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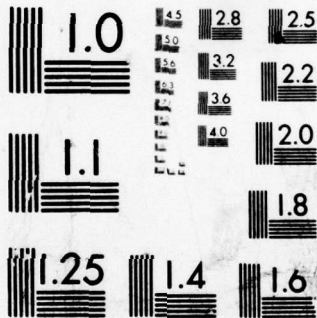
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⁽⁶⁾ METALLOCARBORANES IN CATALYSIS 47.
THE MOLECULAR STRUCTURE OF $3\text{-PPH}_3\text{-3-CO-4-C}_5\text{H}_5\text{N-3,1,2-RhC}_2\text{B}_2\text{H}_4$.

by

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M. Frederick Hawthorne*

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METALLOCARBORANES IN CATALYSIS 4.

THE MOLECULAR STRUCTURE OF 3-PPh₃-3-CO-4-C₅H₅N-3,1,2-RhC₂B₉H₁₀

By

Raymond G. Teller, Joseph J. Wilczynski, and
M. Frederick Hawthorne*

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Sir:

The utility of rhodium carborane complexes as catalysts for industrially important processes has been demonstrated.¹⁻⁵ As part of our research effort in this area¹⁻⁵ we recently prepared $3,3-(PPh_3)_2-4-C_5H_5N-3,1,2-RhC_2B_9H_{10}$ (I) and its carbonyl derivative $3-PPh_3-3-CO-4-C_5H_5N-3,1,2-RhC_2B_9H_{10}$ (II) in order to ascertain their catalytic activity. Structural parameters for either of these molecules are of interest due to the paucity of data on formal Rh(I) carboranes, and the renewed interest in the orientation of ML_2 fragments of d^8 metals with respect to the open face of a carborane anion⁶⁻¹⁰ in metallocarborane complexes. We therefore undertook the structure determination of (II) by single crystal X-ray diffraction.

The parent complex (I) was prepared in the following manner: NaH and $9-C_5H_5N-7,8-C_2B_9H_{11}$ ¹¹ were stirred in tetrahydrofuran (THF) until H_2 ceased to evolve. This solution was then immediately introduced to a THF solution of $RhCl(PPh_3)_3$ and was heated at reflux for one hour in an inert atmosphere. The product was isolated as blue-black crystals from ethanol/THF. An infrared spectrum of the complex showed bands due to coordinated phosphine and carborane fragments. The carbonyl adduct (II) is rapidly formed in high yield by passing CO through a THF solution of (I).

Crystal data: $[P(C_6H_5)_3]CORhC_2B_9H_{10}C_5H_5N(II)$ $M = 603.7$, triclinic, space group $P\bar{1}$, $a = 10.743(4)$, $b = 10.339(4)$, $c = 14.210(5)$ Å, $\alpha = 96.11(2)^\circ$, $\beta = 79.11(2)^\circ$, $\gamma = 115.25(2)^\circ$, $Z = 2$, $\mu(Mo)_{K\alpha} = 7.56$ cm⁻¹. Data were collected on a Picker FACS-I four circle diffractometer at $-154^\circ C$ and the structure was solved by standard Patterson and Fourier techniques. Full matrix least squares refinement of all atomic positions converged to an R factor of 0.037 (2874 reflections).

The molecule is illustrated in the figure along with some pertinent interatomic distances. The most noteworthy feature of the structure is the configuration of the $\text{Rh}(\text{CO})(\text{PPh}_3)$ fragment with respect to the carborane monoanion. A comparison of bond distances of the rhodium atom from the C_2B_3 face ($\text{Rh-C}(\text{average})-\text{Rh-B}(\text{average}) = 0.031 \text{ \AA}$) and the small value of the slip parameter⁷ ($\Delta = 0.02 \text{ \AA}$) enables us to classify this structure as *closo*. Additionally the C-C bond length ($1.630(7) \text{ \AA}$) is consistent with the non-slipped nature of this metallocarborane.¹⁰ This result is in agreement with other work which has illustrated that in addition to the electronic configuration of the metal and the heteroatom nature of the cluster, the π acidity of the ML_2 ligands affects the degree of slip in metallocarboranes.^{7,8} A comparison of slip parameters of three d^8 complexes displays this trend which is in accord with the relative π acidity

| <u>Complex</u> | <u>L₂ Ligand(s)</u> | <u>Δ</u> |
|--|--|----------------------------|
| $3-[\text{C}_2\text{H}_4(\text{NMe}_2)_2]-3,1,2-\text{PdC}_2\text{B}_9\text{H}_{11}$ | $\text{C}_2\text{H}_4(\text{NMe}_2)_2$ | 0.52 \AA |
| $3,3-(\text{PMe}_3)_2-3,1,2-\text{PdC}_2\text{B}_9\text{H}_{11}$ | $(\text{PMe}_3)_2$ | 0.26 \AA |
| (II) | $(\text{CO})(\text{PPh}_3)$ | 0.02 \AA |

of the ligands. This trend also illustrates the effect of the $5e_1(y)-d_{yz}^*$ molecular orbital on the ML_2 fragment slip. As the degree of backbonding from this metal orbital increases, its energy and effect on the geometry of the complex decreases. This trend is also in accord with the smaller d-p promotion energy of Rh relative to Pd.

The orientation of the $\text{Rh}(\text{CO})(\text{PPh}_3)$ moiety is unexpected. Theoretical studies have shown that the most stable conformation of $d^8 \text{ML}_2$ fragments is parallel to a line joining the two ortho carbon atoms.⁹ In the present structure the $\text{Rh}(\text{CO})(\text{PPh}_3)$ fragment is rotated approximately 90° from this expected

orientation. Presumably this is due to steric interactions between the ligands and pyridine ring.

The pyridine moiety can be regarded as an "innocent" ligand. The boron atom bonded to this aromatic ring exhibits an average B-B distance ($1.813(6) \text{ \AA}$) which compares favorably to the average B-B distances of the other boron atoms of the C_2B_3 face ($1.795(6) \text{ \AA}$). The distance of the ring from the Rh atom (Rh-N $3.144(8) \text{ \AA}$) precludes any interaction and the tilt of the aromatic ring with respect to the carborane cage is dictated entirely by crystal packing forces, rather than electronic interactions. Presumably the pyridine ring exhibits unhindered rotation in solution.

Solutions of (1) and (2) are catalysts for the hydroformylation reaction. Detailed studies aimed at determining the active catalysts in these reactions are underway.

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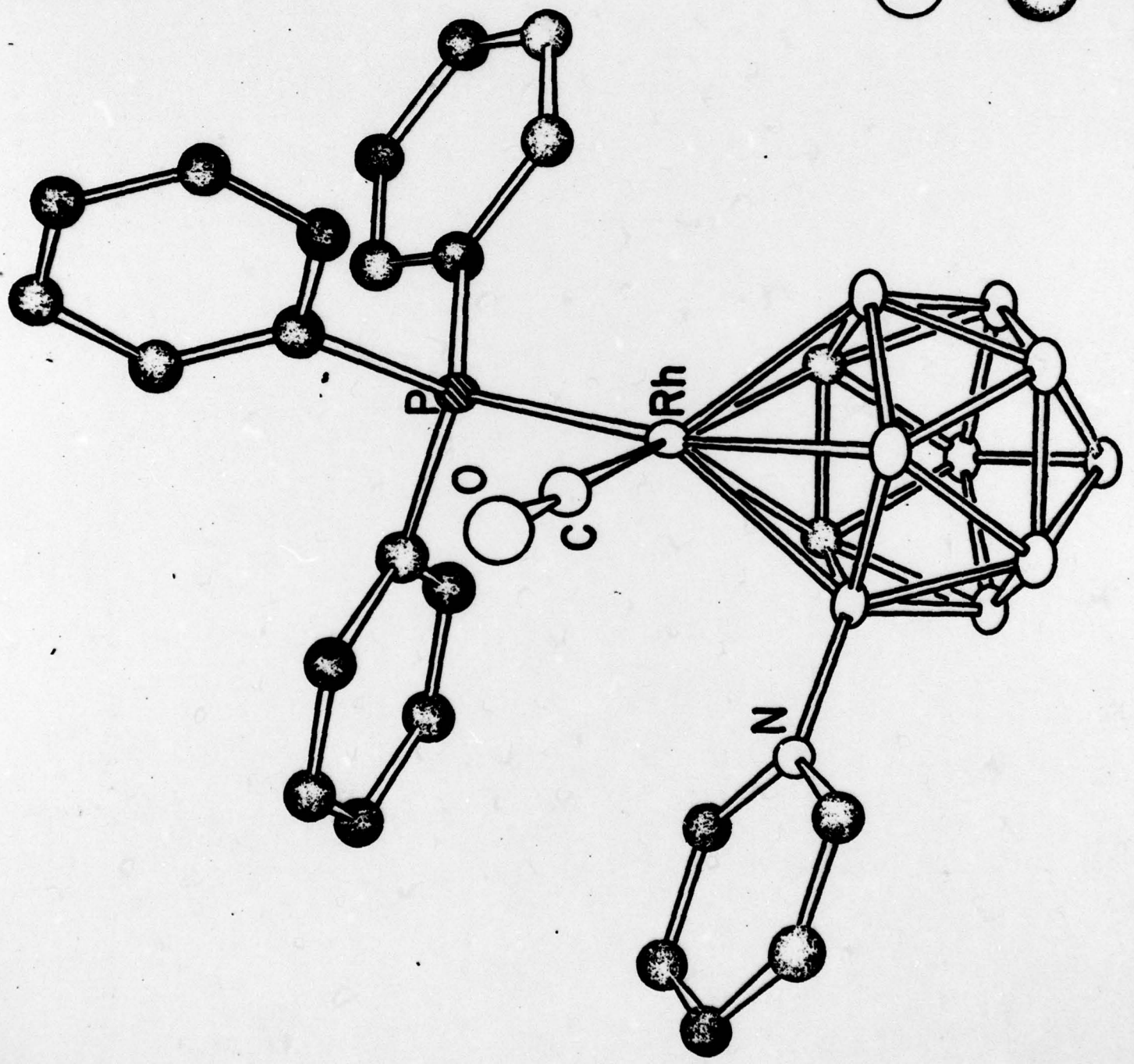
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Figure 1. A molecular plot of (I). Some pertinent distances are Rh-P 2.284(2), Rh-C(O) 1.795(6) Rh-C(cage)_{ave} 2.298(5), Rh-B_{ave} = 2.263(6), B-B_{ave} 1.783(5), C-B_{aveo} 1.706(22) Rh...N 3.144(8), B-N 1.545(7) Å.

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