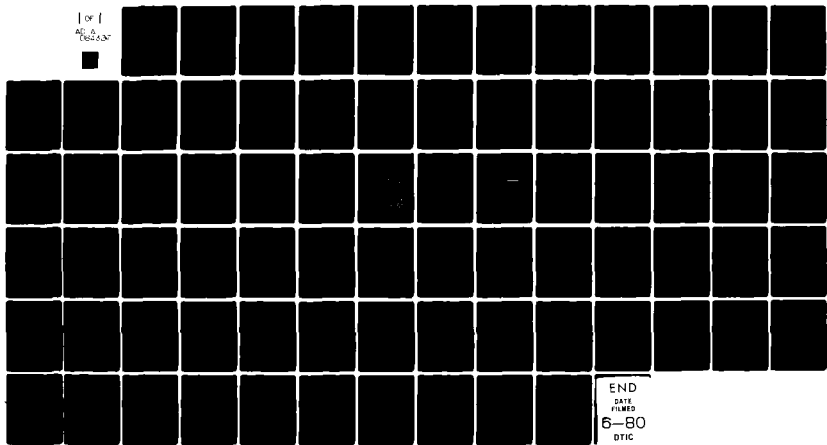


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CLOSO AND HYPER-CLOSO TEN-VERTEX RUTHENACARBORANES CONTAINING C-ETC(U)
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6 Closo and Hyper-Closo Ten-Vertex Ruthenacarboranes Containing
Chelating Alkenyl Phosphine Ligands

By

10 C.W. Jung, R.T. Baker, C.B. Knobler ~~and~~ M.F. Hawthorne*

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Department of Chemistry
University of California
Los Angeles, California 90024

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C. W. Jung, R. T. Baker, C. B. Knobler and M. F. Hawthorne*

Department of Chemistry
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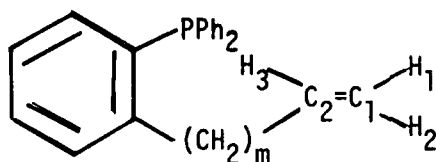
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ABSTRACT

Reactions of [hyper-closo-2-R¹-3-R²-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₇](I) with (o-styryl)diphenylphosphine (R^{1,2}=H,CH₃; R¹=H,R²=Ph), (o-allylphenyl)diphenylphosphine (R^{1,2}=H,CH₃) and Ph_{3-n}P(CH₂CH₂CH=CH₂)_n (n=1,2; R^{1,2}=CH₃) afforded the 16e⁻ ruthenacarborane complexes [hyper-closo-RuL(C₂B₇H₇R¹R²)] (IIa-g), in which the alkenyl phosphine (L) functions as a bidentate ligand. The crystal structure of [2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇](IIId) was determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group P2₁/c with $a=11.740(3)$ Å, $b=15.185(5)$ Å, $c=21.748(7)$ Å, $\beta=137.43(2)^\circ$ and $Z=4$. Refinement of 4168 independent reflections with $I>3\sigma(I)$ led to a final value of $R=4.0\%$. The structure of this complex may best be described in terms of a C₂B₇ fragment of arachno-geometry which occupies nine vertices of an eleven-vertex octadecahedron with a ruthenium atom in a "non-vertex" position and within bonding distance of six atoms in the open face. The observed distortion from the common ten-vertex bicapped square antiprismatic structure is thought to be a result of the perturbation of the polyhedral skeletal bonding induced by the sixteen-electron Ru^{II} center. Reaction of (IIb) with carbon monoxide displaced the coordinated alkenyl side-chain to yield the 18e⁻ Ru^{II} complex [closo-6,6-(CO)₂-6-L-6,2,3-RuC₂B₇H₉](IIIa) {L=(o-allylphenyl)diphenylphosphine}.

Reactions of Ph_{3-n}P(CH₂CH₂CH=CH₂)_n (n=1,2) with [hyper-closo-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₉] produced the fluxional complexes [closo-6,6-L₂-6,2,3-RuC₂B₇H₉](IVa-b) which exhibit butenyl side-chain exchange and undergo closo-hyper-closo equilibria as evidenced by variable temperature multinuclear FTNMR spectroscopy. The reactions of (IVa-b) with carbon monoxide are also discussed.

As part of our study of metallocarborane-catalyzed homogeneous hydrogenation and isomerization of alkenes,^{1,2} we have attempted to isolate or detect possible intermediates in the catalytic cycle.³ Although we have previously noted that the unsaturated ruthenacarboranes $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_n\text{H}_{n+2})]$ ($n=7^4, 9^2$) react with electron-deficient alkenes we were unable to isolate alkene-metallocarborane complexes because of their instability. To overcome this difficulty, the potentially chelating alkenyl phosphines⁵ (*o*-styryl)-diphenylphosphine (SP),⁶ (*o*-allylphenyl)diphenylphosphine (AP)⁷ and $\text{Ph}_{3-n}\text{P}-$



$m = 0$, SP

$m = 1$, AP

$(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_n$ ($n=1$, but-3-enyldiphenylphosphine {MBP}; $n=2$, di(but-3-enyl)phenylphosphine {DBP})⁸ were used to prepare derivatives of the above ruthenacarboranes. This paper describes the synthesis and properties of such alkenyl phosphine complexes prepared from $[2\text{-R}^1\text{-3-R}^2\text{-6,6-(PPh}_3\text{)-6,2,3-RuC}_2\text{B}_7\text{H}_7]$ (Ia-c ; $\text{R}^1, 2=\text{H}$ or Me ; $\text{R}^1=\text{H}$, $\text{R}^2=\text{Ph}$).

The complex $[2,3\text{-(CH}_3)_2\text{-6-(CH}_2\text{=CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P)-6,2,3-RuC}_2\text{B}_7\text{H}_7]$ was the subject of a single crystal X-ray diffraction study, which revealed several interesting structural features. Unlike previously isolated metal complexes derived from the 1,3-dicarba-arachno-nonaborane(13) cage system,⁹ this complex has the metal within bonding distance of all six atoms in the open face. Distortion from the standard closo-structure was anticipated as this n -vertex polyhedron contains only $2n$ skeletal bonding electrons, as does [hyper-closo]- $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\}_2\text{-C}_2\text{B}_6\text{H}_8$.¹⁰

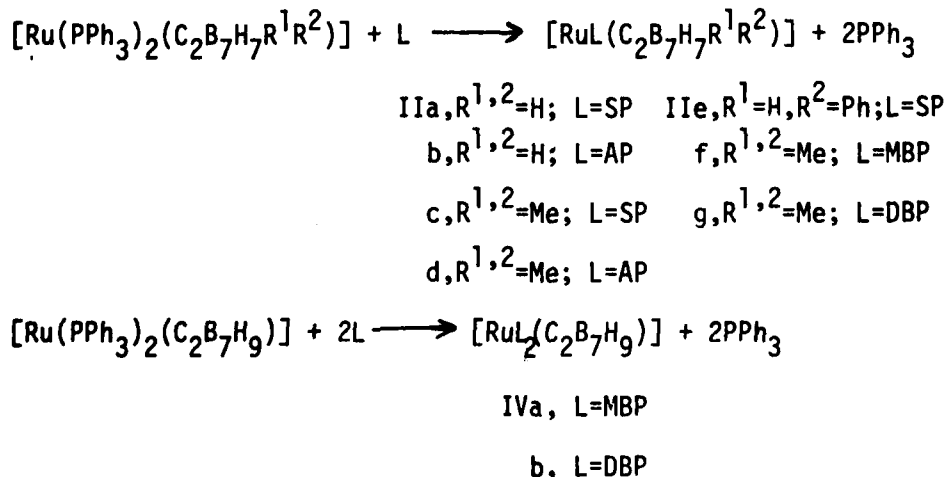
The complexes [closo-6,6-L₂-6,2,3-RuC₂B₇H₉] (L=MBP or DBP) were the subject of a variable temperature multinuclear FTNMR study which demonstrated the existence of two types of exchange processes. The first involves exchange of metal-coordinated and uncoordinated butenyl side-chains, while the second involves phosphine ligand dissociation with concomitant polyhedral rearrangement (closo-hyper-closo equilibrium).

RESULTS AND DISCUSSION

Synthesis, Reactivity and Spectral Data for Hyper-closo Ruthenacarboranes

The reactions of [Ru(PPh₃)₂(C₂B₇H₇R¹R²)] with SP or AP (R^{1,2}=H or Me; R¹=H, R²=Ph SP only) and MBP or DBP (R^{1,2}=Me) afforded the deep-red crystalline compounds [RuL(C₂B₇H₇R¹R²)] (IIa-g; L = alkenyl tertiary phosphine; See Table I). Elemental analyses and mass spectral data agreed with the proposed empirical formulae for IIa-g. Except for L=DBP(IIg), the infrared spectra of IIa-g contained no bands near 1630 cm⁻¹ due to ν_{C=C} for a free alkene group. Instead, medium to weak bands at 1470 and 1260 cm⁻¹ assignable to a coordinated alkene were observed.^{11,12}

TABLE I. Synthesis of Closo and Hyper-closo Ten-Vertex Ruthenacarborane Complexes



The NMR spectra of complexes IIa-g were also consistent with coordination of the alkene side-chain to the ruthenium atom. The alkenyl proton resonances were shifted 1.4 to 3.7 ppm upfield from the corresponding resonances of the free ligand. With ^{31}P -decoupling, the alkenyl proton resonances of $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_9)]$ (IIa) appeared as a first-order AMX spin system with no detectable geminal coupling between H_1 and H_2 (Figure 1). These alkenyl signals were assigned by assuming that the magnitudes of trans-

Figure 1

vicinal couplings (J_{2-3}) remain larger than the corresponding cis-couplings (J_{1-3}) upon complexation of the alkenyl group to ruthenium. The alkenyl coupling constants of IIa-g were smaller than those in the free ligands^{8,13,14} and similar to those found in other transition metal complexes containing chelating alkenyl phosphines or arsines.¹³⁻¹⁶ In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the alkenyl carbons of IIa-g appeared approximately 42 to 60 ppm upfield from those of the free phosphine.¹⁷ Off-resonance decoupled and proton-coupled spectra (for sufficiently soluble compounds) were used to assign these resonances.

The ^{11}B NMR spectra of compounds IIa-g were consistent with the presence of an asymmetric carboranyl ligand (see Figure 2). Those of IIf-g

Figure 2

contained seven doublets ($J_{\text{B-H}} \approx 120 \text{ Hz}$) of roughly equal areas and the spectra of IIa-e were similar, but not as well resolved. As in the parent, $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_7\text{R}^1\text{R}^2)]$,⁴ the complexes IIa-g exhibited resonances at about

107 ppm (relative to external $\text{BF}_3 \cdot \text{OEt}_2$) suggesting that the basic closed polyhedral ruthenacaborane structure was retained in the phosphine metathesis reaction. The ^1H NMR spectra of IIc-d showed two singlets due to two non-equivalent cage-methyl groups, while those of IIa-b contained only one carboranyl C-H singlet, the other carboranyl C-H signal presumably being obscured by the aromatic resonances in the 2.7-3.2 τ range. This notion is supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of IIb which exhibited two broad singlets (ca. 50 Hz halfwidths) at 106.3 and 122.2 ppm due to the two carboranyl carbon atoms. The other complexes either showed only one cage-carbon resonance (the second resonance is presumably buried under the aromatic carbon peaks), or were not sufficiently soluble to yield observable cage-carbon peaks. Cage-bonded methyl signals were not observed in the ^{13}C NMR spectra of IIc-d and may be too broad to detect at ambient temperature.^{18,19}

The spectral data presented for IIa-g are consistent with the alkenyl phosphines acting as bidentate ligands. Since complexes IIa-g are electronically and somewhat coordinatively unsaturated, the two alkenyl groups of the ligand di(but-3-enyl)phenylphosphine could conceivably coordinate to the ruthenium atom.²⁰ However, the infrared, ^1H and ^{13}C NMR spectra of IIg showed the presence of both free and coordinated butenyl side-chains. The ^1H NMR spectrum was essentially temperature-invariant over the range -50 to 40°C, ruling out an equilibrium between free and coordinated alkene.²¹ Steric hindrance and/or the additional metal-cage bonding interactions may prevent both butenyl side-chains from bonding to the ruthenium atom simultaneously.

Complexes IIa-g were air-stable in the solid state, but decomposed slowly in air-saturated solutions. They did not react with hydrogen (1 atm) or dry hydrogen chloride and complex IIa was an ineffective catalyst for alkene hydrogenation under mild conditions. No reduction of the alkenyl side-chain^{21,22} of IIa was discernible even after several days in benzene solution under 1 at-

mosphere pressure of hydrogen.

Treatment of Iib with carbon monoxide rapidly produced a yellow complex with empirical formula $[\text{Ru}(\text{CO})_2(\text{L})(\text{C}_2\text{B}_7\text{H}_9)]$ (IIIa; L=AP). The ^1H NMR spectrum of IIIa indicated that the allyl moiety is not coordinated to the metal atom. The carboranyl C-H resonances were not located, but the ^{11}B NMR spectrum of IIIa was almost identical to that of the complex $[\text{closo-6,6-(CO)}_2\text{-6-PPh}_3\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9]$ ⁴ suggesting that the two Ru^{II} complexes are isostructural.

Complex IIIa and its PPh_3 analog are isoelectronic with $[\text{H}(\text{PPh}_3)_2\text{MC}_2\text{B}_7\text{H}_9]$ ($\text{M}=\text{Rh}, \text{Ir}$)⁴ and $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Co}\}_2\text{C}_2\text{B}_6\text{H}_8]$,²³ and they presumably possess bicapped square antiprismatic structures, consistent with their formulation as saturated, ten-vertex closo polyhedra.²⁴ Complexes IIa-g and $[(\text{PPh}_3)_2\text{RuC}_2\text{B}_7\text{H}_9]$,⁴ however, are unsaturated complexes, all of which exhibit a low-field ^{11}B NMR resonance at about 105 ppm and are isoelectronic with $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\}_2\text{C}_2\text{B}_6\text{H}_8]$, the structure of which has been determined.¹⁰ Nishimura has recently proposed²⁵ that the structure of $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\}_2\text{C}_2\text{B}_6\text{H}_8]$ can be rationalized in terms of a "hyperpolyhedral" metal-metal bond between the two $17e^-\text{Fe}^{\text{III}}$ centers of the cluster. In order to resolve this question by determining if an isoelectronic, unsaturated, monometallic ten-vertex cluster is, in fact, isostructural, an X-ray diffraction study of IId was undertaken.

The Molecular Structure of $[\text{Hyper-closo-2,3-(CH}_3)_2\text{-6-(CH}_2\text{=CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P)}\text{-6,2,3-Ru-C}_2\text{B}_7\text{H}_7]$, IId.

Intramolecular distances and their estimated standard deviations are listed in Table VI. Average bond lengths are collected in Table VII. Bond angles and their associated estimated standard deviations are listed in Table VIII. The structure of $[\text{2,3-(CH}_3)_2\text{-6-(CH}_2\text{=CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P)}\text{-6,2,3-RuC}_2\text{B}_7\text{H}_7]$ is shown in Figure 2, together with the numbering system employed.

The structure of this compound may be described in terms of a $\text{C}_2\text{B}_7\text{H}_7\text{Me}_2$ fragment of arachno geometry which occupies 9 vertices of an 11-vertex octadecahedron. The ruthenium atom occupies a position between the two empty vertices and is bound to the four boron atoms and two carbon atoms of the chair-shaped six-atom open face.

The ruthenium atom is thus bound to B(10), B(9), B(7), C(2), C(3), and B(1) of the carborane cage and to P, C(28) and C(29) of the (o-allylphenyl)diphenylphosphine ligand. The polyhedral carbon atoms occupy positions 2 and 3 in the fragment and are formally five coordinate. The structure of $[6,6-(PPh_3)_2-6,2,3-RuC_2B_7H_9]^4$ is probably similar with the ruthenium atom bonded to all six atoms in the open face (vide infra).

The ruthenium to cage distances can be compared to those in $[2,2-(PPh_3)_2-2,2-H_2-2,1,7-RuC_2B_9H_{11}]$ which range from 2.22(2) Å to 2.32(2) Å for the five atoms of the carborane open face.² However, in the title compound, Ru-B distances involve bonds to boron atoms of different coordination numbers; Ru to 6-coordinate boron B(7), B(9), and B(1) are 2.466(5), 2.340(5), and 2.488(5) Å, respectively, and Ru to 5-coordinate B(10) is 2.023(5) Å. A similar change in Fe-B bond lengths is noted in a compound with comparable cage geometry, [hyper-closo-1,6-($\eta^5-C_5H_5$)₂-1,6,2,3-Fe₂C₂B₆H₈].¹⁰

As expected, the polyhedral carbon atoms occupy nonadjacent positions in this compound; they occupy two of the three low-coordinate positions and are related by a noncrystallographic mirror plane through Ru, B(10), B(8) and B(1). Variations from mirror symmetry are within three standard deviations in related bond distances with the exception of B(1)-C(3) and B(1)-C(2), Ru(6)-C(2) and Ru(6)-C(3), and Ru(6)-B(7) and Ru(6)-B(9). Two of these exceptions can be explained by trans-influence.²⁶ The phosphorous atom is trans- to B(9) and C(28)=C(29) is trans-to C(3). Ru-C(3) is significantly longer than Ru-C(2) and Ru-B(9) is significantly shorter than Ru-B(7).

Unlike $[1,6-(\eta^5-C_5H_5)_2-1,6,2,3-Fe_2C_2B_6H_8]$, boron-boron distances and carbon-boron distances within the polyhedron do not reflect the coordination of the various atoms; the shortest boron-boron distance, B(4)-B(5)=1.743 Å, is between two 6-coordinate boron atoms, and the longest distances, B(1)-B(4), B(1)-B(5) and B(8)-B(9), 1.814, 1.820, and 1.814 Å, respectively, are also between two 6-coordinate boron atoms.

In general, the bond lengths and angles within the C₂B₇ fragment correlate well with the analogous bonds in arachno-C₂B₇H₁₁Me₂.²⁷ The largest deviation is found for B(7)-C(3) and B(9)-C(2). The corresponding distances in the arachno compound are 0.13 Å longer than those in the metallocarborane.

B(9), C(3), P, and the midpoint of C(28)=C(29) are in a square planar conformation about Ru and C(28)=C(29) is nearly perpendicular to this plane. The Ru-P distance of $2.418(1) \text{ \AA}$ is within the range of distances found for ruthenium bonded to phosphines, but is longer than those found in $[2,2-(\text{PPh}_3)_2-2,2-(\text{H}_2)-2,1,7-\text{RuC}_2\text{B}_9\text{H}_{11}]$ ($2.342(4)$ and $2.301(4) \text{ \AA}$).² The longer bond in the title compound may be due to the bulky phosphine ligand with its allyl group. The Ru-C distances of $2.167(4)$ and $2.191(4) \text{ \AA}$ are well within the range of distances for Ru π -bonded to an alkene.

Angles and distances involving the phosphorus atom are unexceptional. Although the phenyl ring of the *o*-allylphenyl moiety is planar, the dihedral angle C(27)-C(26)-C(21)-P is 4.4° and C(27), C(28), H(28), C(29), H(291) and H(292) are not coplanar. The linkage C(27)-C(28) is a normal single bond ($1.5306(6) \text{ \AA}$) and the distance C(28)-C(29) ($1.406(7) \text{ \AA}$) is within the range for π -bonded C=C distances. The distance of $1.498(6) \text{ \AA}$ for C(26)-C(27) and distances and angles in the phenyl ring are not unusual.

The only intermolecular distance less than $2.5 \text{ \AA}$ is between H(292) and H(513) and is $2.44 \text{ \AA}$. Only two nonhydrogen-hydrogen intermolecular distances are less than $3.0 \text{ \AA}$ and they are between phenyl carbon atoms and a phenyl hydrogen atom and a methyl hydrogen atom, respectively; each distance is $2.96 \text{ \AA}$.

The polyhedral geometry of the title compound is significantly different from the bicapped square antiprism found for ten-vertex closo-borane species such as $(\text{B}_{10}\text{H}_{10})^{2-}$ ²⁸ and $[(\text{C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_6\text{H}_8]$ ²³ but is very similar to $[(\text{C}_5\text{H}_5)_2\text{Fe}_2\text{C}_2\text{B}_6\text{H}_8]$ ¹⁰ and does adopt a fully triangulated closed polyhedral structure. If the title compound was constrained to have the bicapped square antiprism form, a new bond would be needed between C(2) and C(3) and the Ru-B(1) bond would be broken. Then B(1) would be in a lower coordinate position and C(2) and C(3) would be located in 6-coordinate positions.

The structures of the two hyper-closo ten-vertex metallocarboranes mentioned above also do not correspond to the predicted capping of the closo nine-vertex tricapped trigonal prism²⁹⁻³¹ but are instead a result of completely capping the six-membered open-face of the arachno C_2B_7 fragment, presumably to compensate for the electronic unsaturation of the metal center.

Synthesis, Reactivity and Variable Temperature Multinuclear FTNMR Studies of Closo-Ruthenacarboranes

Complex $[6,6-(PPh_3)_2-6,2,3-RuC_2B_7H_9](Ia)$ reacted with MBP and DBP to produce yellow complexes with empirical formulae $[RuL_2C_2B_7H_9]$ (IVa-b; L=MBP and DBP, respectively). The infrared spectra of IVa-b in the solid state contained both free and coordinated butenyl absorptions.¹² Solutions of IVa in toluene or dichloromethane were prepared at or above room temperature and the solution infrared spectrum in dichloromethane at 22°C exhibited two additional peaks assignable to a coordinated butenyl side-chain at 1325 and 1285 cm^{-1} along with those at 1630(free), 1300 and 1250 cm^{-1} (coordinated) observed in the solid state spectrum.³⁵

Complex IVb did not yield red solutions until the temperature was above about 60°C. As the ligand cone angle³⁶ of MBP (140°) is larger than that of DBP (135°) it was presumed that phosphine ligand dissociation occurs to yield the unsaturated, red hyper-closo- $LRuC_2B_7H_9$ species. This proposal was supported by the observation of a low-field ^{11}B NMR resonance at 107.5 ppm in a d_2 -dichloromethane solution of IVa at 44°C, which was absent at -40°C. In addition, while treatment of IVb with carbon monoxide yielded closo-(CO) $L_2RuC_2B_7H_9$ in high yield, the yield of the analogous monocarbonyl complex of IVa decreased with increasing temperature due to the formation of the dicarbonyl complex closo-(CO) $_2LRuC_2B_7H_9$ (vide infra).

The variable temperature $^{31}P\{^1H\}$ FTNMR spectrum of IVa in dichloromethane shown in Figure 3 indicated that the closo- $L_2RuC_2B_7H_9$ species which predominates

Figure 3

at low temperatures is itself fluxional. At -73°C the spectrum consisted of a doublet for the chelated alkenyl phosphine ligand^{12,37} at 68.5 ppm ($^2J_{\text{P-P}} = 32$ Hz) and a doublet for the unidentate phosphine ligand at 47.2 ppm. As the temperature was raised, these resonances broadened, but before coalescence was attained, phosphine dissociation started to occur, as evidenced by the change in chemical shift of the unidentate phosphine ligand towards the free ligand limit. The spectrum at 60°C in 10% $\text{C}_6\text{D}_6\text{-C}_6\text{H}_5\text{CH}_3$ represented the high-temperature limit and exhibited a singlet at 49.8 ppm for the [hyper-closo-L $\text{RuC}_2\text{B}_7\text{H}_9$] species and a singlet at 15 ppm for the free alkenyl phosphine ligand.⁸ The presence of two exchange processes was more evident in the variable temperature $^{31}\text{P}\{^1\text{H}\}$ -FTNMR spectra of IVb in dichloromethane, as the temperature domains for the two processes were not overlapping. Thus, at -8°C , coalescence of the two inequivalent phosphorus nuclei occurred cleanly and the change in chemical shift of the unidentate phosphine ligand did not begin until above 27°C . (Figure 4)

Figure 4

The variable temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra of IVa were also complicated due to the overlap of the temperature domains of the two dynamic processes. At -78°C the $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectrum in dichloromethane exhibited free alkenyl carbons at 138.4 and 115.3 ppm, coordinated alkenyl carbons at 79.3 and 58.5 ppm and carboranyl carbons at 72.7 and 41.2 ppm.³⁸ Broad, free alkenyl carbon resonances were observed at -23°C and at 27°C the only resonances observed were due to exchange-averaged phenyl and methylene carbons of the alkenyl phosphine ligand. The ^1H FTNMR spectrum of IVa in d_2 -dichloromethane at -68°C consisted of three broad resonances at 5.39, 5.78 and 6.11 τ , in addition to three resonances at 4.34, 5.09 and 5.16 τ which can be assigned to the coordinated and free alkenyl protons of

butenyl side-chains, respectively.¹⁶ At -38°C these signals broadened and at 33°C only one set of three alkenyl protons was observed, suggesting that the low temperature exchange process is due to exchange of free and coordinated butenyl side-chains,²¹ as depicted in Figure 5.

Figure 5

The variable temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra of IVb in dichloromethane were more informative, although the presence of three inequivalent butenyl side-chains at the low temperature limit led to overlapping resonances and precluded complete spectral assignments. The $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra are shown in Figure 6.

Figure 6

At -83°C three sets of alkenyl carbons were observed at 142.3 and 119.2 (C_2' and C_1'), 138.5 and 115.6 (C_2 and C_1) and 74.8 and 52.5 (coordinated C_2' and C_1'), where the primed carbons refer to those butenyl side-chains attached to the chelating phosphine ligand. The carboranyl carbons were observed at 75.9 and 39.2 ppm.³⁸ At -23°C only the C_1 and C_2 alkenyl carbon resonances were observed and at 27°C , again, only the exchange-averaged phenyl and methylene carbon resonances of the alkenyl phosphine ligand were present. The ^1H FTNMR spectra of IVb in d_2 -dichloromethane are presented in Figure 7.

Figure 7

At 88°C two sets of three free alkenyl proton resonances were observed

at 4.41, 4.60(H_3 and H_3'), 5.15 and 5.31 τ (H_1, H_2, H_1' and H_2' , overlapping), in addition to three coordinated alkenyl proton resonances at 6.00, 6.39 and 6.68. At 7°C two overlapping sets of three alkenyl proton resonances were present, while at 22°C only three alkenyl proton resonances were observed. It appears, then, from the $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H FTNMR spectral data, that there are, in fact, two low temperature exchange processes occurring for IVb in solution. The first involves exchange of one butenyl side-chain on each phosphine ligand between free and metal-coordinated sites, yielding equivalent phosphine ligands, one set of alkenyl carbon resonances due to the two non-fluxional butenyl side-chains and two sets of alkenyl proton resonances due to the two non-fluxional butenyl side-chains and the two exchange-averaged butenyl side-chains. The second process involves exchange of all four butenyl side-chains, yielding equivalent phosphine ligands, one set of exchange-averaged alkenyl protons and no observed alkenyl carbon resonances. The activation energy ($\Delta G^\ddagger$) for the exchange of the first two butenyl side-chains is easily obtained from the $^{31}\text{P}\{^1\text{H}\}$ FTNMR spectra and is found to be 10.0 ± 0.5 kcal/mol.³⁹ The second process may be due to the onset of rotation about the ruthenium-phosphorus bond which would interchange the two butenyl side-chains on each phosphine ligand, thus enabling all four butenyl side-chains to exchange between free and coordinated sites.

The $^{11}\text{B}\{^1\text{H}\}$ FTNMR of IVb in d_2 -dichloromethane at -71°C resembled that of IVa at -40°C and illustrated the asymmetry induced in the carborane ligand when the phosphine ligands become inequivalent.

Complexes IVa-b reacted with carbon monoxide to form the yellow complexes $[\text{closo-6-CO-6,6-L}_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9]$ (IVa-b; L=MBP or DBP). The infrared spectra of IVa-b included ν_{CO} absorptions at 1932 and 1930 cm^{-1} and $\nu_{\text{C}=\text{C}}$ (uncoordinated) at 1628 and 1632 cm^{-1} , respectively. The ^1H NMR spectra in d_2 -dichloromethane contained alkenyl proton resonances due to uncoordinated butenyl side-chains and exhibited no temperature-dependent behavior.⁴⁰ The presence of a mirror-plane was

indicated by the $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data suggesting that the carboranyl cage mirror plane bisects the P-Rh-P angle in a static structure or, alternatively, that the $\{\text{RhP}_2\text{CO}\}$ vertex is rapidly rotating about the five-membered face of the carboranyl ligand as has been proposed for $[\text{closo-}\{\text{P}(\text{C}_2\text{H}_5)_3\}_3\text{RuC}_2\text{B}_7\text{H}_9]$ at -88°C .⁴

The carbonylation of IVa produced Va in quantitative yield when monitored by $^{31}\text{P}\{^1\text{H}\}$ FTNMR at -78°C . At temperatures above 25°C , however, the carbonylation of IVa produced two additional singlet resonances at -15.3 and 45.4 ppm which were assigned to free but-3-enyldiphenylphosphine and to $[\text{closo-6,6-(CO)}_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9]$ (IIIb; L=MPB), respectively. The infrared spectrum of IIIb in the $2100\text{-}1900\text{ cm}^{-1}$ region was very similar to that of the analogous complex, IIIa.

Conclusions

Reactions of $[\text{hyper-closo-2-R}^1\text{-3-R}^2\text{-6,6-(PPh}_3)_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_7]$ (I) with $\text{SP}(\text{R}^1,^2=\text{H,CH}_3; \text{R}^1=\text{H}; \text{R}^2=\text{Ph})$; $\text{AP}(\text{R}^1,^2=\text{H,CH}_3)$, MBP and $\text{DBP}(\text{R}^1,^2=\text{CH}_3)$ yielded the unsaturated ruthenacarborane complexes $[\text{hyper-closo-RuL}(\text{C}_2\text{B}_7\text{H}_7\text{R}^1\text{R}^2)]$ (IIa-g), in which the alkenyl phosphine (L) functions as a bidentate ligand. The molecular structure of IIId (L=AP, $\text{R}^1,^2=\text{CH}_3$) was determined by X-ray diffraction to be similar to that of $[(\eta^5\text{-C}_5\text{H}_5\text{Fe})_2\text{C}_2\text{B}_6\text{H}_8]$ ¹⁰ and represents a new structural class of ten-vertex metallocarboranes containing ten skeletal electron pairs. The term "hyper-closo" has been adopted to describe this structural class of which $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_4\text{H}_4]$,³¹ $[(\eta^5\text{-C}_5\text{H}_5)\text{CoFe}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8]$ ⁴¹ and $[\text{EFe}(\text{CH}_3)_4\text{-C}_4\text{B}_8\text{H}_8]$ ⁴¹ (E=Sn,Ge) are also members, in order to differentiate these species from undistorted, unsaturated metallocarboranes, in which the electronic unsaturation is presumably largely metal-based. Studies are now underway in this laboratory to isolate and determine the molecular structure of twelve and eleven-vertex hyper-closo metallocarboranes in order to elucidate the nature

of the polyhedral distortions induced by the unsaturated metal vertices.

Reactions of [hyper-closo-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₉] with MBP and DBP yielded the saturated ruthenacarborane complexes [closo-RuL₂(C₂B₇H₉)](IVa,b). A variable temperature multinuclear FTNMR study of IVa,b indicated that the complexes undergo butenyl side-chain exchange in solution at lower temperatures and undergo closo-hyper-closo equilibria with concomitant polyhedral rearrangement at higher temperatures. This facile rearrangement demonstrates the remarkable mobility of transition metal vertices in cluster complexes and the flexibility of carborane cages in accommodating both electronic and coordinative unsaturation in the transition metal vertex.

Several interesting metallocarboranes containing carboranyl cage-bonded alkenyl side-chains have recently been prepared in this laboratory and the chemistry of these catalytically active species is currently under investigation.⁴²

EXPERIMENTAL SECTION

Crystal Structure

Crystals of IIId suitable for X-ray studies were obtained as black needles from CH₂Cl₂/pentane. A preliminary examination of several crystals by means of oscillation and Weissenberg photographs showed them to have monoclinic symmetry and systematic absences 0k0, k = 2n + 1, and h0ℓ, ℓ = 2n + 1, space group P2₁/c.⁴³ The specimen selected for data collection was bounded by {102}, {010}, {110} and {110}. Crystal dimensions normal to these faces were 0.20, 0.16, 0.19, and 0.075 mm, respectively. The crystal was mounted on a Syntex P1 autodiffractometer equipped with a scintillation counter and a graphite monochromator. Lattice parameters, determined by a least-squares fit of 15 accurately centered high-angle reflections, were a = 11.740(3) Å, b = 15.185(5) Å, c = 21.748(7) Å, and β = 137.43(2)°. The density measured by flotation in aqueous potassium iodide

was $1.36(1) \text{ g cm}^{-3}$, in good agreement with the calculated density of 1.368 g cm^{-3} based on $Z = 4$.

Intensity measurements were made with $\text{MoK}\alpha$ radiation scan rate of $2.0^\circ/\text{min}$ from 1.25° below the $\text{K}\alpha_1$ reflection to 1.25° above the $\text{K}\alpha_2$ reflection. The background was counted for one half of the scan time at each end of the scan range. Data were collected with a θ - 2θ scan technique to a limit of $2\theta = 55^\circ$. Three strong reflections were checked after each 97 intensity measurements and these showed only random variations consistent with their respective $\sigma(I)$ values. Of the 6052 unique reflections not excluded by the space group, 1884 for which $I < 3\sigma(I)$ were considered unobserved. The remaining 4168 reflections were used in the structure determination and refinement. All measured reflections were corrected for Lorentz and polarization effects and processed to give $|F_o|$ values as previously reported.⁴⁴ An absorption correction was applied ($\mu = 6.60$; maximum and minimum transmission factors were .9559 for $\bar{1}3\ 0\ 18$ and .9479 for $\bar{1}\bar{1}\ 0\ 28$).

Determination and Refinement of the Structure

Trial positions for the ruthenium and phosphorus atoms were obtained from a three-dimensional Patterson summation. The other atoms, including hydrogen atoms, were located by means of difference Fourier maps. Refinement, without the contribution of hydrogen atoms to calculated structure factors, of positional and anisotropic thermal parameters of the ruthenium and phosphorus atoms and of positional and isotropic thermal parameters of all other nonhydrogen atoms, converged to a conventional R^{45} index of 5.5% and a weighted index, R_w , of 7.5%. For reasons of economy, the two C_6H_5 moieties were then constrained to be rigid groups⁴⁶ containing C_6 hexagons of $\text{C}-\text{C} = 1.39 \text{ \AA}$ and $\text{C}-\text{H} = 1.0 \text{ \AA}$. Maxima in the range of $0.5 \pm 0.2 \text{ e \AA}^{-3}$ at positions close to those calculated for the remaining hydrogen atoms were found on a difference Fourier map. The two methyl groups were also constrained to be rigid groups containing an sp^3 carbon atom and $\text{C}-\text{H} =$

1.0 Å. Positional and anisotropic thermal parameters of all nonhydrogen nongroup atoms, positional and isotropic thermal parameters of all carbon group atoms and positional parameters of all nongroup hydrogen atoms were refined. Isotropic thermal parameters for all hydrogen atoms were assigned as follows: for all non-group hydrogen atoms $B = 5.0$, for all phenyl group hydrogen atoms $B = 0.5$ plus the B value on the adjacent carbon atom, and for all methyl group hydrogen atoms $B = 1.0$ plus the B value on the adjacent carbon atom. The refinement converged at $R = 4.0\%$ and $R_w = 4.8\%$. In the final least-squares cycle, the largest shift in a positional or thermal parameter for a nonhydrogen atom was 0.4σ . The final "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2 / (No - Nv)]^{1/2}$ was 1.47. In this expression $No = 4168$, the number of observed reflections, and $Nv = 267$, the number of variable parameters. No maxima $> 0.75 \text{ e } \text{\AA}^{-3}$ were found on a final difference Fourier map.

The final positional and thermal parameters are listed in Tables I, II, and III. A listing of the root-mean-square amplitudes of vibration of the nonhydrogen nongroup atoms along the three principal axes of the vibrational ellipsoids, together with the corresponding B values, is given in Table IV.⁴⁷ A set of structure factors was calculated on the basis of the tabulated parameters and is available as Table V.⁴⁷ The atomic scattering factors were those given in Table 2.2A of ref. 48 and the real and imaginary components of anomalous dispersion from Table 2.3.1 of ref. 43 were applied to the scattering factors of ruthenium and phosphorus.

Synthesis of Metallocarboranes

Unless indicated otherwise, all operations were conducted under purified nitrogen or argon using standard inert atmosphere techniques.⁴⁹

Infrared spectra were determined as mineral oil mulls or KBr pellets on a Perkin-Elmer 421 dual-grating spectrometer. Proton NMR spectra were measured using Varian A60D and HA100D spectrometers. ¹³C NMR spectra were recorded on

a Varian CFT-20 spectrometer. The 80.5 and 111.8 MHz ^{11}B FTNMR spectra were obtained with an instrument designed and constructed by Professor F. A. L. Anet of this department. All other FTNMR spectra were recorded on a Brüker WP-200 spectrometer equipped with a B-ST-100/700C variable temperature unit. ^{11}B and ^{31}P chemical shifts were referenced to external $\text{BF}\cdot\text{OEt}_2$ and D_3PO_4 , respectively, with positive values assigned to low-field shifts and all reported coupling constants are absolute values. All NMR solvents were vacuum distilled from P_4O_{10} into the NMR sample tube prior to sealing under vacuum ($< 5 \times 10^{-5}$ torr). Mass spectra were obtained on an Associated Electrical Industries MS-9 spectrometer.

Melting points were determined in open capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

The complex [hyper-closo-2-R¹-3-R²-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₇]⁻ was prepared by a previously described procedure.⁴ SP⁶, AP⁷, MBP⁸ and DBP⁸ were prepared by literature methods. Toluene, benzene and petroleum ether (30-60°C) were distilled from calcium hydride. Other solvents were reagent grade and deoxygenated with bubbling nitrogen or argon immediately before use. All other chemicals were reagent grade and used as supplied.

Preparation of [hyper-closo-6-(SP)-6,2,3-RuC₂B₇H₉](IIa)

A toluene (2 ml) solution of $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_9)]$ (0.101 g, 0.138 mmol) and SP (0.0875 g, 0.304 mmol) was stirred overnight at room temperature yielding a deep blood-red solution. Pentane (10 ml) was gently layered above the toluene solution and the mixture was cooled to -15°C for 3 d. The resulting red-brown crystals of $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_9)]$ (IIa) (0.049 g, 68%) were filtered off in air, washed with methanol and pentane and vacuum dried, m.p.: $193-197^\circ\text{C}$. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{B}_7\text{PRu}$: C, 53.04; H, 5.26; B, 15.19. Found: C, 53.10; H, 5.42; B, 15.36. ^1H NMR (100 MHz, CD_2Cl_2): 7.85 (dd [$J_{13}=8.4$, $J_{\text{P-H}_1}=1.3$ Hz], H_1),

7.20 (d{ $J_{23}=11.9$, $J_{P-H_2} < 0.5$ Hz}, H_2), 4.87 (q{ $J_{P-H_3} < 0.5$ Hz}, H_3), 3.96 τ (br, s, carborane C-H). $^{13}C\{^1H\}$ NMR (20.5 MHz, 20% CD_2Cl_2/CH_2Cl_2): 66.25 (s, C_1 , $J_{C_1-H} = 152.5$, 159.8 Hz), 92.55 (s, C_2 , $J_{C_2-H} = 158.8$ Hz), and 110.1 ppm (br, s, carborane C{ $W_{1/2} \approx 50$ Hz}). ^{11}B NMR (80.5 MHz, CD_2Cl_2): 106.8(1); 18.9(1); 5.59(1); -3.75, -4.55, -5.94 (3, overlapping peaks); -8.82 ppm(1).

Analogous $[RuL(C_2B_7H_7R^1R^2)]$ complexes were prepared similarly by reactions of $[2-R^1-3-R^2-6,6-(PPh_3)_2-6,2,3-RuC_2B_7H_7]$ with the appropriate alkenyl phosphine: $[Ru(AP)(C_2B_7H_9)]$ (IIb), AP (0.208 g, 0.685 mmol), $[Ru(PPh_3)_2(C_2B_7H_9)]$ (0.251 g, 0.342 mmol), 85% yield, m.p.: 157-160°C. Anal. Calcd for $C_{23}H_{28}B_7PRu$: C, 53.94; H, 5.51; B, 14.78; P, 6.05; Ru, 19.73. Found: C, 53.79; H, 5.65; B, 14.93; P, 6.28; Ru, 19.53. 1H NMR (100 MHz, CD_2Cl_2): 8.37 (dd{ $J_{13}=7.8$, $J_{P-H_1}=2.5$ Hz}, H_1), 7.53 (dd{ $J_{23}=13.0$, $J_{P-H_2} \approx 1$ Hz}, H_2), 5.53 (m, H_3), 6.13 (m, CH_2), 4.88 τ (br, s, carborane C-H). $^{13}C\{^1H\}$ NMR (20.5 MHz, 20% CD_2Cl_2/CH_2Cl_2): 66.52 (s, C_1); 88.66 (d{ $^4J_{P-C_2}=5.0$ Hz}, C_2); 39.54 (d{ $^3J_{P-C}=14.0$ Hz}, CH_2); 106.3 and 122.2 ppm (br, s, carborane C). ^{11}B NMR (80.5 MHz, CD_2Cl_2): 108.4(1), 15.0(1), 4.80(1), -5.18(1), 7.01(2), -10.3(1) ppm. $[Ru(SP)(C_2B_7H_7Me_2)]$ (IIc), SP (0.15 g, 0.52 mmol), $[Ru(PPh_3)_2(C_2B_7H_7Me_2)]$ (0.206 g, 0.270 mmol). Anal. Calcd for $C_{24}H_{30}B_7PRu$: C, 54.78; H, 5.75; P, 5.88. Found: C, 55.61; H, 6.31; P, 5.65. 1H NMR (100 MHz, CD_2Cl_2): 7.51 (dd{ $J_{13}=8.6$, $J_{P-H_1}=2.0$ Hz}, H_1 (upfield half obscured by Me singlet)); 8.01 (dd{ $J_{23}=12.2$, $J_{P-H_2}=1.6$ Hz}, H_2); 5.14 (q{ $J_{P-H_3} < 0.5$ Hz}, H_3); 7.53 and 8.77 τ (s, CH_3). ^{11}B NMR (CD_2Cl_2): 107.6(1), 17.9(1), 11.9(1), -0.12(1), -2.21(2), -9.56 ppm(1). $[Ru(AP)(C_2B_7H_7Me_2)]$ (IId), AP (0.091 g, 0.301 mmol), $[Ru(PPh_3)_2(C_2B_7H_7Me_2)]$ (0.153 g, 0.201 mmol), 70% yield. Anal. Calcd for $C_{25}H_{32}B_7PRu$: C, 55.58; H, 5.97; P, 5.73. Found: C, 55.92; H, 6.07; P, 5.38. 1H NMR (100 MHz, CD_2Cl_2): 7.52 (dd{ $J_{12}=3.5$, $J_{13}=7.5$, $J_{P-H_1} < 0.5$ Hz}, H_1); 8.01 (dd{ $J_{23}=8.2$, $J_{P-H_2} < 0.5$ Hz}, H_2); 5.58 (m, H_3); 6.14 (m, CH_2); 7.69 and 8.77 τ (s, CH_3). $^{13}C\{^1H\}$ (20% CD_2Cl_2/CH_2Cl_2): 55.73 (s, C_1), 88.76 (d{ $^4J_{P-C_2}=4.1$ Hz}, C_2),

39.49 ppm ($d\{^3J_{P-C}=15.2\text{ Hz}\}$, CH_2). ^{11}B NMR (CD_2Cl_2): 108.0(1), 19.2(1), 14.6(1), -2.06(3), -11.0 ppm(1). $[Ru(SP)(C_2B_7H_8Ph)](IIE)$, SP (0.149 g, 0.517 mmol), $[Ru(PPh_3)_2(C_2B_7H_8Ph)]$ (0.279 g, 0.344 mmol), 58% yield. Anal. Calcd for $C_{28}H_{30}B_7PRu$: C, 58.56; H, 5.26; P, 5.39. Found: C, 58.58; H, 5.42; P, 5.70. 1H NMR (100 MHz, CD_2Cl_2): 8.55 (dt($J_{12}\approx 1$, $J_{13}=8.8$, $J_{P-H_1}\approx 1\text{ Hz}$), H_1), 7.70 (dt($J_{23}=12.0$, $J_{P-H_2}\approx 1\text{ Hz}$), H_2), 4.83 (q($J_{P-H_3}< 0.5\text{ Hz}$), H_3), 4.19 τ (br,s, carborane C-H). $^{13}C\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2): 65.44 (s($J_{C_1-H}=155, 162\text{ Hz}$), C_1), 92.35 (s($J_{C_2-H_3}=159\text{ Hz}$), C_2), 104.2 ppm (br,s, carborane C). ^{11}B NMR (CD_2Cl_2): 106.8(1), 15.2(1), 9.09(1), -4.82(3), -10.4 ppm(1). $[Ru(MBP(C_2B_7H_7Me_2))](IIf)$, MBP (0.21 g, 0.87 mmol), $[Ru(PPh_3)_2(C_2B_7H_7Me_2)]$ (0.301 g, 0.395 mmol), 77.5% yield, m.p.: 250-280°C (dec). Anal. Calcd for $C_{20}H_{30}B_7PRu$: C, 50.24; H, 6.32; P, 6.48. Found: C, 50.33; H, 6.55; P, 6.55. 1H NMR (100 MHz, CD_2Cl_2): 7.87 (d($J_{13}=8.5\text{ Hz}$), H_1); ca. 7.3 (peak partially obscured by CH_2 resonances, H_2); 5.59(m, H_3); 6.8-7.5(m, CH_2); 7.61 and 8.42 τ (s, CH_3). $^{13}C\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2): 55.42 (s, C_1), 94.98 (d($^3J_{P-C_2}=2.6\text{ Hz}$), C_2), 30.1-33.4 ppm (CH_2). ^{11}B NMR (CD_2Cl_2): 107.5(1), 17.5(1), 10.6(1), 0.19(1), -2.30(1), -3.59(1), -9.65 ppm(1). $[Ru(DBP(C_2B_7H_7Me_2))](IIg)$, DBP (0.19 g, 0.87 mmol), $[Ru(PPh_3)_2(C_2B_7H_7Me_2)]$ (0.302 g, 0.396 mmol), 56% yield, m.p.: 119-130°C (dec). Anal. Calcd for $C_{18}H_{32}B_7PRu$: C, 47.39; H, 7.07; P, 6.79. Found: C, 47.46; H, 7.08; P, 6.79. 1H NMR (100 MHz, CD_2Cl_2): ca. 8.0 and 7.2 (H_1 and H_2 respectively, peaks partially obscured by CH_2 resonances); 5.07(m, H_3); 6.8-8.2(m, CH_2); 7.66 and 8.30(s, CH_3); 4.16 (m, uncoordinated H_3); 4.88 τ (m, uncoordinated H_1 and H_2). ^{13}C NMR (20% CD_2Cl_2/CH_2Cl_2): 54.53 (s($J_{C_1-H}=142.5, 165\text{ Hz}$), C_1), 94.65 (s($J_{C_2-H_3}=156.5\text{ Hz}$), C_2), 23.2-32.8 (alkyl), 116.28 (d($^4J_{P-C_1}=22.2\text{ Hz}$), uncoordinated C_1), 137.5 ppm (d($^3J_{P-C_2}=14\text{ Hz}$), uncoordinated C_2). ^{11}B NMR (CD_2Cl_2): 106.8(1), 17.2(1), 9.73(1), -0.11(1), -2.30(1), -4.48(1), -9.85 ppm(1). Infrared spectrum (KBr): free $\nu_{C=C}$ at 1629 cm^{-1} .

Reaction of [6-(AP)-6,2,3-Ru $C_2B_7H_9$] with Carbon Monoxide

A toluene (1 ml) solution of $[Ru(AP)(C_2B_7H_9)]$ (54.0 mg, 0.105 mmol) was

stirred under a carbon monoxide atmosphere, and the initial blood-red color turned yellow instantly. After 5 minutes petroleum ether (20 ml) was layered on top of the toluene, and the mixture was allowed to stand for 4 h undisturbed. The resulting yellow crystals were filtered in air, washed with petroleum ether, methanol and recrystallized from dichloromethane/petroleum ether affording [closo-6,6-(CO)₂-6-AP-6,2,3-RuC₂B₇H₉](IIIg)](27%), m.p.: 172-176°C. Anal. Calcd for C₂₅H₂₈B₇P₂O₂Ru: C, 52.84; H, 4.97; P, 5.45. Found: C, 53.06; H, 5.21; P, 4.97. ¹H NMR (100 MHz, CD₂Cl₂): 5.09(m, H₁), 4.96(m, H₂), 4.40(m, H₃), and 6.62 τ(m, CH₂). ¹¹B{¹H} NMR (CD₂Cl₂): 1.40(2), -9.33(1), -20.4 and -23.2 ppm (4, overlapped peaks). Infrared spectrum (KBr): ν_{CO} at 2037(s) and 1980 cm⁻¹(s) and free ν_{C=C} at 1630 cm⁻¹.

Preparation of [closo-6,6-(MBP)₂-6,2,3-RuC₂B₇H₉](IVa)

To a stirred suspension of [Ru(PPh₃)₂(C₂B₇H₉)] (0.102 mg, 0.138 mmol) in toluene (2 ml) was added (but-3-enyl)diphenylphosphine (0.078 g, 0.32 mmol). The blue solution instantly turned red. After 15 min, pentane (60 ml) was layered above the toluene solution. After standing undisturbed overnight the mixture was cooled to -15°C for 2 d, precipitating yellow crystals of [closo-6,6-(MBP)₂-6,2,3-RuC₂B₇H₉](IVa) (0.066 g, 69%) which were filtered quickly in air, washed with methanol and petroleum ether and vacuum dried, m.p.: 115-126°C (dec, darkens at 100°C). Anal. Calcd for C₃₄H₄₃B₇P₂Ru: C, 59.15; H, 6.28; P, 8.97. Found: C, 60.45; H, 6.56; P, 8.53.

¹H FTNMR (200.133 MHz, CD₂Cl₂, 33°C): 2.60(m, phenyl protons), 4.7, 6.3, 6.7(br, alkenyl protons) and 7.58 τ(br, methylene protons). At -38°C: 2.70(br, m, phenyl protons), 4.90(br, alkenyl protons) and 7.65 τ(br, methylene protons). At -68°C: 2.27, 2.56, 2.73, 2.90(m, phenyl protons), 3.54, 4.88(br, s, carborane C-H protons), 4.34(br, m, uncoordinated H₃), 5.09(br, s) and 5.16(d, J₂₋₃=10 Hz)(uncoordinated H₁ and H₂, respectively), 5.39, 5.78, 6.11(br, coordinated alkenyl protons), 7.23

and 8.17 τ (br,m, methylene protons). $^{13}\text{C}\{^1\text{H}\}$ FTNMR (50.32 MHz, 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$, 22°C): 133.7 (d, $^2J_{\text{P-C}}=13$ Hz, ortho phenyl carbon), 131.3 (s, para carbon), 129.8 (d, $^3J_{\text{P-C}}=10$ Hz, meta carbon) and 31.6 ppm (overlapping doublets, $J_{\text{P-C}_4}=18$ Hz, $^2J_{\text{P-C}_3}=11$ Hz, methylene carbons). At -23°C : 138 (br, uncoordinated C_2), 134-129 (complex multiplet, phenyl carbons), 115 (br, uncoordinated C_1) and 28 ppm (br, methylene carbons). At -78°C : 138.4 (d, $^3J_{\text{P-C}_2}=12$ Hz, uncoordinated C_2), 133.4-127.8 (complex multiplet, phenyl carbons), 115.3 (s, coordinated C_1), 79.3 (s, coordinated C_2), 72.7 (br, carborane carbon), 58.5 (s, coordinated C_1), 41.2 (br, carborane carbon), 35.4 (d, $J_{\text{P-C}_4}'=25$ Hz) and 29.8(s)(methylene carbons of coordinated butenyl side-chain), 27.5 (d, $J_{\text{P-C}_4}=20$ Hz) and 23.2 ppm(s)(methylene carbons of uncoordinated butenyl side-chain). $^{31}\text{P}\{^1\text{H}\}$ FTNMR (81.02 MHz, 20% $\text{C}_6\text{D}_6\text{-C}_6\text{H}_5\text{CH}_3$, 60°C : 59.8(s) and -13.7 ppm(s). At 32°C in 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$: 60.3 and -14.0 ppm (br,s, $W_{1/2} \approx 200$ Hz). At -23°C : 66.8 (br,s, $W_{1/2} \approx 200$ Hz) and 42.3 ppm (br,s, $W_{1/2} \approx 650$ Hz). At -73°C : 68.5 (d, $^2J_{\text{P-P}}=32$ Hz) and 47.2 ppm(d). $^{11}\text{B}\{^1\text{H}\}$ FTNMR (111.8 MHz, CD_2Cl_2 , 44°C): 107.5(1), 17.3(1), 2.5(1), -5.0(2), -6.5(1) and -8.7 ppm(1). At -40°C : 20.4(2), -6.0(2) and -23.2 ppm(3). Infrared spectrum (Nujol): 3045(w), 3525(s,br), 1941(w), 1630(m), 1578(w), 1563(w), 1424(s), 1300(w), 1250(w), 1174(w), 1149(w), 1093(m,sh), 1077(m), 1053(m,sh), 1019(w), 980(m,br), 933(w), 897(m), 886(w), 786(w), 738(s), 692 cm^{-1} (s). In CH_2Cl_2 solution: Two additional weak bands at 1325 and 1285 cm^{-1} .

The complex $[\text{closo-6,6-(DBP)}_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9](\text{IVb})$ was synthesized from DBP (0.080 g, 0.367 mmol) and $[\text{Ru}(\text{PPh}_3)_2\text{C}_2\text{B}_7\text{H}_9]$ (0.100 g, 0.136 mmol) in 2 ml of toluene and worked up as described above. Yield: 0.062 g (70%), m.p.: $91-96^\circ\text{C}$ (dec). Anal. Calcd for $\text{C}_{33.5}\text{H}_{51}\text{B}_7\text{P}_2\text{Ru}$ (IVb-0.5 $\text{C}_6\text{H}_5\text{CH}_3$): C, 58.10; H, 7.47; P, 8.95. Found: C, 57.02; H, 7.39; P, 8.89. ^1H FTNMR (200.133 MHz, CD_2Cl_2 , 22°C): 2.66, 2.82 (m, phenyl protons), 4.82, 5.65, 6.42 (br, alkenyl protons) 7.92 and 8.17 τ (br, methylene protons). At 7°C : 2.61, 2.85 (m, phenyl protons), 4.42, 5.17, 5.98, 6.55 (br, overlapping alkenyl proton resonances), 7.93 and

8.15 τ (br, methylene protons). At -88°C : 2.57, 2.71 (m, phenyl protons), 3.07 (br, carborane C-H), 4.41 (br, uncoordinated H_3), 4.68 (br, uncoordinated H_3'), 4.90 (br, carborane C-H), 5.25 (complex multiplet, uncoordinated H_1 , H_2 , H_1' , H_2'), 6.00, 6.39, 6.68 (br, coordinated H_1' , H_2' , H_3'), 7.99, 8.15 and 8.77 ppm (br, methylene protons). $^{31}\text{C}\{^1\text{H}\}$ FTNMR (50.32 MHz, 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$, 27°C): 132.9 (d, $^2\text{J}_{\text{P-C}}=8$ Hz, ortho phenyl carbon), 131.0 (s, para carbon) 129.6 (d, $^3\text{J}_{\text{P-C}}=8$ Hz, meta carbon) and 28.5 ppm (overlapping doublet and singlet, $\text{J}_{\text{P-C}_4}=15$ Hz, methylene carbons). At -23°C : 138.7 (d, $^4\text{J}_{\text{P-C}_2}=12$ Hz, uncoordinated C_2), 132.4, 130.7, 129.3 (s, phenyl carbons), 115.5 (s, uncoordinated C_1), 28.9 (overlapping doublet and singlet, $\text{J}_{\text{P-C}}=19$ Hz) and 26.6 ppm (d, $\text{J}_{\text{P-C}}=20$ Hz) (methylene carbons). At -83°C : 141.8 (s, uncoordinated C_2'), 138.3 (s, uncoordinated C_2), 133.6, 132.2, 131.0, 130.3, 129.5, 128.6 (br,s, phenyl carbons), 118.8 (s, uncoordinated C_1'), 115.2 (s, uncoordinated C_1), 75.9 and 39.2 (br,s, carborane carbons), 73.3 and 51.5 (s, coordinated C_2' and C_1' respectively), 32.5, 30.9, 29.1, 27.6, 25.1 and 21.3 ppm (br,s, methylene carbons). $^{31}\text{P}\{^1\text{H}\}$ FTNMR (81.02 MHz, 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$, 47°C): 42.8 ppm (br,s, $\text{W}_{1/2} \approx 160$ Hz). At -3°C : 46.4 ppm (br,s, $\text{W}_{1/2} \approx 1200$ Hz). At -88°C : 61.0 (d, $^2\text{J}_{\text{P-P}}=37$ Hz) and 36.5 ppm(d). $^{11}\text{B}\{^1\text{H}\}$ FTNMR (111.8 MHz, CD_2Cl_2 , 44°C): 2.6(3) and -15.8 ppm(4). At -71°C : 24.9(2), -3.4(2) and -19.9 ppm(3). Infrared spectrum (KBr): $\nu_{\text{C}=\text{C}}$ (uncoordinated) at 1633 cm^{-1} .

Preparation of $[\text{closo-6-CO-6,6-(DBP)}_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9](\text{Vb})$

Dry carbon monoxide was bubbled through a solution of $[\text{Ru}(\text{DBP})_2\text{C}_2\text{B}_7\text{H}_9]$ (IIIb) (0.150 g, 0.232 mmol) in toluene (5 ml) yielding a bright yellow solution. Upon addition of petroleum ether (10 ml) and cooling to -15°C for 1 d, yellow crystals of $[\text{closo-6-CO-6,6-(DBP)}_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9](\text{Vb})$ (0.133 g, 87%) were obtained, m.p.: $121\text{-}123^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{31}\text{H}_{47}\text{B}_7\text{P}_2\text{ORu}$: C, 55.21; H, 7.02; P, 9.18. Found: C, 54.78; H, 7.14; P, 9.66. ^1H FTNMR (200.133 MHz, C_6D_6):

2.40 (m, 2H), 2.60 and 2.98 (m, 4H) (phenyl protons), 4.52 (m, 4H, H₃), 5.11 (d, J₁₃ = 11 Hz, 4H, H₁), 5.17 (d, J₂₃ = 24 Hz, 4H, H₂), 6.59 (br, s, 2H, carborane C-H), 8.11 and 8.60 τ (m, 8H, methylene protons). ³¹P{¹H} FTNMR (81.02 MHz, 20% CD₂Cl₂-CH₂Cl₂): 29.7 ppm(s). ¹¹B{¹H} FTNMR (80.5 MHz, CD₂Cl₂): 0.00(2), -9.13(1) and -23.4 ppm(4). Infrared spectrum (KBr): ν_{CO} at 1930(s, br), and $\nu_{\text{C=C}}$ (uncoordinated) at 1632 cm⁻¹(s).

The complex [closo-6-CO-6,6-(MBP)₂-6,2,3-RuC₂B₇H₉](Va) (70 mg, 77%) was similarly prepared from [Ru(MBP)₂(C₂B₇H₉)] (93 mg, 0.13 mmol) at -78°C. m.p.: 174-176°C (melts to a red liquid, darkens at 165°C). Anal. Calcd for C₃₅H₄₃B₇P₂ORu: C, 58.52; H, 6.03; P, 8.62. Found: C, 58.18; H, 6.15; P, 8.33. ¹H FTNMR (200.133 MHz, C₆D₆): 2.42 (m, 4H), 2.89 and 3.08 (m, 8H) (phenyl protons), 4.63 (m, 2H, H₃), 5.18 (d, J₁₃ = 10 Hz, 2H, H₁), 5.25 (d, J₂₃ = 17 Hz, 2H, H₂), 6.70 (br, s, 2H, carborane C-H), 7.79 and 8.04 τ (m, 4H, methylene protons). ³¹P{¹H} FTNMR (81.02 MHz, 20% C₆D₆/C₆H₆): 42.5(s). ¹¹B{¹H} FTNMR (80 MHz, CD₂Cl₂): 0.4(2), -8.2(1) and -22.0 ppm(4). Infrared spectrum (KBr): ν_{CO} at 1932 (s, br) and $\nu_{\text{C=C}}$ (uncoordinated) at 1628 cm⁻¹(w). The carbonylation of IVa was monitored by ³¹P{¹H} FTNMR at several temperatures using rubber septa and a syringe needle. ([IVa] $\approx$ 0.03M). At -78°C in 10% C₆D₆-C₆H₅CD₃: 45.0 ppm(s). At 30°C in 10% C₆D₆-C₆H₆: 45.4 (s, 1), 42.5 (s, 5) and -15.3 ppm (s, 1) ($\approx$ 30% IIb). At 60°C in 10% C₆D₆-C₆H₅CD₃: (The sample was carbonylated at 60°C and the spectrum recorded at 30°C) 45.5 (s, 1), 42.5 (s, 2) and -15.3 ppm (s, 1) ($\approx$ 50% IIb). Infrared spectrum of IIb (Nujol): ν_{CO} at 1970 and 2025 cm⁻¹.

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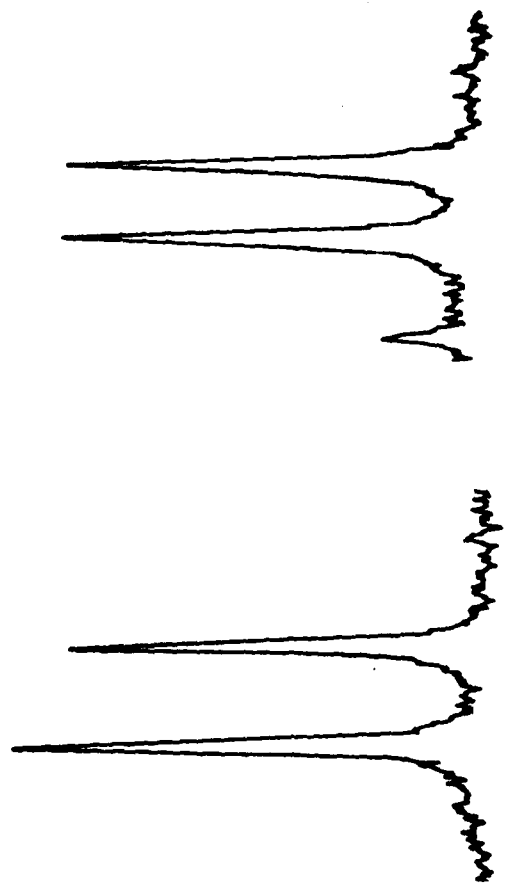
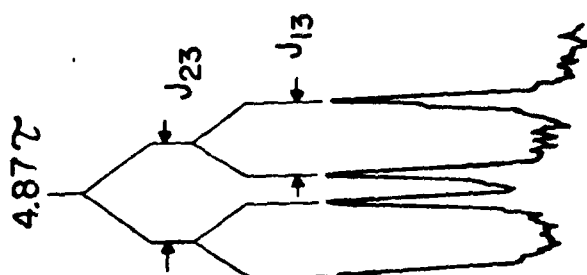
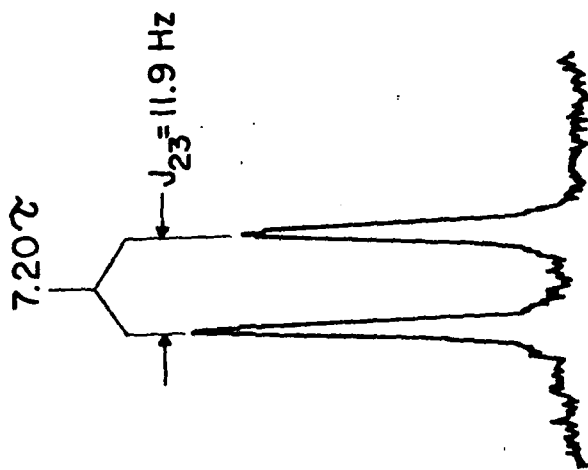
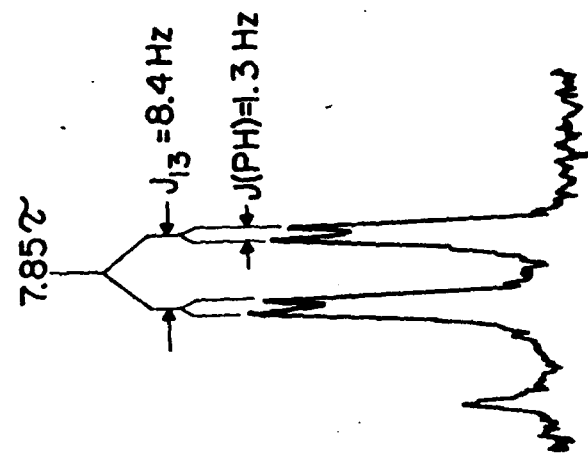
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45. $R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$; $R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/(\sigma F)^2$. The function $\sum w||F_o| - |F_c||^2$ was minimized in least-squares refinement.
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- Figure 1
- A. The 100 MHz ^1H NMR spectrum of $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_9)](\text{IIa})$ in CD_2Cl_2 .
- B. Same with ^{31}P -decoupling (triplet at 4.72 τ is due to residual CHDCl_2)



A

B

Figure 2 Structure of [hyper-closo-2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-Ru-C₂B₇H₇](IIId) and the numbering system employed. Atoms are shown as 50% probability ellipsoids. For the two phenyl rings, only the positions are indicated, and all hydrogen atoms have been removed for clarity.

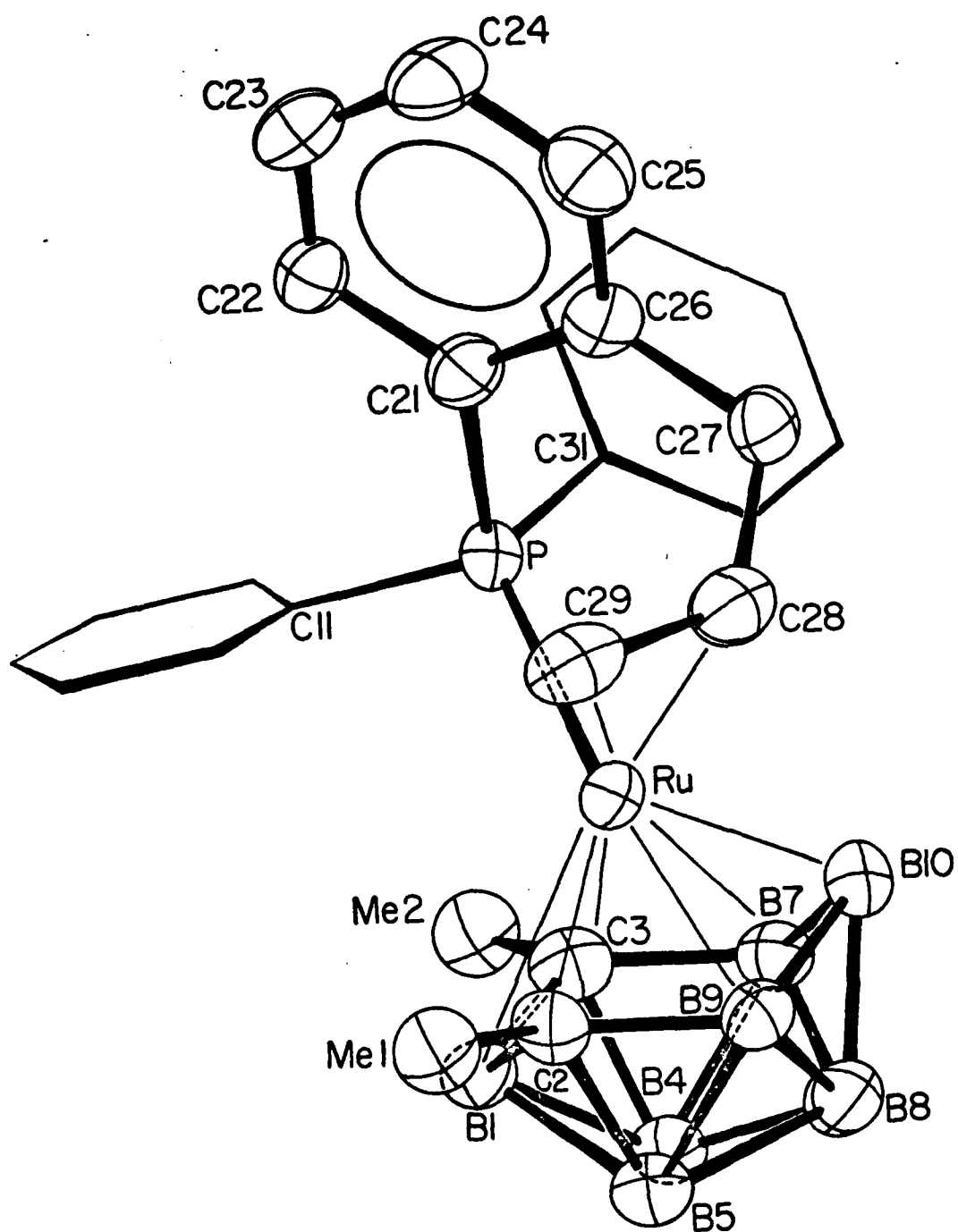


Figure 3 $^{31}\text{P}\{^1\text{H}\}$ FTNMR spectra of [closo-Ru(MBP) $_2\text{C}_2\text{B}_7\text{H}_9$], IVa, in 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$. The spectrum marked by asterisk was recorded in 10% $\text{C}_6\text{D}_6\text{-C}_6\text{H}_5\text{CH}_3$. Scale is in ppm downfield from D_3PO_4 .

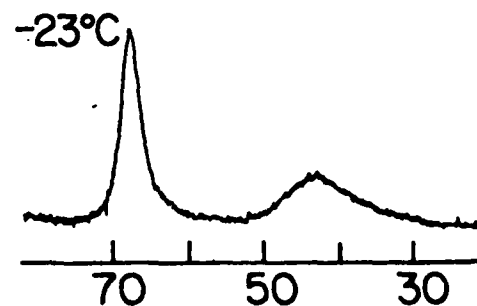
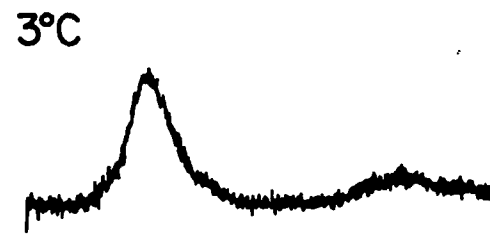
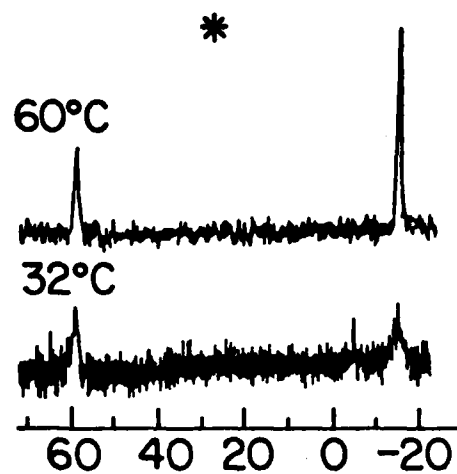
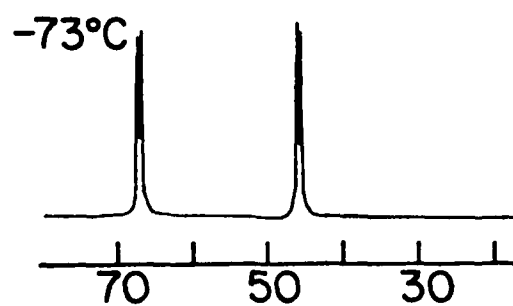
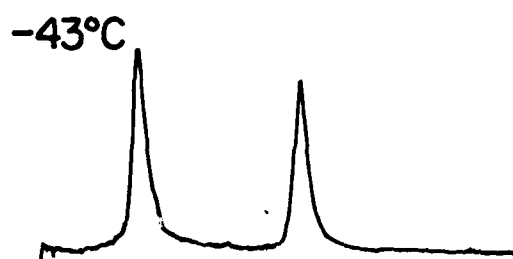
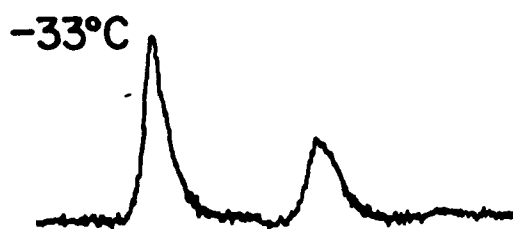


Figure 4 $^{31}\text{P}\{^1\text{H}\}$ FTNMR spectra of [closo-Ru(DBP) $_2\text{C}_2\text{B}_7\text{H}_9$], IVb, in 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$. Scale is in ppm downfield from D_3PO_4 .

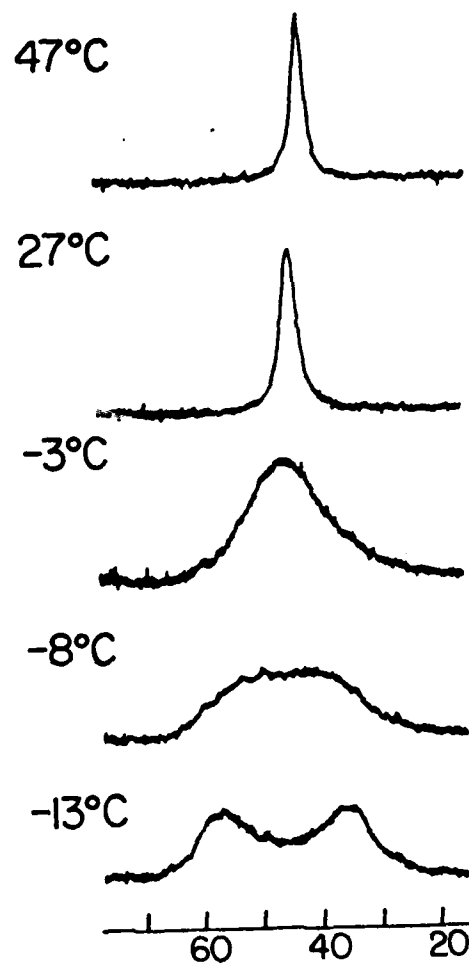
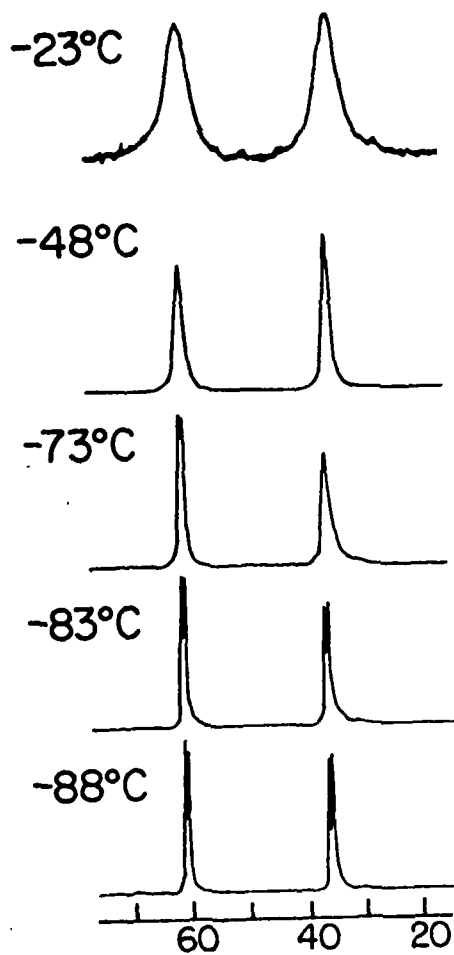
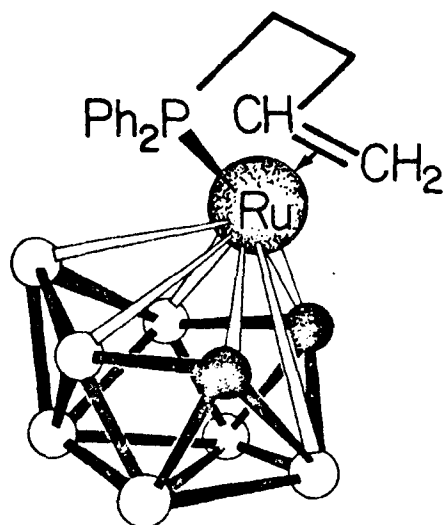


Figure 5 Proposed dynamic processes for [closo-Ru(MBP)₂C₂B₇H₉], IVa.



30°C red solution
hyper-closo



-50°C yellow
solution — closo

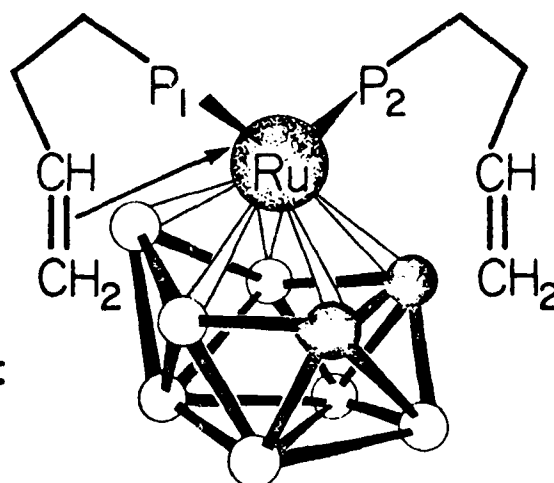
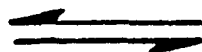
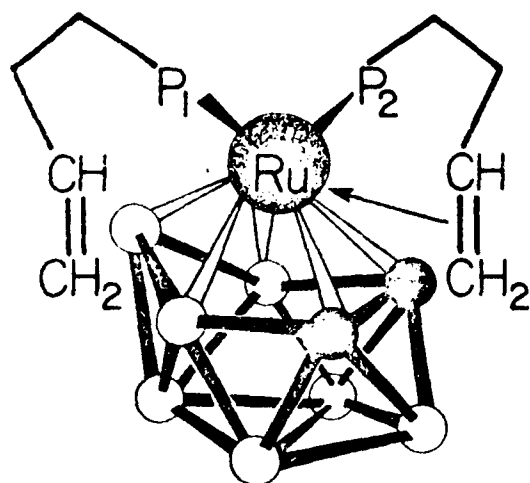


Figure 6 $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra of [closo-Ru(DBP) $_2\text{C}_2\text{B}_7\text{H}_9$], IVb, in 20% $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$ (extra solvent peak at -83°C is due to small amounts of solid $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$).

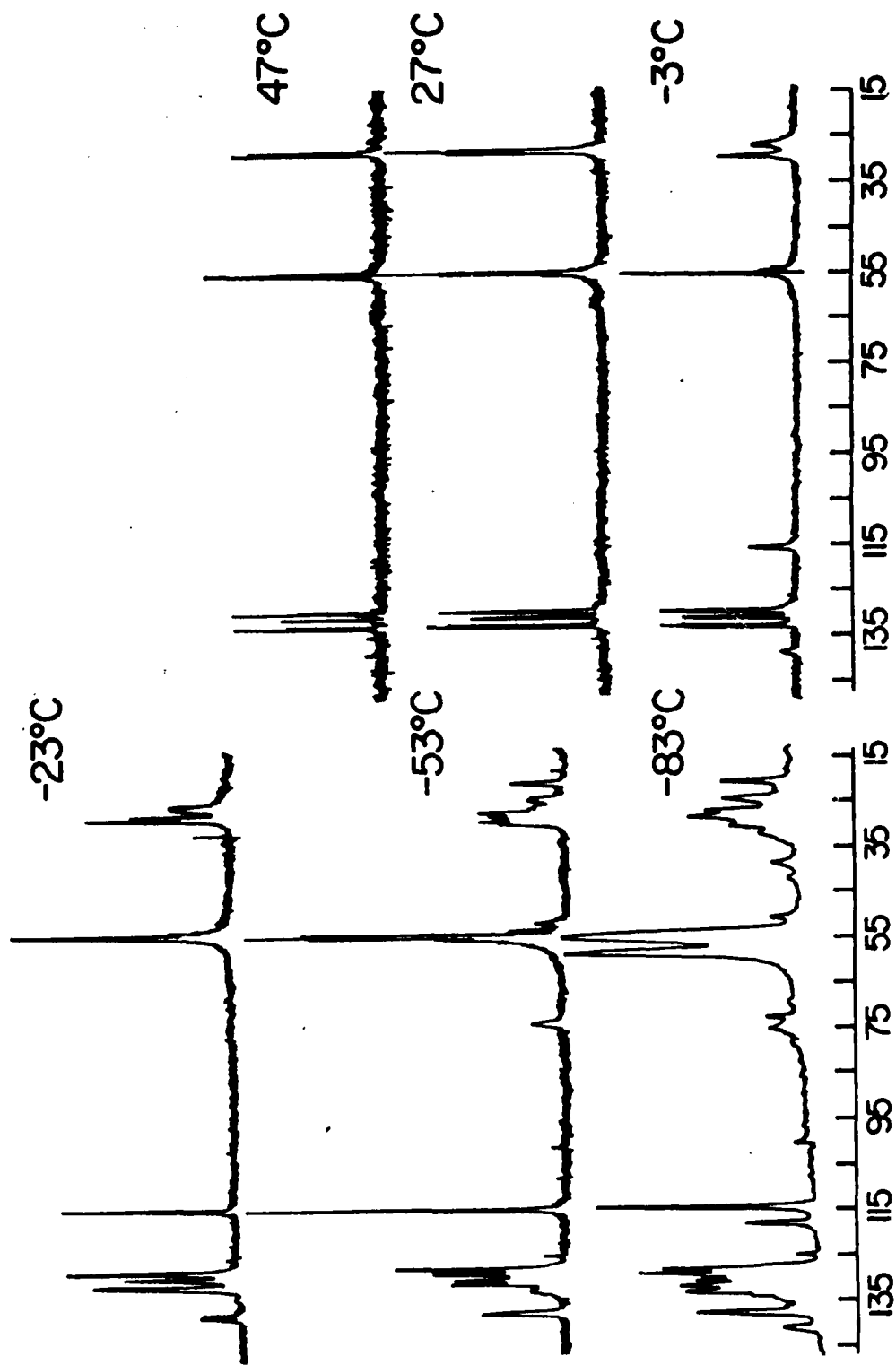


Figure 7 ^1H FTNMR spectra of IVb in CD_2Cl_2 . Resonances marked by asterisks are due to residual CH_2Cl_2 and toluene of crystallization.

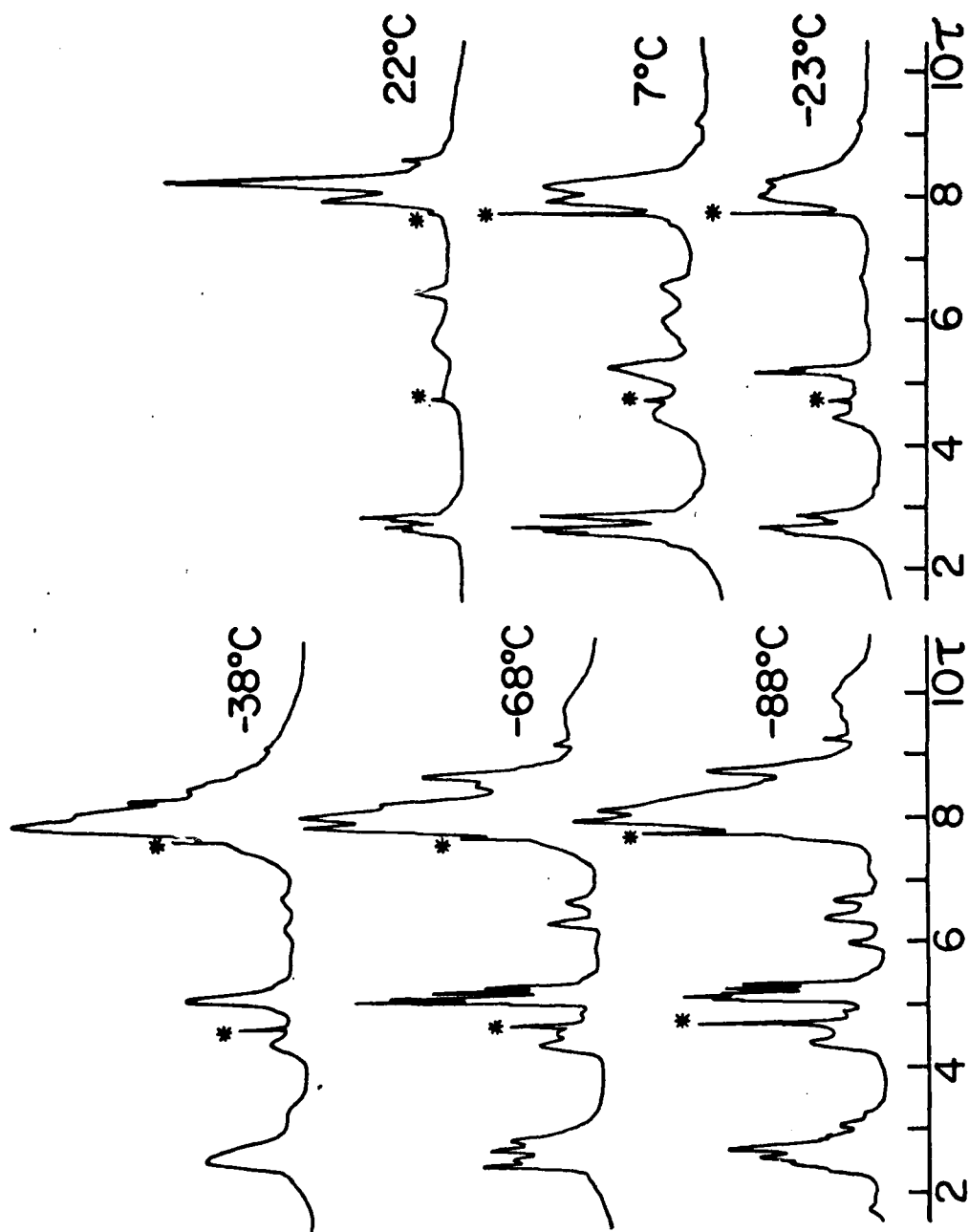
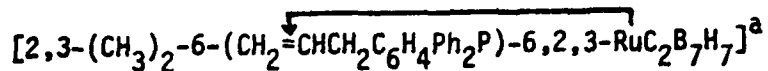


TABLE I

Atomic Positional Parameters in



Atom	<u>x</u>	<u>y</u>	<u>z</u>
Ru	-0.08832(4) ^b	0.23399(2)	0.17700(2)
P	-0.15648(11)	0.23507(7)	0.04155(6)
B(1)	-0.1975(6)	0.3612(3)	0.1937(3)
B(4)	-0.3551(6)	0.2987(4)	0.1727(3)
B(5)	-0.1548(6)	0.3089(3)	0.2843(3)
B(7)	-0.3555(6)	0.2025(4)	0.1242(4)
B(8)	-0.2486(7)	0.2009(4)	0.2395(4)
B(9)	-0.0303(6)	0.2185(3)	0.3050(3)
B(10)	-0.1602(6)	0.1430(3)	0.2111(3)
C(2)	-0.0176(5)	0.3131(3)	0.2798(3)
C(3)	-0.3263(5)	0.2968(3)	0.1072(3)
C(21)	0.0166(5)	0.1999(3)	0.0609(3)
C(22)	0.0605(5)	0.2452(3)	0.0248(3)
C(23)	0.1907(6)	0.2151(3)	0.0393(3)
C(24)	0.2768(6)	0.1394(4)	0.0894(4)
C(25)	0.2346(6)	0.0944(3)	0.1256(4)
C(26)	0.1052(5)	0.1233(3)	0.1126(3)
C(27)	0.0672(6)	0.0757(3)	0.1562(4)
C(28)	0.0936(5)	0.1316(3)	0.2244(3)
C(29)	0.1741(5)	0.2140(3)	0.2580(3)
H(1) ^c	-0.199(7)	0.431(4)	0.184(4)
H(4)	-0.466(7)	0.322(4)	0.150(4)
H(5)	-0.119(7)	0.345(4)	0.341(4)

Table I (cont'd)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
H(7)	-0.470(7)	0.164(4)	0.068(4)
H(8)	-0.295(7)	0.162(4)	0.259(4)
H(9)	0.078(7)	0.184(4)	0.368(4)
H(10)	-0.134(7)	0.074(4)	0.225(4)
H(22)	0.001(8)	0.299(4)	-0.007(4)
H(23)	0.221(8)	0.242(4)	0.015(4)
H(24)	0.360(7)	0.118(4)	0.100(4)
H(25)	0.292(8)	0.044(4)	0.162(4)
H(271)	0.143(7)	0.022(4)	0.188(4)
H(272)	-0.052(8)	0.055(4)	0.109(4)
H(28)	0.121(7)	0.097(4)	0.274(4)
H(291)	0.196(8)	0.242(4)	0.230(4)
H(292)	0.231(8)	0.225(4)	0.316(4)

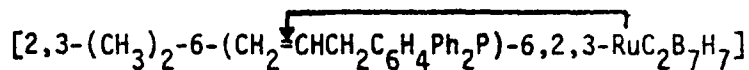
^aAtomic positional parameters for atoms which have been treated as members of rigid groups are listed in Table II.

^bThe numbers given in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits.

^cHydrogen atoms are numbered according to the number of the atom to which they are bonded.

TABLE II

a) Atomic Positional Parameters for Members of Rigid Groups in



<u>Group</u>	<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Phenyl 1	C(11)	-0.1902	0.3495	0.0058
	C(12)	-0.3348	0.3804	-0.0805
	C(13)	-0.3540	0.4699	-0.0995
	C(14)	-0.2285	0.5286	-0.0321
	C(15)	-0.0839	0.4977	0.0543
	C(16)	-0.0647	0.4082	0.0732
	H(12)	-0.425	0.338	-0.129
	H(13)	-0.458	0.492	-0.162
	H(14)	-0.242	0.593	-0.046
	H(15)	0.006	0.540	0.103
	H(16)	0.039	0.386	0.135
Phenyl 3	C(31)	-0.3302	0.1692	-0.0579
	C(32)	-0.3778	0.1763	-0.1381
	C(33)	-0.5033	0.1220	-0.2114
	C(34)	-0.5813	0.0606	-0.2044
	C(35)	-0.5337	0.0536	-0.1242
	C(36)	-0.4081	0.1079	-0.0509
	H(32)	-0.322	0.220	-0.143
	H(33)	-0.538	0.127	-0.269
	H(34)	-0.672	0.022	-0.257
	H(35)	-0.590	0.009	-0.119
	H(36)	-0.374	0.103	0.007
Methyl 1	C(41)	0.1430	0.3679	0.3493
	H(411)	0.149	0.410	0.317
	H(412)	0.143	0.401	0.389
	H(413)	0.243	0.328	0.388

Table II (cont'd)

<u>Group</u>	<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Methyl 2	C(51)	-0.4622	0.3372	0.0130
	H(511)	-0.564	0.336	0.000
	H(512)	-0.438	0.399	0.010
	H(513)	-0.484	0.300	-0.033

b) Group Parameters for Rigid Groups^a

<u>Group</u>	<u>x (Å)</u>	<u>y (Å)</u>	<u>z (Å)</u>	<u>φ (deg)</u>	<u>θ (deg)</u>	<u>ρ (deg)</u>
Phenyl 1	-0.1902(3)	0.3495(1)	0.0058(2)	-59.2(3)	-110.1(1)	-144.2(3)
Phenyl 3	-0.3302(3)	0.1692(2)	-0.0579(2)	120.6(1)	-147.8(1)	-113.6(1)
Methyl 1	0.1429(6)	0.3679(3)	0.3493(3)	138(3)	-132(3)	91(4)
Methyl 2	-0.4622(6)	0.3372(3)	0.0130(3)	-81(2)	172(3)	-114(3)

^aThese parameters are defined in reference 34.

TABLE III

Atomic Thermal Parameters in $[2,3-(\text{CH}_3)_2-6-(\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P})-6,2,3-\text{RuC}_2\text{B}_7\text{H}_7]^a$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	802(5)	255(1)	239(1)	7(2)	310(2)	20(1)
P	866(14)	226(4)	265(4)	-16(7)	349(7)	7(4)
B(1)	1223(80)	301(24)	327(23)	29(33)	467(38)	9(18)
B(4)	1219(81)	429(25)	374(24)	1(36)	527(40)	-29(20)
B(5)	1339(83)	350(25)	344(23)	-8(36)	519(40)	-17(19)
B(7)	1075(77)	423(25)	405(26)	-125(36)	499(41)	-86(21)
B(8)	1497(90)	376(24)	408(26)	-148(38)	623(44)	-56(20)
B(9)	1320(79)	326(26)	305(22)	10(34)	483(37)	24(18)
B(10)	1409(86)	272(23)	411(25)	-105(34)	589(43)	-28(19)
C(2)	1141(66)	293(20)	276(18)	-49(28)	397(31)	-19(14)
C(3)	913(62)	409(21)	289(19)	54(28)	367(31)	10(16)
C(21)	923(60)	271(17)	316(19)	-17(25)	403(30)	-13(14)
C(22)	1176(66)	348(23)	312(19)	-20(28)	445(32)	14(15)
C(23)	1348(74)	496(28)	449(24)	-69(34)	653(39)	6(19)
C(24)	1394(85)	616(31)	555(29)	155(40)	725(46)	54(23)
C(25)	1704(92)	413(26)	576(29)	303(38)	778(47)	136(21)
C(26)	1299(72)	303(20)	415(22)	74(29)	576(36)	27(16)
C(27)	1858(90)	291(21)	591(28)	248(35)	879(47)	149(19)
C(28)	1396(78)	377(23)	426(24)	321(33)	610(39)	161(18)
C(29)	969(67)	539(30)	327(21)	193(33)	381(34)	90(19)

Group	Atom	$B (\text{\AA}^2)$
Phenyl 1	C(11)	2.58(7)
	C(12)	3.48(8)
	C(13)	4.66(11)
	C(14)	5.11(11)
	C(15)	4.75(11)
	C(16)	3.50(8)

Group	Atom	$B (\text{\AA}^2)$
Phenyl 3	C(31)	2.61(7)
	C(32)	3.48(8)
	C(33)	4.44(10)
	C(34)	4.38(10)
	C(35)	4.26(10)
	C(36)	3.37(8)
Methyl 1	C(41)	3.74(9)
Methyl 2	C(51)	3.97(9)

Table III (cont'd)

^aAll values of β have been multiplied by 10^5 . The anisotropic temperature factor expression is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The hydrogen atoms were assigned fixed isotropic thermal parameters: all cage hydrogen atoms had B values fixed at $5.0 \text{ \AA}^2$, all other hydrogen atoms which are not members of rigid groups also were assigned $B=5.0 \text{ \AA}^2$, all methyl group hydrogen atoms were assigned B values $1.0 \text{ \AA}^2$ greater than the B value on the adjacent carbon atom, and all phenyl group hydrogen atoms were assigned B values $0.5 \text{ \AA}^2$ greater than those of the adjacent carbon atoms.

Supplementary Material

TABLE IV

Root-Mean-Square Amplitudes of Vibration and Equivalent B Values^a

Atom	R.M.S. Amplitude ($\text{\AA}$)			Equivalent B ($\text{\AA}^2$)		
	<u>Min.</u>	<u>Median</u>	<u>Max.</u>	<u>Min.</u>	<u>Median</u>	<u>Max.</u>
Ru	0.1581(5)	0.1636(5)	0.1791(5)	1.97	2.11	2.53
P	0.158(2)	0.168(1)	0.176(1)	1.97	2.22	2.45
B(1)	0.186(7)	0.187(7)	0.201(6)	2.72	2.77	3.19
B(4)	0.178(7)	0.202(7)	0.227(7)	2.52	3.22	4.08
B(5)	0.183(7)	0.204(7)	0.207(6)	2.64	3.28	3.39
B(7)	0.173(7)	0.198(7)	0.239(7)	2.37	3.10	4.52
B(8)	0.184(7)	0.195(7)	0.235(7)	2.70	3.00	4.36
B(9)	0.170(7)	0.198(8)	0.208(6)	2.27	3.10	3.42
B(10)	0.168(7)	0.201(7)	0.219(6)	2.24	3.18	3.78
C(2)	0.171(6)	0.184(6)	0.203(6)	2.31	2.68	3.25
C(3)	0.169(6)	0.184(6)	0.220(6)	2.25	2.66	3.84
C(21)	0.167(6)	0.177(6)	0.190(6)	2.20	2.47	2.85
C(22)	0.180(6)	0.193(6)	0.207(6)	2.56	2.94	3.40
C(23)	0.161(6)	0.223(6)	0.244(7)	2.04	3.93	4.70
C(24)	0.172(6)	0.243(6)	0.274(7)	2.34	4.68	5.95
C(25)	0.179(7)	0.226(6)	0.272(6)	2.52	4.05	5.83
C(26)	0.178(6)	0.194(6)	0.216(6)	2.50	2.97	3.68
C(27)	0.163(7)	0.194(6)	0.272(6)	2.09	2.96	5.83
C(28)	0.157(6)	0.192(6)	0.257(6)	1.95	2.91	5.21
C(29)	0.164(6)	0.206(6)	0.259(7)	2.13	3.35	5.29

^aThe equivalent B values are related to the root-mean-square amplitudes of vibration, $(\bar{U}^2)^{1/2}$, by the expression $B = 8\pi^2(\bar{U}^2)$.

Supplementary Material

TABLE V

Structure Factor Amplitudes for $[2,3-(\text{CH}_3)_2-6-(\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P})-6,2,3-\text{RuC}_2\text{B}_7\text{H}_7]$

C. W. Jung, R. T. Baker, C. B. Knobler, and M. F. Hawthorne

The table lists the values of h , k , l , $10 F_o$ and F_c for each observed reflection.

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	
K = 0																
-15	18	222	213	-7	2	500	510	-1	20	184	168	-12	20	506	483	
-15	20	323	300	-7	4	201	223	00	2	450	436	-12	22	218	228	
-15	22	158	131	-7	6	255	269	00	6	824	819	-12	24	217	226	
-14	12	226	228	-7	8	586	608	00	8	927	936	-12	26	310	323	
-14	16	301	302	-7	10	1273	1286	00	10	86	49	-11	2	231	220	
-14	18	174	160	-7	12	508	514	00	12	96	54	-11	4	344	342	
-14	20	153	173	-7	14	751	766	00	14	558	588	-11	6	303	291	
-14	22	301	292	-7	16	779	771	00	16	174	182	-11	8	437	432	
-14	24	186	224	-7	18	295	272	00	18	189	193	-11	10	382	394	
-13	8	283	303	-7	20	485	525	1	2	492	465	-11	11	106	139	
-13	12	293	295	-7	22	341	326	1	4	894	860	-11	12	468	469	
-13	14	411	393	-6	24	306	314	1	6	188	1205	-11	14	319	313	
-13	16	296	311	-6	0	312	308	1	8	485	498	-11	16	403	399	
-13	18	107	93	-6	2	432	446	1	10	451	432	-11	18	262	269	
-13	22	369	358	-6	4	754	766	1	12	528	534	-11	19	168	225	
-12	6	513	531	-6	6	1261	1301	1	14	434	425	-11	22	417	407	
-12	8	561	535	-6	8	208	215	2	16	186	172	-11	24	287	282	
-12	14	131	168	-6	10	887	846	2	2	735	697	-11	26	159	142	
-12	16	375	345	-6	12	698	690	2	4	382	424	-11	28	177	172	
-12	20	401	394	-6	14	549	559	2	6	1083	1091	-10	0	233	207	
-12	22	222	237	-6	16	240	219	2	8	161	154	-10	2	266	262	
-12	26	465	446	-6	18	563	544	2	10	553	563	-10	4	328	314	
-12	28	556	540	-6	20	257	278	2	12	290	290	-10	6	429	411	
-11	6	195	198	-5	22	174	177	2	16	185	193	-10	7	101	115	
-11	8	100	136	-5	24	680	676	3	2	1071	1061	-10	8	361	360	
-11	10	512	488	-5	0	615	619	3	4	1218	1222	-10	10	575	573	
-11	12	636	685	-5	2	1121	1054	3	8	378	370	-10	11	123	152	
-11	14	727	713	-5	4	454	465	3	10	465	470	-10	12	120	112	
-11	18	351	367	-5	6	1232	1292	3	12	409	417	-10	14	401	418	
-11	20	281	297	-5	8	568	549	4	14	123	112	-10	15	317	324	
-11	22	283	282	-5	10	1034	1068	4	2	474	502	-10	16	519	536	
-11	26	264	247	-5	12	661	667	4	4	292	297	-10	18	284	250	
-11	28	647	669	-5	14	211	230	4	6	442	431	-10	19	117	127	
-10	4	124	143	-5	16	736	776	4	8	499	494	-10	20	362	362	
-10	6	129	144	-5	18	482	492	4	10	350	347	-10	22	360	360	
-10	8	544	542	-4	20	173	187	5	2	461	458	-10	24	187	201	
-10	10	529	499	-4	22	155	102	5	4	122	111	-10	26	269	271	
-10	12	836	858	-4	24	1039	1053	5	6	442	450	-9	28	247	244	
-10	14	343	355	-4	0	160	125	5	8	207	225	-9	0	319	308	
-10	18	103	53	-4	2	1339	1337	5	10	296	296	-9	2	117	102	
-10	20	151	159	-4	4	519	545	6	2	209	227	-9	4	122	129	
-10	22	260	260	-4	6	219	217	6	4	228	233	-9	6	714	728	
-10	24	181	158	-4	8	1385	1407	6	6	558	537	-9	8	480	478	
-9	4	825	822	-4	10	713	716	6	8	133	116	-9	9	96	84	
-9	6	320	309	-4	12	743	688	6	10	538	515	-9	10	309	300	
-9	8	609	607	-4	14	547	541	6	12	406	417	-9	12	545	556	
-9	10	839	824	-4	16	699	722	7	14	359	349	-9	14	484	487	
-9	12	178	213	-4	18	226	223	7	16	363	372	-9	15	103	133	
-9	14	119	120	-4	20	499	499	9	18	299	326	-9	16	669	687	
-9	16	905	894	-4	0	1058	1058		20	299	326	-9	17	299	337	
-9	18	319	323	-4	2	553	553	***K = 1***	22	1	257	257	-9	18	125	99
-9	20	155	126	-4	4	1442	1452	-15	24	423	423	-9	20	530	548	
-9	22	225	229	-4	6	980	966	-15	26	441	436	-9	22	132	137	
-9	24	385	373	-4	8	1355	1405	-14	28	428	406	-9	24	206	212	
-9	26	212	210	-4	10	337	320	-14	30	280	278	-9	26	226	228	
-9	28	374	368	-4	12	220	241	-14	32	162	167	-9	28	185	187	
-8	0	902	912	-4	14	610	594	-14	34	154	143	-9	30	399	396	
-8	2	547	543	-4	16	429	425	-14	36	316	323	-9	32	167	180	
-8	4	1043	1038	-4	18	568	551	-13	38	350	355	-9	34	581	596	
-8	6	346	315	-4	20	2110	2152	-13	40	239	224	-9	36	805	798	
-8	8	337	290	-4	22	81	91	-13	42	240	227	-9	38	317	329	
-8	10	492	536	-4	24	1509	1519	-13	44	332	326	-9	40	101	91	
-8	12	830	876	-4	26	1452	1463	-13	46	117	99	-9	42	166	181	
-8	14	106	104	-4	28	593	624	-13	48	106	118	-9	44	104	100	
-8	16	210	211	-4	30	2157	2232	-13	50	139	148	-9	46	227	231	
-8	18	474	490	-4	32	1361	1346	-12	52	223	237	-9	48	482	476	
-8	20	229	208	-4	34	1949	1929	-12	54	350	360	-9	50	131	166	
-8	22	494	501	-4	36	425	422	-12	56	192	206	-9	52	604	621	
-7	0			-4	38	1623	1618	-12	58	161	160	-9	54	130	138	
				-4	40	261	258	-12	60	506	515	-9	56	566	560	
				-4	42	533	535	-12	62	100	74	-9	58	116	149	
				-4	44	472	454	-12	64	319	337	-9	60	480	491	
				-4	46			-12	66	303	302	-9	62	126	154	

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-7	6	637	636	-3	9	124	100	2	8	1096	1073	-11	9	113	127
-7	8	110	100	-3	10	83	64	2	9	103	105	-11	12	414	412
-7	9	114	100	-3	11	233	233	2	10	511	519	-11	13	168	177
-7	10	899	922	-3	12	453	458	2	14	444	439	-11	14	578	564
-7	12	1152	1164	-3	14	568	569	2	16	137	163	-11	15	119	102
-7	13	193	195	-3	15	99	126	3	2	266	282	-11	17	288	310
-7	14	325	358	-3	16	387	405	3	3	148	145	-11	18	125	91
-7	18	664	653	-3	18	312	302	3	4	149	156	-11	20	729	734
-7	20	366	357	-3	20	225	233	3	5	147	145	-11	22	264	268
-7	21	101	109	-3	22	367	362	3	6	131	140	-11	26	224	222
-7	24	198	213	-2	0	433	436	3	8	415	422	-11	26	224	222
-7	26	417	427	-2	1	664	630	3	9	134	135	-10	28	301	324
-6	0	113	80	-2	2	313	784	3	12	317	291	-10	3	165	134
-6	2	807	818	-2	3	176	166	3	14	387	389	-10	4	488	487
-6	3	233	223	-2	4	265	247	4	1	264	240	-10	5	107	82
-6	4	926	936	-2	5	708	692	4	2	280	269	-10	6	584	570
-6	5	102	94	-2	6	1175	1173	4	2	885	913	-10	10	254	237
-6	6	408	410	-2	7	626	575	4	4	222	215	-10	11	106	138
-6	8	276	247	-2	8	996	981	4	6	594	598	-10	12	669	697
-6	10	1239	1286	-2	9	82	80	4	8	159	158	-10	13	308	303
-6	11	516	554	-2	10	450	431	4	10	151	116	-10	14	232	249
-6	12	369	366	-2	11	119	111	4	12	471	476	-10	16	110	113
-6	13	238	237	-2	12	409	432	5	2	137	128	-10	17	109	103
-6	14	173	167	-2	13	104	126	5	4	669	684	-10	18	486	468
-6	15	113	118	-2	14	436	437	5	5	133	118	-10	19	257	291
-6	16	475	472	-2	18	456	436	5	6	278	269	-10	20	441	450
-6	18	650	866	-2	20	215	206	5	10	230	211	-10	22	122	90
-6	20	139	138	-1	0	1798	1818	6	1	150	143	-10	24	145	154
-6	22	187	187	-1	1	61	61	6	2	316	326	-9	26	291	283
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-5	6	225	221	-1	9	80	58	7	6	166	164	-9	11	171	191
-5	7	345	332	-1	10	661	672	7	7	145	106	-9	12	763	777
-5	8	274	283	-1	11	133	109	8	2	386	391	-9	14	131	150
-5	9	264	310	-1	12	434	442					-9	16	120	85
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-5	11	487	487	-1	15	214	222					-9	19	203	198
-5	12	119	116	-1	16	256	255					-9	20	160	160
-5	14	485	468	-1	18	385	396					-9	22	192	194
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-4	13	190	196	1	4	326	349					-8	16	354	335
-4	14	599	601	1	5	102	88					-8	17	102	137
-4	16	991	1028	1	6	177	149					-8	18	703	699
-4	17	142	97	1	7	194	165					-8	19	194	208
-4	20	302	306	1	8	1162	1176					-8	20	195	179
-4	22	430	426	1	10	584	574					-8	22	300	313
-3	0	1422	1431	1	12	199	209					-8	24	390	383
-3	1	229	220	1	14	236	239					-8	26	232	214
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-3	3	547	814	2	1	275	259					-7	0	261	260
-3	4	1024	1018	2	2	863	843					-7	1	242	248
-3	5	1149	1136	2	3	272	251					-7	2	797	809
-3	6	245	242	2	4	474	452					-7	4	305	307
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-7	8	609	617	-4	0	232	239	1	10	190	176	-13	18	232	248
-7	9	109	112	-4	1	210	201	1	11	239	246	-13	20	527	511
-7	10	907	922	-4	2	986	995	1	12	446	451	-13	21	161	178
-7	11	273	291	-4	4	691	711	1	13	107	71	-13	22	139	130
-7	12	260	252	-4	5	291	274	1	14	410	398	-13	23	131	107
-7	14	526	537	-4	6	83	88	1	16	226	197	-13	26	220	213
-7	16	748	763	-4	7	158	155	1	2	555	550	-12	5	197	207
-7	18	403	416	-4	8	628	603	2	3	179	142	-12	6	313	293
-7	20	470	461	-4	9	470	459	2	4	932	941	-12	8	121	100
-7	22	360	372	-4	10	1559	1580	2	5	422	407	-12	10	209	209
-7	24	310	286	-4	11	232	249	2	6	920	940	-12	12	511	520
-6	0	140	137	-4	12	661	652	2	7	374	379	-12	14	156	112
-6	1	288	286	-4	14	106	113	2	8	224	220	-12	16	304	274
-6	2	825	837	-4	15	226	200	2	10	305	311	-12	17	105	102
-6	3	134	136	-4	16	783	785	2	11	231	215	-12	18	283	287
-6	4	421	419	-4	17	224	252	2	12	397	405	-12	20	483	484
-6	5	219	212	-4	18	336	341	2	13	119	97	-12	22	162	162
-6	6	512	536	-4	0	201	215	2	16	223	213	-12	23	114	148
-6	7	262	235	-4	1	706	685	2	2	424	478	-12	24	204	210
-6	8	782	779	-4	2	1057	1071	2	3	162	156	-12	25	140	120
-6	9	266	250	-4	3	254	243	2	4	1203	1202	-12	26	306	287
-6	10	643	667	-4	4	1384	1374	2	5	162	175	-11	4	359	358
-6	11	290	282	-4	5	150	139	2	6	150	147	-11	8	398	396
-6	12	1002	1057	-4	6	289	263	2	8	437	449	-11	10	294	301
-6	13	133	150	-4	7	148	144	2	10	421	425	-11	11	145	148
-6	14	638	652	-4	8	1459	1435	2	12	323	315	-11	12	447	461
-6	16	471	461	-4	10	1038	1031	2	14	179	150	-11	13	138	142
-6	19	248	261	-4	11	233	234	2	1	145	125	-11	14	212	225
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-6	5	122	136	-4	3	242	242	2	10	306	306	-11	23	133	135
-6	6	883	871	-4	4	892	884	2	11	161	153	-11	24	223	227
-6	7	883	94	-4	5	469	454	2	12	145	153	-11	26	228	217
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-6	14	591	592	-4	11	172	174	2	8	307	322	-10	8	439	450
-6	15	240	248	-4	12	173	196	2	10	287	270	-10	9	252	238
-6	16	236	235	-4	14	637	652	2	11	260	266	-10	10	453	449
-6	18	517	507	-4	15	188	224	2	12	401	410	-10	11	138	119
-6	19	129	111	-4	16	542	549	2	3	115	129	-10	14	395	386
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-6	22	211	201	-4	2	785	757	2	6	573	572	-10	18	182	174
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-6	16	311	300	-4	4	229	249	2	13	183	170	-9	14	640	645
-6	17	232	237	-4	5	310	316	2	14	358	354	-9	16	184	172
-6	18	523	517	-4	6	937	969	2	1	170	170	-9	17	226	242
-6	19	169	168	-4	7	375	380	2	2	316	316	-9	19	219	237
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-9	22	193	203	-5	13	167	173	-1	12	459	452	6	8	170	165
-9	24	186	201	-5	14	190	216	-1	14	333	342	7	1	144	138
-9	26	249	259	-5	15	285	292	-1	16	370	359	7	2	453	464
-9	27	218	200	-5	16	596	610	-1	17	134	136	7	4	311	330
-8	0	375	377	-5	17	240	238	-1	18	360	365	7	6	173	180
-8	1	203	203	-5	18	556	576	-1	20	238	260	8	2	377	390
-8	2	328	330	-5	22	245	245	0	1	152	1123	9	2	168	164
-8	3	122	138	-5	23	117	118	0	1	1415	1411				
-8	4	370	355	-5	24	300	293	0	2	585	588	***	K	=	4
-8	6	630	633	-4	0	720	714	0	3	474	472	-14	13	116	91
-8	7	104	117	-4	1	527	526	0	4	819	840	-14	15	155	143
-8	8	194	174	-4	2	1873	1865	0	6	534	502	-14	16	355	370
-8	9	129	115	-4	3	537	521	0	8	851	845	-14	18	181	161
-8	10	116	115	-4	4	173	156	0	9	344	337	-14	20	114	106
-8	11	314	338	-4	6	586	578	0	10	632	624	-14	22	272	266
-8	12	928	944	-4	7	1083	1037	0	11	341	343	-14	23	290	286
-8	13	241	217	-4	8	1328	1295	0	12	495	495	-14	24	236	245
-8	14	651	692	-4	10	834	825	0	15	148	152	-13	9	115	115
-8	16	375	365	-4	12	150	178	0	16	508	502	-13	10	135	131
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-8	19	180	176	-4	14	563	558	1	1	303	282	-13	13	119	123
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-8	25	144	151	-4	18	98	119	1	5	147	133	-13	16	383	383
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-7	18	637	630	-3	15	407	406	2	7	261	273	-12	17	119	107
-7	19	371	376	-3	16	354	376	2	8	756	781	-12	18	149	123
-7	20	442	445	-3	17	122	150	2	9	136	122	-12	20	298	297
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-6	6	457	413	-2	2	198	191	3	4	264	249	-11	8	227	235
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-6	9	201	229	-2	4	1098	1078	3	6	1024	1025	-11	12	330	331
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-6	11	705	678	-2	6	1230	1208	3	8	261	259	-11	14	555	552
-6	12	595	635	-2	7	1036	973	3	12	214	217	-11	15	267	264
-6	15	207	232	-2	8	850	862	3	13	150	177	-11	16	99	89
-6	16	389	377	-2	10	474	457	3	14	377	362	-11	18	202	199
-6	17	384	410	-2	11	323	336	4	1	99	76	-11	19	122	141
-6	18	746	744	-2	12	604	615	4	4	443	447	-11	20	577	550
-6	19	165	195	-2	14	692	709	4	5	197	187	-11	21	211	225
-6	20	125	107	-2	15	178	194	4	6	707	707	-11	22	244	241
-6	21	122	109	-2	17	197	227	4	10	131	121	-11	24	108	96
-6	24	333	354	-2	18	417	443	4	12	416	412	-11	26	182	197
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-5	1	235	236	-1	0	1473	1487	5	4	793	799	-10	4	434	433
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-5	3	532	547	-1	2	542	494	5	6	240	243	-10	7	177	166
-5	4	1021	1011	-1	3	209	198	5	10	174	174	-10	10	270	290
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-5	7	177	192	-1	5	836	809	6	1	194	180	-10	12	677	687
-5	8	354	377	-1	6	1218	1217	6	2	95	112	-10	13	274	270
-5	9	259	273	-1	7	347	351	6	3	150	152	-10	14	104	108
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H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
3	7	232	213	-11	15	250	251	-8	25	130	111	-3	1	988	983
3	8	261	242	-111	16	273	277	-7	0	201	207	-3	2	575	581
3	9	156	144	-111	17	223	217	-7	1	214	215	-3	3	153	156
3	10	188	171	-111	18	235	230	-7	2	122	85	-3	4	335	326
3	11	286	292	-111	19	131	109	-7	3	263	275	-3	5	113	116
3	12	215	219	-111	20	105	100	-7	4	265	256	-3	6	437	413
4	1	404	400	-111	21	189	180	-7	5	234	227	-3	7	752	739
4	2	199	198	-111	22	304	301	-7	6	331	331	-3	8	958	958
4	3	519	530	-111	23	187	189	-7	7	147	160	-3	9	331	349
4	4	152	153	-111	24	167	135	-7	8	195	168	-3	10	198	218
4	5	163	166	-111	25	132	113	-7	9	369	372	-3	11	312	316
4	6	311	308	-111	26	249	256	-7	10	694	680	-3	12	334	293
4	7	326	304	-110	1	150	154	-7	11	557	567	-3	13	502	504
4	8	388	393	-110	2	211	205	-7	12	329	310	-3	14	537	534
4	9	368	375	-110	3	112	108	-7	13	188	187	-3	15	162	166
5	1	186	189	-110	4	255	266	-7	14	332	346	-3	16	229	211
5	2	220	220	-110	5	202	211	-7	15	606	638	-3	17	138	116
5	3	474	475	-110	6	122	165	-7	16	410	386	-3	18	139	135
5	4	266	243	-110	7	226	251	-7	17	226	216	-3	19	801	827
5	5	160	135	-110	8	351	347	-7	18	163	153	-3	20	327	330
5	6	245	240	-110	9	329	336	-7	19	154	133	-3	21	166	143
5	7	241	251	-110	10	347	348	-7	20	126	132	-3	22	535	491
5	8	198	192	-110	11	126	115	-6	21	163	166	-3	23	830	799
5	9	258	261	-110	12	170	194	-6	22	376	380	-3	24	223	236
6	1	372	379	-110	13	472	472	-6	23	842	862	-3	25	622	646
6	2	150	171	-110	14	206	192	-6	24	790	802	-3	26	565	585
6	3	139	150	-110	15	330	341	-6	25	364	341	-3	27	561	589
6	4	112	130	-110	16	202	201	-6	26	150	135	-3	28	328	323
6	5	396	395	-110	17	220	228	-6	27	475	486	-3	29	288	286
6	6	178	176	-110	18	126	127	-6	28	745	735	-3	30	435	445
6	7	187	174	-110	19	181	176	-6	29	608	596	-3	31	410	385
6	8	160	176	-110	20	275	264	-6	30	482	458	-3	32	339	357
6	9	316	310	-110	21	235	258	-6	31	197	196	-3	33	278	294
6	10	288	285	-110	22	235	240	-6	32	143	116	-3	34	217	225
7	1	127	128	-99	23	122	135	-6	33	480	481	-3	35	256	237
7	2	203	187	-99	24	265	262	-6	34	567	551	-3	36	140	149
7	3	247	261	-99	0	231	214	-6	35	209	224	-3	37	199	179
7	4	187	192	-99	1	245	264	-6	36	217	206	-3	38	164	188
7	5	123	132	-99	2	227	240	-6	37	134	151	-3	39	221	186
7	6	184	182	-99	3	194	195	-5	38	293	293	-3	40	861	830
7	7	254	248	-99	4	420	427	-5	39	696	716	-3	41	273	311
7	8	254	268	-99	5	306	288	-5	40	791	788	-3	42	351	361
7	9	182	170	-99	6	226	202	-5	41	139	148	-3	43	469	454
7	10	232	217	-99	7	351	360	-5	42	134	115	-3	44	1042	1025
7	11	296	239	-99	8	298	289	-5	43	198	196	-3	45	428	427
7	12	172	141	-99	9	295	298	-5	44	650	657	-3	46	363	343
7	13	195	193	-99	10	389	372	-5	45	960	944	-3	47	514	509
7	14	148	131	-99	11	253	238	-5	46	859	865	-3	48	410	417
7	15	174	160	-99	12	328	331	-5	47	462	464	-3	49	231	248
7	16	159	171	-99	13	206	202	-5	48	239	243	-3	50	393	406
7	17	144	137	-99	14	479	468	-5	49	210	247	-3	51	273	270
7	18	327	315	-99	15	260	238	-5	50	655	657	-3	52	219	214
7	19	194	173	-99	16	200	190	-5	51	387	389	-3	53	213	240
7	20	213	223	-99	17	227	217	-5	52	272	279	-3	54	226	204
7	21	194	205	-99	18	123	183	-5	53	162	152	-3	55	159	153
7	22	105	106	-99	19	190	200	-5	54	191	193	-3	56	885	863
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7	24	284	271	-99	21	239	226	-5	56	558	562	-3	58	200	225
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8	2	193	193	-99	23	635	650	-5	58	453	468	-3	60	686	661
8	3	196	191	-99	24	105	120	-5	59	93	80	-3	61	337	359
8	4	169	150	-99	25	158	172	-5	60	171	183	-3	62	157	174
8	5	248	246	-99	26	342	367	-5	61	735	711	-3	63	294	295
8	6	275	262	-99	27	584	562	-5	62	628	626	-3	64	535	520
8	7	226	237	-99	28	584	260	-5	63	490	485	-3	65	263	261
8	8	192	181	-99	29	228	213	-5	64	187	164	-3	66	211	191
8	9	180	164	-99	30	172	186	-5	65	372	386	-3	67	298	275
8	10	239	249	-99	31	151	128	-5	66	443	412	-3	68	197	208
8	11	190	200	-99	32	429	442	-5	67	526	537	-3	69	157	137
8	12	238	252	-99	33	456	483	-5	68	150	185	-3	70	315	287
8	13	157	166	-99	34	166	165	-5	69	202	184	-3	71	694	696
8	14	156	152	-99	35	138	116	-5	70	176	186	-3	72	627	646
8	15	156	152	-99	36	138	116	-5	71	661	663	-3	73	269	288

H	L	PO	PC	H	L	PO	PC	H	L	PO	PC	H	L	PO	PC
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1	5	334	352	-12	15	267	273	-7	6	383	364	-4	12	180	194
1	6	245	247	-12	20	247	245	-7	8	529	551	-4	13	319	347
1	7	365	360	-12	21	346	348	-7	9	505	524	-4	14	372	395
1	8	697	702	-12	22	257	259	-7	10	722	749	-4	16	157	136
1	9	589	606	-11	5	213	171	-7	11	268	281	-4	17	245	258
1	10	166	170	-11	6	209	212	-7	12	98	106	-4	18	436	445
1	11	207	203	-11	7	218	239	-7	13	187	210	-4	19	223	241
1	12	173	182	-11	10	120	113	-7	14	228	227	-4	21	114	78
1	14	297	304	-11	12	265	248	-7	15	349	361	-4	22	130	104
1	15	343	317	-11	13	432	441	-7	16	234	253	-3	0	553	561
1	16	227	241	-11	14	359	362	-7	17	364	365	-3	1	174	198
2	1	572	572	-11	15	150	140	-7	18	215	221	-3	2	457	462
2	2	423	417	-11	19	300	307	-7	19	169	161	-3	3	742	757
2	3	319	290	-11	20	229	204	-7	20	183	213	-3	4	513	545
2	4	162	171	-11	21	305	306	-7	21	237	243	-3	5	304	301
2	5	174	182	-10	4	225	231	-7	22	176	172	-3	6	360	345
2	6	394	420	-10	5	323	329	-7	23	153	141	-3	8	209	195
2	7	542	521	-10	6	250	250	-7	24	210	207	-3	9	704	712
2	8	462	466	-10	7	170	188	-6	0	421	418	-3	10	800	829
2	9	343	354	-10	9	135	152	-6	1	538	558	-3	11	216	204
2	13	302	286	-10	10	98	60	-6	2	239	250	-3	13	574	553
2	14	381	393	-10	11	319	321	-6	3	333	330	-3	15	179	171
2	15	269	264	-10	12	441	430	-6	4	120	151	-3	16	303	309
3	1	271	233	-10	13	420	450	-6	5	563	578	-3	17	443	435
3	2	181	212	-10	14	245	235	-6	6	143	156	-3	18	329	329
3	3	227	225	-10	17	249	253	-6	7	282	282	-2	1	490	509
3	5	372	369	-10	18	253	268	-6	8	554	567	-2	2	1170	1180
3	6	439	418	-10	19	377	374	-6	9	604	606	-2	3	667	664
3	7	338	337	-10	20	339	347	-6	10	251	254	-2	4	529	535
3	8	341	328	-10	21	158	166	-6	11	99	98	-2	5	144	137
3	12	227	230	-10	25	180	169	-6	12	228	235	-2	6	363	353
3	13	300	290	-9	3	331	335	-6	13	499	505	-2	7	249	286
4	1	222	223	-9	4	403	408	-6	14	437	465	-2	8	499	508
4	4	321	316	-9	5	393	387	-6	15	322	297	-2	9	861	871
4	5	369	342	-9	8	216	213	-6	16	418	414	-2	10	541	512
4	6	529	539	-9	10	354	378	-6	18	301	319	-2	11	241	269
4	7	179	174	-9	11	530	516	-6	19	239	236	-2	13	116	98
4	11	218	210	-9	12	621	617	-6	20	351	345	-2	14	205	199
5	1	295	304	-9	16	171	188	-6	21	234	251	-2	15	312	309
5	2	113	141	-9	17	268	273	-6	22	260	238	-2	16	370	373
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5	4	506	488	-9	19	412	406	-5	0	616	612	-1	0	921	933
5	5	329	328	-9	20	251	259	-5	1	394	393	-1	1	944	941
5	6	235	245	-9	23	172	173	-5	2	413	397	-1	2	384	409
5	9	128	112	-9	25	272	273	-5	3	114	131	-1	3	309	284
6	1	172	146	-8	1	127	94	-5	4	381	386	-1	4	115	114
6	2	382	394	-8	2	117	121	-5	5	609	621	-1	5	106	114
6	3	350	354	-8	3	497	503	-5	6	97	110	-1	6	274	252
6	4	412	408	-8	4	439	428	-5	7	503	521	-1	7	775	753
6	5	268	259	-8	5	330	318	-5	8	561	550	-1	8	728	713
7	1	372	389	-8	7	306	286	-5	9	218	245	-1	9	372	372
7	2	336	337	-8	8	284	294	-5	10	356	354	-1	10	183	229
7	3	313	305	-8	9	201	199	-5	11	604	607	-1	11	100	79
7	4	200	206	-8	10	608	603	-5	12	411	403	-1	13	297	304
7	6	159	158	-8	11	541	571	-5	13	333	314	-1	14	327	324
8	1	324	314	-8	12	266	261	-5	14	182	188	-1	15	483	477
8	2	337	328	-8	13	214	209	-5	15	224	254	-1	16	279	274
8	3	132	160	-8	14	143	122	-5	17	262	255	0	0	921	904
9	1	209	194	-8	15	133	110	-5	18	400	387	0	1	957	956
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-13	14	194	198	-8	18	400	396	-5	21	149	145	0	6	474	514
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-13	16	159	174	-8	20	111	71	-4	1	334	327	0	8	641	635
-13	17	151	119	-8	21	153	169	-4	2	193	180	0	9	126	119
-13	18	118	117	-8	23	183	180	-4	3	543	573	0	11	110	76
-13	21	202	222	-8	24	209	212	-4	4	540	543	0	12	138	158
-13	22	291	297	-7	25	161	162	-4	5	495	482	0	13	290	286
-13	23	224	230	-7	0	199	209	-4	6	312	295	0	14	386	397
-13	24	165	171	-7	1	349	344	-4	7	338	328	0	15	335	323
-12	8	218	206	-7	2	449	422	-4	8	84	66	0	1	468	466
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H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
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1	6	902	896	-12	17	127	104	-8	20	250	254	-3	6	454	435
1	7	601	597	-12	19	339	343	-8	21	168	178	-3	7	527	581
1	10	119	140	-12	22	220	201	-8	22	175	195	-3	8	497	513
1	11	267	246	-12	23	208	226	-7	1	195	197	-3	9	388	380
1	12	138	131	-11	5	196	218	-7	2	173	162	-3	10	212	235
1	13	329	313	-11	7	108	135	-7	3	227	242	-3	11	234	233
1	14	401	382	-11	9	132	145	-7	4	437	452	-3	12	355	368
1	15	124	115	-11	10	166	162	-7	5	695	681	-3	13	304	322
2	2	502	513	-11	11	313	302	-7	6	321	301	-3	14	291	318
2	3	319	317	-11	12	233	217	-7	10	173	172	-3	15	244	247
2	4	366	398	-11	14	171	165	-7	11	669	657	-3	16	170	196
2	5	779	781	-11	15	331	325	-7	12	409	396	-2	17	647	691
2	6	567	553	-11	17	172	171	-7	13	433	437	-2	18	501	503
2	7	129	113	-11	18	200	195	-7	14	134	153	-2	19	518	490
2	8	159	153	-11	19	190	183	-7	15	104	100	-2	0	621	626
2	9	135	147	-11	21	210	202	-7	17	198	198	-2	5	502	493
2	10	276	266	-11	22	194	169	-7	18	470	426	-2	6	881	860
2	11	189	210	-11	23	180	153	-7	19	351	343	-2	7	438	422
2	12	270	267	-10	3	217	222	-7	20	299	300	-2	8	108	110
2	13	227	204	-10	4	238	250	-7	22	135	122	-2	10	376	379
2	14	156	167	-10	6	253	255	-7	23	128	111	-2	11	265	255
3	1	491	486	-10	7	235	214	-6	2	330	328	-2	12	337	331
3	2	421	423	-10	8	134	116	-6	3	640	634	-2	13	327	334
3	3	231	238	-10	9	232	228	-6	4	217	234	-2	14	240	215
3	4	422	434	-10	10	273	267	-6	5	110	92	-2	15	273	263
3	5	407	405	-10	11	306	321	-6	7	257	271	-2	17	201	208
3	7	180	184	-10	13	243	231	-6	9	294	298	-2	18	150	134
3	8	330	315	-10	14	377	383	-6	10	560	598	-1	19	222	264
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3	10	230	240	-10	16	196	175	-6	12	379	378	-1	2	481	488
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3	2	190	195	-10	22	114	122	-6	17	570	602	-1	6	685	722
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3	1	162	155	-9	16	194	197	-5	12	131	93	0	6	734	725
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3	3	129	109	-9	19	263	256	-5	15	261	260	0	8	239	219
3	4	153	137	-9	20	267	265	-5	16	516	515	0	9	421	427
3	5	398	406	-9	21	323	332	-5	17	324	334	0	11	296	275
3	6	230	237	-9	22	161	165	-5	18	175	169	0	12	277	287
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3	1	150	147	-8	1	212	207	-4	2	583	584	0	15	254	277
3	2	125	118	-8	2	164	161	-4	3	486	510	0	16	176	161
3	3	137	159	-8	3	106	99	-4	5	159	134	0	17	221	224
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-13	19	272	252	-8	11	414	420	-4	17	321	297	1	9	438	419
-13	20	241	248	-8	12	498	522	-4	21	179	181	1	10	121	85
-13	21	218	215	-8	13	469	482	-3	0	408	371	1	11	143	142
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-12	13	259	239	-8	16	119	79	-3	3	93	89	1	15	250	256
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H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
2	2	280	271	-	10	257	270	-	7	331	322	-	10	109	81	-	10	109	81
2	3	337	320	-	11	540	532	-	8	303	306	-	13	117	105	-	13	117	105
2	4	201	195	-	12	398	410	-	9	227	213	-	14	188	210	-	14	188	210
2	5	195	157	-	15	108	136	-	10	286	270	-	15	462	459	-	15	462	459
2	6	477	476	-	16	130	92	-	11	459	474	-	0	363	383	-	0	363	383
2	7	538	554	-	17	304	288	-	12	348	334	-	1	978	963	-	1	978	963
2	8	346	321	-	18	267	251	-	13	359	346	-	2	126	60	-	2	126	60
2	9	263	270	-	19	405	403	-	14	372	367	-	3	131	116	-	3	131	116
2	10	140	130	-	20	172	175	-	15	397	387	-	6	605	600	-	6	605	600
2	11	253	239	-	0	139	139	-	18	294	290	-	7	570	588	-	7	570	588
2	12	309	288	-	3	436	457	-	19	379	377	-	8	222	252	-	8	222	252
2	13	221	202	-	4	366	332	-	20	159	156	-	9	240	231	-	9	240	231
2	14	453	431	-	5	316	290	-	21	137	137	-	10	131	134	-	10	131	134
2	15	460	450	-	6	100	107	-	22	155	152	-	12	109	110	-	12	109	110
2	16	224	207	-	7	332	336	-	0	155	152	-	13	256	280	-	13	256	280
2	17	257	254	-	8	378	388	-	1	267	283	-	14	235	232	-	14	235	232
2	18	124	83	-	9	476	486	-	2	694	694	-	15	245	232	-	15	245	232
2	19	306	309	-	10	287	310	-	3	391	383	-	1	494	492	-	1	494	492
2	20	435	423	-	11	118	128	-	4	425	421	-	2	94	75	-	2	94	75
2	21	407	410	-	12	176	175	-	5	150	150	-	4	246	270	-	4	246	270
2	22	186	197	-	13	194	206	-	6	234	233	-	5	432	426	-	5	432	426
2	23	294	283	-	14	187	176	-	7	364	364	-	6	660	658	-	6	660	658
2	24	408	409	-	15	345	349	-	8	527	543	-	7	441	432	-	7	441	432
2	25	181	202	-	16	340	340	-	9	490	486	-	12	320	328	-	12	320	328
2	26	164	159	-	17	209	191	-	10	115	138	-	13	271	298	-	13	271	298
2	27	248	254	-	18	225	227	-	11	222	180	-	14	238	215	-	14	238	215
2	28	415	413	-	19	121	111	-	12	139	136	-	2	218	226	-	2	218	226
2	29	256	252	-	20	137	151	-	13	380	343	-	3	203	230	-	3	203	230
2	30	212	222	-	21	123	104	-	14	260	239	-	4	492	472	-	4	492	472
2	31	169	162	-	22	289	270	-	15	265	260	-	5	472	491	-	5	472	491
2	32	158	174	-	23	249	246	-	16	112	122	-	6	260	304	-	6	260	304
2	33	384	372	-	24	322	321	-	17	485	468	-	7	188	170	-	7	188	170
2	34	194	196	-	25	219	237	-	18	324	329	-	8	191	228	-	8	191	228
2	35	196	213	-	26	324	338	-	19	535	551	-	9	296	305	-	9	296	305
2	36			-	27	106	86	-	20	466	449	-	10	128	131	-	10	128	131
2	37			-	28	223	244	-	21	343	370	-	11	206	189	-	11	206	189
2	38			-	29	576	576	-	22	356	357	-	12	243	235	-	12	243	235
2	39			-	30	419	417	-	23	343	357	-	13	209	213	-	13	209	213
2	40			-	31	142	141	-	24	929	931	-	14	180	173	-	14	180	173
2	41			-	32	280	276	-	25	347	312	-	15	454	426	-	15	454	426
2	42			-	33	169	140	-	26	490	499	-	16	358	331	-	16	358	331
2	43			-	34	317	298	-	27	141	107	-	17	450	456	-	17	450	456
2	44			-	35	280	300	-	28	179	204	-	18	123	149	-	18	123	149
2	45			-	36	393	372	-	29	180	170	-	19	224	249	-	19	224	249
2	46			-	37	150	123	-	30	449	436	-	20	173	193	-	20	173	193
2	47			-	38	242	239	-	31	182	195	-	21	293	297	-	21	293	297
2	48			-	39	277	247	-	32	131	117	-	22	359	362	-	22	359	362
2	49			-	40	179	200	-	33	781	765	-	23	382	398	-	23	382	398
2	50			-	41	437	423	-	34	745	743	-	24	379	385	-	24	379	385
2	51			-	42	396	395	-	35	614	627	-	25	181	159	-	25	181	159
2	52			-	43	293	299	-	36	285	280	-	26	108	129	-	26	108	129
2	53			-	44	405	399	-	37	281	258	-	27	325	339	-	27	325	339
2	54			-	45	294	295	-	38	802	812	-	28	150	165	-	28	150	165
2	55			-	46	257	281	-	39	208	256	-	29	266	256	-	29	266	256
2	56			-	47	384	388	-	40	390	386	-	30	190	152	-	30	190	152
2	57			-	48	520	522	-	41	161	178	-	31	432	436	-	31	432	436
2	58			-	49	233	237	-	42	134	159	-	32	287	275	-	32	287	275
2	59			-	50	241	225	-	43	355	353	-	33	220	231	-	33	220	231
2	60			-	51	349	341	-	44	300	280	-	34	129	119	-	34	129	119
2	61			-	52	298	297	-	45	315	321	-	35	200	200	-	35	200	200
2	62			-	53	228	243	-	46	122	95	-	36	200	223	-	36	200	223
2	63			-	54	141	121	-	47	310	328	-	37	301	300	-	37	301	300
2	64			-	55	158	161	-	48	798	804	-	38	226	219	-	38	226	219
2	65			-	56	302	288	-	49	390	388	-	39	179	194	-	39	179	194
2	66			-	57	268	268	-	50	365	388	-	40	143	125	-	40	143	125
2	67			-	58	163	155	-	51	194	179	-	41	436	424	-	41	436	424
2	68			-	59	140	155	-	52	388	354	-	42	141	123	-	42	141	123
2	69			-	60	276	310	-	53	160	147	-	43	186	183	-	43	186	183
2	70			-	61	244	258	-	54	657	645	-	44			-	44		
2	71			-	62	380	363	-	55	409	416	-	45			-	45		
2	72			-	63	362	352	-	56	595	590	-	46			-	46		
2	73			-	64	312	328	-	57			-	47			-	47		
2	74			-	65			-	58			-	48			-	48		
2	75			-	66			-	59			-	49			-	49		
2	76			-	67			-	60			-	50			-	50		
2	77			-	68			-	61			-	51			-	51		
2	78			-	69			-	62			-	52			-	52		
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2	82			-	73			-	66			-	56			-	56		
2	83			-	74			-	67			-	57			-	57		
2	84			-	75			-	68			-	58			-	58		
2	85			-	76			-	69			-	59			-	59		
2	86			-	77			-	70			-	60			-	60		
2	87			-	78			-	71			-	61			-	61		
2	88			-	79			-	72			-	62			-	62		
2	89			-	80			-	73			-	63			-	63		
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2	91			-	82			-	75			-	65			-	65		
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2	93			-	84			-	77			-	67						

H	L	PO	PC	H	L	PO	PC	H	L	PO	PC	H	L	PO	PC
-12	15	136	99	-6	8	211	224	-1	7	448	452	-10	12	391	380
-12	16	119	71	-6	9	331	319	-11	9	486	483	-10	14	123	78
-12	17	137	138	-6	10	393	391	-11	10	175	210	-10	19	340	343
-12	19	286	274	-6	11	620	614	-11	11	279	306	-10	21	157	157
-11	9	246	240	-6	12	206	199	-11	12	116	144	-9	3	257	243
-11	11	245	260	-6	14	137	145	-11	13	199	188	-9	5	321	333
-11	12	211	220	-6	16	242	232	-11	14	122	98	-9	9	122	102
-11	14	115	123	-6	17	490	486	-11	17	290	294	-9	11	414	412
-11	15	282	281	-6	18	248	266	0	1	546	521	-9	13	187	185
-11	17	203	228	-6	19	238	227	0	2	239	231	-9	15	127	129
-11	18	155	158	-6	1	469	442	0	3	454	443	-9	17	272	273
-11	19	234	231	-5	2	240	236	0	4	289	281	-9	18	203	184
-11	21	183	158	-5	3	703	729	0	5	386	415	-9	19	455	436
-10	4	182	176	-5	5	126	133	0	8	360	354	-8	0	130	110
-10	7	226	231	-5	8	240	235	0	9	149	183	-8	1	127	133
-10	9	158	170	-5	9	443	463	0	9	527	507	-8	3	415	393
-10	10	247	244	-5	10	518	533	0	10	217	184	-8	4	135	171
-10	11	206	197	-5	11	336	346	0	11	243	256	-8	5	179	180
-10	13	208	188	-5	13	128	102	0	12	169	179	-8	7	112	85
-10	14	121	119	-5	15	311	296	0	13	161	189	-8	9	267	257
-10	15	342	352	-5	17	586	574	0	15	258	272	-8	11	423	417
-10	16	162	149	-4	1	650	668	1	1	909	883	-8	13	146	136
-10	17	273	274	-4	2	440	431	1	2	212	226	-8	14	162	162
-10	18	243	242	-4	3	435	444	1	4	169	183	-8	15	295	283
-10	21	340	320	-4	4	190	163	1	6	541	517	-8	17	321	318
-10	22	136	158	-4	6	103	108	1	7	138	106	-8	19	138	112
-10	23	170	160	-4	7	388	395	1	8	433	437	-8	21	166	166
-9	3	209	198	-4	8	456	460	1	9	281	297	-7	2	249	241
-9	5	201	189	-4	9	762	762	1	9	484	470	-7	3	144	142
-9	6	221	233	-4	10	199	198	1	11	139	129	-7	6	448	418
-9	7	378	396	-4	11	173	177	1	12	168	143	-7	7	144	149
-9	9	285	261	-4	12	93	74	2	2	692	672	-7	8	441	430
-9	10	277	273	-4	13	187	213	2	2	222	209	-7	9	122	78
-9	12	127	136	-4	14	114	80	2	3	268	294	-7	11	347	347
-9	13	471	476	-4	15	479	502	2	7	624	614	-7	13	170	154
-9	14	294	296	-4	16	326	331	2	8	250	260	-7	15	309	294
-9	15	347	327	-4	17	351	347	2	9	214	222	-7	16	225	217
-9	17	251	236	-4	19	137	148	2	11	370	360	-7	17	291	275
-9	19	227	234	-3	0	152	167	3	2	105	78	-7	19	403	403
-9	20	129	128	-3	1	1040	1029	3	5	305	306	-7	21	214	213
-9	21	255	246	-3	2	421	421	3	6	223	230	-6	0	237	231
-9	22	162	163	-3	4	120	109	3	7	513	523	-6	1	358	370
-8	1	122	125	-3	5	256	252	3	9	108	100	-6	2	220	210
-8	5	416	418	-3	7	658	654	3	10	110	66	-6	5	216	235
-8	6	243	226	-3	8	238	260	4	1	102	101	-6	6	209	207
-8	7	263	251	-3	9	525	534	4	2	119	120	-6	7	430	432
-8	9	165	184	-3	11	498	501	4	3	152	150	-6	8	220	236
-8	11	289	293	-3	12	258	259	4	5	481	488	-6	9	432	438
-8	12	168	152	-3	13	224	231	4	6	212	199	-6	11	296	300
-8	13	582	582	-3	14	123	130	4	7	273	279	-6	12	121	95
-8	15	259	258	-3	15	417	383	5	1	197	182	-6	13	392	392
-8	18	226	216	-3	16	240	221	5	3	347	346	-6	14	126	140
-8	19	461	465	-3	19	189	192	5	4	276	295	-6	15	300	301
-8	20	175	167	-2	0	687	669	5	5	423	431	-6	16	117	136
-8	21	172	168	-2	1	357	363	5	5	193	177	-6	17	187	193
-7	1	160	150	-2	3	328	311	6	2	136	138	-6	19	316	293
-7	2	115	87	-2	4	282	313	6	3	414	392	-6	21	179	145
-7	3	207	213	-2	5	390	417	6	5	194	195	-6	0	171	163
-7	4	461	440	-2	6	266	267	7	1	153	148	-5	1	492	477
-7	5	554	575	-2	7	674	671	7	2	162	161	-5	3	121	143
-7	6	136	156	-2	8	119	111	7	3	227	266	-5	5	423	402
-7	7	384	341	-2	9	122	118	7	1	212	202	-5	6	209	202
-7	11	528	544	-2	11	433	417	8	8			-5	7	326	329
-7	12	251	250	-2	12	199	159					-5	8	365	362
-7	13	314	326	-2	13	289	317					-5	9	279	277
-7	17	212	253	-2	14	246	245	-12	15	290	293	-5	10	271	259
-7	18	144	153	-2	15	246	249	-11	13	113	124	-5	11	447	434
-7	19	320	322	-2	17	303	279	-11	15	432	397	-5	12	132	141
-7	20	182	185	-1	0	233	235	-11	19	131	128	-5	13	340	337
-6	3	116	127	-1	2	360	390	-11	21	249	238	-5	14	230	231
-6	4	457	473	-1	3	533	532	-11	2	368	348	-5	15	382	367
-6	5	236	212	-1	4	291	285	-10	6	133	134	-5	16	155	161
-6	7	356	340	-1	5	384	373	-10	7	131	142	-5	17	110	103
-6		364	363	-1	6	371	357	-10	12	280	275	-5	19	362	339
										214	234				

H	L	PO	PC	H	L	PO	PC	H	L	PO	PC	H	L	PO	PC
-4	0	156	139	1	12	123	133	-7	3	336	343	-2	14	176	168
-4	1	119	154	1	13	332	328	-7	5	468	462	-2	15	228	190
-4	2	140	116	2	2	265	267	-7	6	182	156	-1	0	158	174
-4	3	470	485	2	3	233	207	-7	7	146	166	-1	1	190	218
-4	4	156	167	2	5	539	530	-7	8	136	121	-1	2	348	348
-4	5	411	400	2	6	220	213	-7	10	113	97	-1	3	522	524
-4	6	112	74	2	7	172	178	-7	11	482	490	-1	5	226	227
-4	7	399	413	2	9	226	269	-7	12	110	103	-1	7	318	318
-4	8	435	458	2	11	194	188	-7	13	289	269	-1	9	287	296
-4	9	279	277	2	12	174	165	-7	17	196	160	-1	10	257	228
-4	10	377	368	3	1	317	305	-7	19	378	364	-1	11	145	106
-4	11	653	658	3	3	270	288	-6	0	131	105	-1	12	273	257
-4	13	202	213	3	5	478	479	-6	2	147	129	0	13	337	354
-4	14	111	112	3	6	134	116	-6	3	576	564	0	1	424	448
-4	15	233	245	3	7	132	117	-6	4	129	104	0	3	117	121
-4	17	359	364	3	9	264	256	-6	5	432	442	0	4	328	310
-4	19	247	232	3	10	175	141	-6	6	184	169	0	5	109	70
-3	1	235	219	4	1	524	506	-6	9	262	262	0	8	185	178
-3	2	353	365	4	2	124	131	-6	10	105	58	0	9	502	547
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-3	7	215	196	5	1	267	262	-6	18	121	103	1	3	421	393
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-3	10	133	94	5	4	110	116	-5	2	197	195	1	8	242	233
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-3	16	148	128	6	4	121	118	-5	10	333	331	2	3	277	264
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-2	1	673	697	***K	=	13	****	-5	17	512	487	2	11	193	151
-2	2	370	361	-11	11	331	334	-4	1	548	571	3	1	390	424
-2	3	572	583	-11	15	260	262	-4	3	504	487	3	3	192	157
-2	6	96	70	-11	16	115	125	-4	5	96	69	3	5	277	257
-2	7	139	135	-11	17	140	146	-4	6	123	108	3	7	378	412
-2	8	122	106	-11	18	156	120	-4	7	166	168	4	2	130	124
-2	9	730	710	-11	19	246	213	-4	8	243	247	4	5	503	509
-2	11	111	92	-10	7	245	254	-4	9	588	583	4	7	219	216
-2	15	256	262	-10	9	176	200	-4	10	293	277	5	3	230	256
-2	17	335	310	-10	10	141	126	-4	11	157	152	5	5	406	383
-1	0	307	272	-10	11	232	217	-4	13	307	305	6	2	145	112
-1	1	826	851	-10	13	222	207	-4	15	417	413	6	3	333	330
-1	2	107	111	-10	14	142	126	-4	16	135	148	6	4	119	63
-1	3	388	387	-10	15	271	253	-4	17	301	281	7	1	206	205
-1	4	179	185	-10	17	221	221	-3	0	366	354	***K	=	14	****
-1	7	471	479	-10	18	165	140	-3	1	645	644	-10	11	235	238
-1	8	234	246	-10	19	181	135	-3	2	310	310	-10	13	355	347
-1	9	511	507	-9	5	258	222	-3	4	157	166	-9	5	399	386
-1	10	128	113	-9	7	194	184	-3	5	163	172	-9	11	366	383
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-1	14	166	162	-9	9	195	209	-3	7	450	440	-9	15	120	123
-1	15	350	359	-9	13	422	442	-3	8	164	163	-9	17	169	199
0	1	734	748	-9	14	144	138	-3	9	493	500	-9	19	326	303
0	2	152	177	-9	15	232	243	-3	11	303	301	-8	3	406	385
0	6	317	346	-9	17	180	180	-3	13	180	178	-8	4	162	129
0	7	740	729	-9	19	183	160	-3	15	376	412	-8	5	185	159
0	8	231	213	-9	21	274	277	-3	16	203	193	-8	9	158	183
0	9	159	140	-8	5	444	455	-2	0	160	167	-8	11	430	427
0	10	123	99	-8	6	106	86	-2	1	601	604	-8	15	320	307
0	13	264	248	-8	7	201	231	-2	3	285	296	-8	17	353	341
0	15	244	236	-8	9	191	194	-2	4	175	159	-8	19	136	158
1	1	493	470	-8	11	179	197	-2	5	377	346	-7	1	175	196
1	3	143	117	-8	13	533	525	-2	6	135	142	-7	3	353	356
1	5	274	301	-8	15	149	159	-2	7	272	294	-7	7	265	285
1	6	301	319	-8	18	117	136	-2	8	136	110	-7	8	111	69
1	7	492	472	-8	19	318	340	-2	10	169	144	-7	9	345	327
1	8	122	117	-8	20	121	113	-2	11	252	277	-7	10	123	112
1	9	110	109	-8	21	166	154	-2	12	226	227	-7	11	227	222
1	11	140	132	-7	1	138	111	-2	13	194	213	-7	11	227	222

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-7	13	340	358	2	3	164	159	-2	13	187	155	-2	7	113	120
-7	15	320	319	2	5	464	443	-1	3	317	304	-2	9	436	449
-7	17	272	275	2	9	216	185	-1	5	357	386	-2	11	139	139
-7	18	179	160	3	1	372	366	-1	7	302	270	-1	1	668	644
-6	1	344	332	3	3	321	312	-1	9	172	156	-1	7	386	402
-6	3	155	155	3	4	109	80	-1	11	247	265	-1	9	355	368
-6	5	420	401	3	5	415	385	-1	13	373	371	-1	12	122	58
-6	7	406	391	3	7	192	163	0	1	307	311	0	1	327	324
-6	9	343	328	4	1	333	331	0	2	137	137	0	2	131	106
-6	11	227	236	4	3	307	304	0	3	280	285	0	5	200	218
-6	13	312	288	4	4	154	144	0	5	334	320	0	7	509	502
-6	14	159	121	4	5	121	125	0	9	501	494	0	9	119	168
-6	15	327	307	4	7	338	303	0	11	248	247	1	3	180	172
-6	17	261	254	5	1	132	149	1	1	442	448	1	5	310	314
-6	18	114	97	5	2	143	121	1	3	208	222	1	7	360	358
-6	19	261	264	5	3	245	237	1	5	281	272	1	9	120	159
-5	0	113	75	5	5	151	150	1	7	362	360	2	1	167	155
-5	1	400	404	*** K = 15 ****				1	9	314	316	2	3	158	163
-5	3	200	172	-9	7	183	178	1	11	225	239	2	5	359	376
-5	5	433	425	-9	9	153	166	2	1	438	423	3	1	267	261
-5	7	385	396	-9	13	374	357	2	3	134	139	3	3	212	229
-5	9	173	186	-9	14	119	69	2	7	470	456	3	5	322	316
-5	11	222	219	-9	15	123	159	2	9	131	139	4	1	281	264
-5	13	416	408	-9	17	161	166	3	1	298	306	4	3	299	294
-5	15	362	370	-8	5	362	357	3	3	146	157	5	1	179	175
-5	16	318	304	-8	7	306	287	3	5	235	231	*** K = 17 ****			
-5	18	186	159	-8	9	179	206	4	7	324	301	-7	7	149	169
-4	1	164	134	-8	10	107	86	5	9	408	412	-7	11	384	375
-4	2	111	118	-8	11	160	166	*** K = 16 ****				-7	13	136	132
-4	3	404	400	-8	13	420	411	-8	1	201	203	-6	3	341	331
-4	4	304	287	-8	3	274	252	-8	9	421	388	-6	5	227	202
-4	5	281	284	-7	5	385	385	-8	11	182	186	-6	9	235	234
-4	7	438	446	-7	6	142	145	-8	15	292	333	-6	11	335	339
-4	8	157	155	-7	7	202	187	-7	3	237	224	-5	1	125	180
-4	11	588	593	-7	10	115	108	-7	7	377	383	-5	3	368	350
-4	13	253	258	-7	11	435	427	-7	9	156	157	-5	8	126	103
-4	15	121	100	-7	13	232	235	-7	11	241	269	-5	9	385	388
-4	17	372	372	-7	17	197	187	-7	13	211	215	-5	10	153	144
-3	3	749	734	-6	3	432	440	-7	15	225	233	-4	11	214	214
-3	4	254	246	-6	5	245	242	-6	1	269	262	-4	0	121	119
-3	5	229	199	-6	8	179	162	-6	5	221	231	-4	1	373	383
-3	7	149	154	-6	9	243	250	-6	7	342	332	-4	3	262	236
-3	9	365	371	-6	10	133	138	-6	9	185	188	-4	5	158	147
-3	11	355	362	-6	11	379	392	-6	13	115	83	-4	7	167	187
-3	15	115	109	-6	17	349	317	-6	14	285	299	-4	9	480	498
-3	17	365	358	-5	1	243	221	-6	15	334	343	-4	13	150	128
-2	1	503	519	-5	3	386	395	-5	1	195	205	-3	0	164	179
-2	2	240	228	-5	9	478	510	-5	3	263	285	-3	1	454	436
-2	3	520	536	-5	11	225	209	-5	5	317	328	-3	5	109	132
-2	5	141	157	-5	15	149	152	-5	7	143	151	-3	7	409	376
-2	7	239	232	-5	17	357	362	-5	9	331	346	-3	8	134	112
-2	9	518	509	-4	1	602	584	-5	11	186	175	-3	9	291	285
-2	10	179	167	-4	3	194	223	-5	13	276	270	-3	11	184	195
-2	11	121	124	-4	5	135	123	-5	15	138	151	-3	13	201	196
-2	15	326	302	-4	7	145	156	-4	1	440	445	-2	1	293	288
-1	1	681	682	-4	9	633	616	-4	3	237	236	-2	3	342	313
-1	3	285	295	-4	13	149	162	-4	5	314	310	-2	4	115	131
-1	6	98	50	-4	15	300	302	-4	7	125	102	-2	5	202	199
-1	7	471	479	-4	16	117	84	-4	9	375	389	-2	7	431	438
-1	9	425	424	-3	1	544	542	-4	11	213	190	-2	11	240	236
-1	10	159	155	-3	5	255	264	-4	13	163	148	-1	2	111	80
-1	13	112	127	-3	6	133	127	-3	1	133	130	-1	3	243	264
0	2	583	602	-3	7	329	332	-3	2	531	562	-1	5	291	292
0	3	144	130	-3	9	337	332	-3	4	111	102	-1	7	242	242
0	5	342	345	-3	11	222	224	-3	5	184	201	0	9	133	135
0	7	638	619	-3	12	140	118	-3	7	201	199	0	11	238	243
0	9	166	154	-3	13	173	177	-3	9	471	480	0	1	392	380
0	13	274	261	-3	15	348	338	-3	11	258	260	0	3	290	292
1	2	177	130	-2	1	507	525	-2	13	144	113	0	5	359	328
1	5	404	380	-2	3	204	217	-2	0	385	387	0	9	253	258
1	7	505	523	-2	5	227	198	-2	1	426	404	1	1	372	378
1	9	214	191	-2	7	494	497	-2	3	182	191	1	3	196	170
1	11	124	158	-2	11	265	258	-2	5			1	5	158	174

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
1	7	261	258	-4	5	116	150	-1	1	468	468	-2	6	120	76
2	1	298	323	-4	7	276	272	-1	7	314	306	-2	7	346	309
2	3	236	197	-4	10	137	123	-1	9	229	240	-1	2	151	149
3	1	161	165	-4	11	275	281	0	1	263	267	-1	3	321	313
3	3	185	172	-3	2	125	126	0	7	362	373	-1	3	125	136
***	K = 18	***	***	-3	3	357	357	1	5	265	280	-1	4	180	200
-6	7	186	198	-3	4	143	116	3	1	142	131	0	5	218	246
-6	9	302	283	-3	5	153	153	***	K = 19	***	***	0	1	247	243
-5	3	130	127	-3	7	164	150	-4	7	154	133	0	5	282	281
-5	5	221	209	-3	9	333	346	-3	1	311	306	1	1	373	335
-5	7	205	203	-3	11	230	214	-3	2	120	119	1	3	148	161
-5	9	165	149	-2	1	338	339	-3	2	268	271	2	1	233	235
-5	11	245	234	-2	2	136	160	-3	7	167	168				
-4	1	206	202	-2	3	173	178	-2	1	168	178				
-4	3	333	325	-2	5	123	103	-2	3	207	225				
				-2	9	341	315								

TABLE VI

Interatomic Distances ($\text{\AA}$)

Ru-B10	2.023(5)	B9-H9	1.10(6)
Ru-C2	2.097(4)	B9-B10	1.795(7)
Ru-C29	2.167(4)	B10-H10	1.06(6)
Ru-C3	2.185(4)	C2...C3	2.692(6)
Ru-C28	2.191(4)	B7...B9	2.826
Ru-B9	2.340(5)	B10...C2	2.833
Ru-P	2.418(1)	B10...C3	2.806
Ru-B7	2.466(5)	B10...B4	2.951
Ru-B1	2.488(5)	B10...B5	2.956
P-C21	1.826(4)	C21-C22	1.398(6)
P-C11	1.824	C21-C26	1.405(6)
P-C31	1.828	C22-H22	0.96(6)
B1-H1	1.03(6)	C22-C23	1.390(6)
B1-C3	1.609(6)	C23-H23	0.92(6)
B1-C2	1.635(6)	C23-C23	1.331(7)
B1-B4	1.814(7)	C24-H24	0.89(6)
B1-B5	1.820(7)	C24-C25	1.380(7)
C2-Me1	1.527	C25-H25	0.93(6)
C2-B9	1.584(6)	C25-C26	1.396(6)
C2-B1	1.635(6)	C26-C27	1.498(6)
C2-B5	1.685(6)	C27-H271	1.01(6)
C3-Me2	1.519	C27-H272	0.99(6)
C3-B7	1.578(7)	C27-C28	1.530(6)
C3-B1	1.609(6)	C28-H28	1.02(6)
C3-B4	1.688(6)	C28-C29	1.406(7)
B4-H4	1.06(6)	C29-H291	0.92(6)
B4-B5	1.743(7)	C29-H292	0.92(6)
B4-B3	1.790(8)		
B4-B7	1.800(8)		
B5-H5	1.11(6)		
B5-B9	1.801(7)		
B5-B8	1.808(7)		
B7-H7	1.10(6)		
B7-B8	1.797(7)		
B7-B10	1.807(7)		
B8-H8	1.08(6)		
B8-B10	1.782(7)		
B8-B9	1.814(7)		

TABLE VII

Average Bond Lengths

<u>Atoms</u>	<u>No.</u>	<u>Range, (Å)</u>	<u>Av.^a (Å)</u>
Ru-C	4	2.097(4)-2.191(4)	2.16(4)
Ru-B	4	2.023(5)-2.488(5)	2.33(22)
C-C ^b	6	1.380(7)-1.405(6)	1.392(10)
B-B	12	1.743-1.820	1.80(2)
C-B	8	1.584(6)-1.688(6)	1.63(10)
B-H	7	1.06(6)-1.11(6)	1.08(2)
C-H	9	0.89(6)-1.02(6)	0.95(5)

$$^a \sigma = \left[\sum_{i=1}^N (X_i - \bar{X})^2 / (N-1) \right]^{1/2}$$

^b C-C for distances within phenyl ring of o-allylphenyl group

TABLE VIII

Interatomic Angles (deg)

B10-Ru-C2	86.9(2)	C3-B1-C2	112.1(4)
B10-Ru-C29	109.5(2)	C3-B1-B4	58.7(3)
B10-Ru-C3	83.6(2)	C3-B1-B5	105.8(4)
B10-Ru-C28	82.4(2)	C3-B1-Ru	60.0(2)
B10-Ru-B9	47.9(2)	C2-B1-B4	105.8(3)
B10-Ru-P	126.7(1)	C2-B1-B5	58.1(3)
B10-Ru-B7	46.2(2)	C2-B1-Ru	56.7(2)
B10-Ru-B1	94.5(2)	B4-B1-B5	57.3(3)
C2-Ru-C29	90.2(2)	B4-B1-Ru	95.5(3)
C2-Ru-C28	115.0(2)	B5-B1-Ru	93.3(3)
C2-Ru-C3	77.9(2)		
C2-Ru-B9	41.4(2)	B9-C2-Me1	120.9
C2-Ru-P	144.2(1)	B9-C2-B1	115.5(3)
C2-Ru-B7	88.7(2)	B9-C2-B5	66.9(3)
C2-Ru-B1	40.7(2)	B9-C2-Ru	77.5(2)
C29-Ru-C3	162.0(2)	B1-C2-Me1	120.2
C29-Ru-C28	37.6(2)	B1-C2-B5	66.4(3)
C29-Ru-B9	91.4(2)	B1-C2-Ru	82.6(2)
C29-Ru-P	89.3(1)	B5-C2-Me1	120.0
C29-Ru-B7	155.7(2)	B5-C2-Ru	113.3(3)
C29-Ru-B1	124.5(2)	Ru-C2-Me1	126.7
C3-Ru-C28	160.3(2)		
C3-Ru-B9	88.5(2)	B7-C3-Me2	119.2
C3-Ru-P	92.5(1)	B7-C3-B1	117.2(4)
C3-Ru-B7	39.1(2)	B7-C3-B4	66.8(3)
C3-Ru-B1	39.6(2)	B7-C3-Ru	80.1(2)
C28-Ru-B9	92.3(2)	B1-C3-Me2	118.7
C28-Ru-P	84.9(1)	B1-C3-B4	66.7(3)
C28-Ru-B7	123.1(2)	B1-C3-Ru	80.4(2)
C28-Ru-B1	155.6(2)	B4-C3-Me2	117.9
B9-Ru-P	174.4(1)	B4-C3-Ru	111.7(3)
B9-Ru-B7	72.0(2)	Ru-C3-Me2	150.4
B9-Ru-B1	68.6(2)		
P-Ru-B7	105.5(1)	H4-B4-C3	123(3)
P-Ru-B1	115.4(1)	H4-B4-B5	124(3)
B7-Ru-B1	66.6(2)	H4-B4-B8	123(3)
		H4-B4-B7	122(3)
Ru-P-C11	107.4	H4-B4-B1	128(3)
Ru-P-C21	113.8(1)	C3-B4-B5	105.9(3)
Ru-P-C31	101.2	C3-B4-B8	102.5(3)
C11-P-C21	103.4	C3-B4-B7	53.7(3)
C11-P-C31	108.3	C3-B4-B1	54.6(3)
C21-P-C31	101.2	B5-B4-B8	61.6(3)
		B5-B4-B7	107.9(4)
H1-B1-C3	120(3)	B5-B4-B1	61.5(3)
H1-B1-C2	119(3)	B8-B4-B7	60.1(3)
H1-B1-B4	127(3)	B8-B4-B1	104.9(3)
H1-B1-B5	125(3)	B7-B4-B1	97.7(3)
H1-B1-Ru	132(3)		

Table VIII (cont'd)

H5-B5-C2	117(3)	B10-B9-B5	110.4(4)
H5-B5-B4	128(3)	B10-B9-B8	59.2(3)
H5-B5-B9	121(3)	B10-B9-Ru	56.8(2)
H5-B5-B8	129(3)	B5-B9-B8	60.0(3)
H5-B5-B1	125(3)	B5-B9-Ru	98.9(3)
C2-B5-B4	106.8(3)	B8-B9-Ru	94.3(3)
C2-B5-B9	53.9(3)		
C2-B5-B8	103.4(3)	H10-B10-B8	120(3)
C2-B5-B1	55.5(2)	H10-B10-B9	118(3)
B4-B5-B9	107.1(4)	H10-B10-B7	132(3)
B4-B5-B8	60.5(3)	H10-B10-Ru	132(3)
B4-B5-B1	61.2(3)	B8-B10-B9	60.9(3)
B9-B5-B8	60.3(3)	B8-B10-B7	60.1(3)
B9-B5-B1	97.4(3)	B8-B10-Ru	107.2(3)
B8-B5-B1	103.9(3)	B9-B10-B7	103.3(3)
		B9-B10-Ru	75.3(2)
		B7-B10-Ru	79.9(3)
H7-B7-C3	122(3)		
H7-B7-B8	124(3)	C22-C21-C26	119.7(4)
H7-B7-B4	124(3)	C22-C21-P	122.3(3)
H7-B7-B10	117(3)	C26-C21-P	118.0(3)
H7-B7-Ru	136(3)		
C3-B7-B8	106.8(4)	H22-C22-C23	122(4)
C3-B7-B4	59.5(3)	H22-C22-C21	117(4)
C3-B7-B10	111.8(3)	C21-C22-C23	120.6(4)
C3-B7-Ru	60.8(2)		
B8-B7-B4	59.7(3)	H23-C23-C24	117(4)
B8-B7-B10	59.3(3)	H23-C23-C22	123(4)
B8-B7-Ru	90.6(3)	C24-C23-C22	119.8(4)
B4-B7-B10	109.8(4)		
B4-B7-Ru	96.7(3)	H24-C24-C25	117(4)
B10-B7-Ru	53.9(2)	H24-C24-C23	122(4)
		C25-C24-C23	120.0(4)
H8-B8-B10	117(3)		
H8-B8-B4	121(3)	H272-C27-H271	108(5)
H8-B8-B7	122(3)	H272-C27-C26	110(4)
H8-B8-B5	124(3)	H272-C27-C28	103(4)
H8-B8-B9	127(3)	H271-C27-C26	108(3)
B10-B8-B4	111.4(4)	H271-C27-C28	109(3)
B10-B8-B7	60.6(3)	C26-C27-C28	113.8(4)
B10-B8-B5	110.8(3)		
B10-B8-B9	59.9(3)	H25-C25-C24	123(4)
B4-B8-B7	60.2(3)	H25-C25-C26	115(4)
B4-B8-B5	57.9(3)	C24-C25-C26	121.5(4)
B4-B8-B9	104.7(3)		
B7-B8-B5	105.2(4)	C25-C26-C21	118.5(4)
B7-B8-B9	103.0(3)	C25-C26-C27	120.5(4)
B5-B8-B9	59.7(3)	C21-C26-C27	121.0(4)
H9-B9-C2	123(3)	H28-C28-C29	110(3)
H9-B9-B10	110(3)	H28-C28-C27	115(3)
H9-B9-B5	131(3)	H28-C28-Ru	107(3)
H9-B9-B8	126(3)	C29-C28-C27	125.2(4)
H9-B9-Ru	126(3)	C29-C28-Ru	70.3(2)
C2-B9-B10	113.8(3)	C27-C28-Ru	120.5(3)
C2-B9-B5	59.2(3)		
C2-B9-B8	107.5(4)		
C2-B9-Ru	61.1(2)		

Table VIII (cont'd)

H292-C29-H291	124(6)
H292-C29-C28	114(6)
H292-C29-Ru	104(4)
H291-C29-C28	119(4)
H291-C29-Ru	109(4)
C28-C29-Ru	72.1(2)

TABLE IX

Selected Least-Squares Planes and Interplanar Angles

a) Distances of Atoms from Least-Squares Planes^a, ($\text{\AA} \times 10^3$)

Atom	Plane I ^b	Plane II	Plane III	Plane IV	Plane V	Plane VI	Plane VII ^c
Ru	-1595	-1103	-1776		-2077	-2088	21*
P	-3304	-976	-3464	-48	-2232	-2026	-1483
B(1)	616	864	-1596				-14*
C(2)	6*	1*	-1345		-2138	-2581	1338
C(3)	-6*	-1*	-1351		-4220	-4267	-1353
B(4)	1468	2*	0*				-831
B(5)	1466	-2*	0*				910
B(7)	6*	1424	0*		-4126	-3881	-1423
B(8)	955	-1564	1003				20*
B(9)	-6*	-1439	0*		-1925	-2092	1399
B(10)	-820	-2466	221				-27*
C(21)				2*			-764
C(22)				-1*			-894
C(23)				4*			-357
C(24)				-3*			299
C(25)				-1*			433
C(26)				3*	329	722	-86
C(27)				70	53*	548	129
C(28)	-3255				-184*	19*	939
C(29)	-2968				59*	-80*	1642
H(28)					72*	322	1430
H(291)					239	32*	1538
H(292)					305	29*	2400

b) Interplanar Angles, Deg

[B(7), B(9), B(10)]-[Plane I]	47.2 ^o
[B(1), C(2), C(3)]-[Plane I] ^d	42.7 ^o
[B(7), B(8), B(9)]-[Plane I]	58.2 ^o

^aAtoms used to define the least-squares planes are indicated by asterisks. ^bPlanes are defined as $Ax + By + Cz = D$, where x, y, z are orthogonal coordinates (in Angströms) and the axes parallel a, b , and c^* . Plane I $-0.8734x + 0.4115y + 0.2606z = 7.117$
 Plane II $-0.0396x + 0.9958y - 0.0827z = 4.5789$
 Plane III $-0.7658x - 0.5598y + 0.3164z = 3.5757$

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ABSTRACT

Reactions of [hyper-closo-2- R^1 -3- R^2 -6,6-(PPh_3)₂-6,2,3-RuC₂B₇H₇](I) with (*o*-styryl)diphenylphosphine ($R^1,2=H,CH_3$; $R^1=H, R^2=Ph$), (*o*-allylphenyl)diphenylphosphine ($R^1,2=H,CH_3$) and $Ph_{3-n}P(CH_2CH_2CH=CH_2)_n$ ($n=1,2$; $R^1,2=CH_3$) afforded the 16e⁻ ruthenacarborane complexes [hyper-closo-RuL(C₂B₇H₇R¹R²)] (IIa-g), in which the alkenyl phosphine (L) functions as a bidentate ligand. The crystal structure of [2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇](IIId) was determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a=11.740(3)$ Å, $b=15.185(5)$ Å, $c=21.748(7)$ Å, $\beta=137.43(2)^\circ$ and $Z=4$. Refinement of 4168 independent reflections with $I>3\sigma(I)$ led to a final value of $R=4.0\%$. The structure of this complex may best be described in terms of a C₂B₇ fragment of arachno-geometry which occupies nine vertices of an eleven-vertex octadecahedron with a ruthenium atom in a "non-vertex" position and within bonding distance of six atoms in the open face. The observed distortion from the common ten-vertex bicapped square antiprismatic structure is thought to be a result of the perturbation of the polyhedral skeletal bonding induced by the sixteen-electron Ru^{II} center. Reaction of (IIb) with carbon monoxide displaced the coordinated alkenyl side-chain to yield the 18e⁻ Ru^{II} complex [closo-6,6-(CO)₂-6-L-6,2,3-RuC₂B₇H₉](IIIa) {L=(*o*-allylphenyl)-diphenylphosphine}.

Reactions of $Ph_{3-n}P(CH_2CH_2CH=CH_2)_n$ ($n=1,2$) with [hyper-closo-6,6-(PPh_3)₂-6,2,3-RuC₂B₇H₉] produced the fluxional complexes [closo-6,6-L₂-6,2,3-RuC₂B₇H₉] (IVa-b) which exhibit butenyl side-chain exchange and undergo closo-hyper-closo equilibria as evidenced by variable temperature multinuclear FTNMR spectroscopy. The reactions of (IVa-b) with carbon monoxide are also discussed.

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