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PREPARATION AND MOLECULAR STRUCTURE OF TAH(P(C6H5)2)2(ME2PC2H4M--ETC(U)
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Preparation and Molecular Structure of $TaH[P(C_6H_5)_2]_2[Me_2PC_2H_4PMe_2]_2$, a Metal Hydride of the type MHL_2(bidentate phosphine)$_2$, Having a Pentagonal Bipyramidal Structure

by

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Preparation and Molecular Structure of $TaH[P(C_6H_5)_2]_2[(CH_3)_2PC_2H_4P(CH_3)_2]_2$, a Metal Hydride of the type $MHL_2(\text{bidentate phosphine})_2^{n+}$ Having a Pentagonal Bipyramidal Structure.

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ABSTRACT

Treatment of $TaCl_2(dmpe)_2$ (dmpe = 1,2-bis-(dimethylphosphino)ethane) with $K[PPh_2]\cdot 2$ dioxane affords a seven-coordinate, Ta(III) hydride, $TaH(PPh_2)_2(dmpe)_2$. Crystals of the complex are triclinic, space group $P\bar{1}$, with $a = 10.556(3)$ Å, $b = 11.175(3)$ Å, $c = 18.663(5)$ Å, $\overset{\text{alpha}}{\alpha} = 76.00(3)°$, $\overset{\text{beta}}{\beta} = 74.48(3)°$, $\overset{\text{Gamma}}{\gamma} = 66.60(3)°$. Full-matrix least squares refinement of positional and thermal parameters for all nonhydrogen atoms (including fixed contributions for phenyl H atoms) led to $R = 0.077$ and $\underset{\omega\,(\text{omega})}{R_w} = 0.093$. The molecular structure of the complex consists of a well-defined pentagonal bipyramid, with apical, monodentate PPh_2 moieties, and two dmpe ligands plus a hydride ion in the pentagonal plane. The hydride ion was not refined, but its position was inferred from a peak on a final difference map, as well as from large P-Ta-P angle distortions in the pentagonal plane.

Paramagnetic Ta and Nb organometallic complexes are rare, particularly those having oxidation states II and O. Although $(\eta\text{-}C_5H_5)_2V$[2], $V(CO)_6$[3], and other V(O) compounds[4] are well-known, Ta and Nb analogs are absent or poorly defined. A number of stable Nb(IV)[5] and Ta(IV)[6] cyclopentadienyl derivatives are known and $(\eta\text{-}C_5H_5)_2NbH_2$ has been observed as a short-lived intermediate[7]. The complexes $(LiPh)_4MPh_2(Et_2O)_{3.5}$ (M = Nb, Ta), apparent M(II) derivatives[8], likely contain M(IV)[9]. Monomeric $(\eta\text{-}C_5H_5)_2Nb$ has been claimed in solution but has not been isolated and is incompletely characterized[10]. Isolated "niobocene" is not a simple metallocene but a dimer containing $\eta^5:\eta^1\text{-}C_5H_4$ ligands and M-H bonds[11].

We have investigated the reaction of the stable, monomeric Ta(II) complex $TaCl_2(dmpe)_2$[12] (dmpe = 1,2-bis(dimethylphosphine)ethane) with particular nucleophilic reagents in order to explore the reasons for the apparent instability of Ta(II) complexes. Thus, $TaCl_2(dmpe)_2$ reacts with $Na[C_5H_5]$[13] and $Na[H_2Al(OR)_2]$[14] to form, respectively, Ta(III) and Ta(I) complexes, presumably by disporportionation in the former case and reduction or disproportionation in the latter. This report concerns the reaction of $K[PPh_2]$ with $TaCl_2(dmpe)_2$, which affords the Ta(III) complex, $TaH(PPh_2)_2(dmpe)_2$, apparently by hydrogen abstraction from the solvent.

This hydride represents the only structurally characterized member of the class $MH(L)_2(\text{bidentate phosphine})_2^{n+}$ ($M = Nb^{15}$, Ta^{16}, $n = 0$, $L = CO$, C_2H_4; $M = Cr^{17}$, $Mo^{17a,18}$, $W^{17,19}$, $N = 1$, $L = CO$, N_2, C_2H_4) having a pentagonal bipyramidal structure. Two related complexes, $[WH(N_2)_2(\text{diphos})_2]^{+}$[19b] and $[MoH(C_2H_4)_2(\text{diphos})_2]^{+}$[18b], have been reported to have pentagonal bipyramidal structures. However, the former structure has not been published and the latter has a ligand-hydride interaction which makes structural comparisons of questionable value.

Further, the structure of $TaH[PPh_2]_2(\text{dmpe})_2$ differs from those of other dialkyl- or diarylphosphide complexes in that it contains unidentate, rather than bridging phosphide ligands.

Experimental Section

Manipulations were performed under an atmosphere of prepurified argon or nitrogen or under vacuum. Solvents were purified by distillation from sodium benzophenone ketyl, excepting CH_2Cl_2 which was distilled from P_2O_5. $TaCl_2(\text{dmpe})_2$[12] and $K[PPh_2]\cdot 2$ dioxane[20] were prepared by literature procedures. 100-MHz ^1H and 40.5-MHz ^{31}P NMR and mass spectra were obtained on Varian XL-100 and AEI MS-9 spectrometers, respectively. ^{31}P NMR chemical shifts are relative to 85% external H_3PO_4. Double decoupled $^{13}C\{^{31}P, ^1H\}$ spectra were recorded with a Bruker HFX-90 spectrometer using a Universal probe. In this configuration, the additional tuned 36.43 HMz ^{31}P noise decoupling was introduced onto a separate crossed coil. The elemental analysis was by Dornis and Kolbe, Mülkein, Germany.

$\underline{\text{TaH(PPh}_2)_2\text{(dmpe)}_2}$. Dry THF (250 ml) was added to 7.0 g (0.012 mole) $TaCl_2(dmpe)_2$ and 9.6 g (0.024 mole) $KPPh_2 \cdot 2$ dioxane contained in a flask, cooled in an ice bath. A deep purple color developed instantly. The reaction was allowed to proceed for two hours at 0° with constant stirring. The solvent was then removed under reduced pressure and the resulting solid was extracted with hot toluene until the washings were colorless. The pooled extracts were filtered through celite and concentrated to dryness, affording 5.7 g of crude product (56%). Repeated crystallizations from hot toluene gave an analytically pure compound: MW(cryoscopic in benzene) 820 ± 30, Calcd. 852; IR (nujol mull) ν(Ta-H) 1648 cm^{-1}; ^{31}P NMR (toluene-d_8) 20.52 ppm (s), 10.11 (d, J_{PH} = 83 Hz), -3.85 (s); $^{1}H\{^{31}P\}$ NMR (toluene-d_8) 8.05 and 7.43 δ(aryl, 20H), 1.72 and 1.32 (dmpe methyls, singlets, 24H), 1.51 (dmpe methylenes, br, 8H).

Anal. Calcd. for $C_{36}H_{53}P_6Ta$: C, 50.71; H, 6.27; P, 21.79; Ta, 21.22. Found: C, 50.72; H, 6.14; P. 21.65; Ta, 21.17.

$\underline{\text{Degradation of TaH(PPh}_2)_2\text{(dmpe)}_2}$

$\underline{\text{(A) Reaction with DCl and D}_2\text{O}}$. DCl gas was bubbled into a THF solution containing 100 mg of $TaH(PPh_2)_2(dmpe)_2$. An instantaneous color change from purple to pale blue-green occurred. The solvent was removed by distillation *in vacuo* and 10 ml of 0.1 N KOH solution was added to the residue. The organic components were then extracted into 25 ml of dry pentane. Following evaporation of the solvent, the mass spectrum (appearance potential) of the resultant oil revealed parent peaks for $[^{12}C_{12}{}^{1}H_{10}{}^{2}D_{1}{}^{31}P_{1}]^{+}$ (m/e 187) and $[^{12}C_{12}{}^{1}H_{11}{}^{31}P_{1}]^{+}$ (m/e 186) in the ratio of 1.00:0.95. A similar experiment with D_2O showed the presence of $[^{12}C_{12}{}^{1}H_{10}{}^{2}D_{1}{}^{31}P_{1}]^{+}$ and $[^{12}C_{12}{}^{1}H_{11}{}^{31}P_{1}]^{+}$ in the ratio of 1.00:0.70.

(B) Reaction with CD_2Cl_2. A color change from purple to brown was observed upon adding CD_2Cl_2 to $TaH(PPh_2)_2(dmpe)_2$. A ^{1}H NMR spectrum indicated the presence of diphenylphosphine; $\underline{H}P\phi_2$ at 5.17δ, J_{PH} = 219 Hz (Lit.[21]: $\underline{H}P\phi_2$ 5.14δ, J_{PH} = 216 Hz). Integration of the phenyl region versus $\underline{H}P\phi_2$ gave a ratio of 20:1.

Collection and Reduction of Diffraction Data. Purple-red prismatic crystals were isolated from a toluene solution which had been cooled slowly, and were mounted in capillary tubes sealed under N_2. Several batches of crystals were examined and about twenty were mounted, from which six crystals were selected for use on the basis of Laué photographs. Preliminary Weissenberg photographs indicated that the crystal was probably triclinic. However, during this time half of the crystals decomposed suddenly and unpredictably, after each had been exposed to x-rays for different periods. The remaining crytals were transferred sequentially to a Syntex $P2_1$ diffractometer. Unfortunately, two of these decomposed during the first 4-6 hr, and it was suspected that a structure determination would be impossible due to crystal instability. Nevertheless the last crystal was mounted on the diffractometer, and appeared to be somewhat more stable than the others. Hence we decided to begin a data collection. All operations were carried out as described previously[22] and details of the structure analysis[23] are given in Table I. All operations and refinement were carried out using locally modified versions of the machine-language or Fortran diffractometer program, and the Syntex XTL Structure Determination System (24 K Nova configuration)[24]. Within minutes of the end of data collection, the crystal decomposed to a colorless powder. Absorption corrections were not made.

Solution and Refinement of the Structure. The Patterson function was rather complicated owing to a large peak at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, implying a pseudo-body centered arrangement in either $P\bar{1}$ or $P1$. Such a vector distribution immediately precluded the possibility of bridging phosphide moieties, as the Ta-Ta distance (~11 Å) was far too great. The structure was solved, with considerable difficulty, by careful consideration of chemical and spectroscopic data and "manual trial-and-error" shifting of the tantalum atom away from $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in $P\bar{1}$. Structure factor calculations based on tantalum and the six phosphorus atoms gave $R = 0.204$; atomic positional parameters of all carbon atoms were obtained from two successive difference Fourier syntheses. A difference map calculated after anisotropic refinement of all dmpe C atoms (except C33), 6P and Ta showed evidence for the hydride H atom and phenyl H atoms. The phenyl H atoms were included as fixed contributions in the final refinement. The hydride H atom did not refine successfully and was not included in the calculations (but see further below). The analytical scattering factors of Cromer and Waber were used[25a]; real and imaginary components of anomalous scattering were included in the calculation for Ta and P[25b]. At convergence ($\Delta/\sigma \leq 0.01$), a weighting scheme analysis revealed large discrepancies for reflections (mainly $0k\ell$) measured between 18.5 and 22.5 hours of "shutter open" time. Other reflections showed no unusual dependence on sequence number, angle, index, or the magnitude of $|F_o|$. Regrettably, owing to the difficulty of obtaining diffraction-quality crystals and their instability (apparent x-ray damage), we were unable to repeat the structure analysis, or to remeasure the affected reflections. The large discrepancies mentioned above ($F_o \cong 1.3\ F_c$) led, apparently, to five large peaks of height $\sim 2.5\ e^-/\mathring{A}^3$. These were near the Ta and P atoms, but all had locations of the type $(X, \sim\frac{1}{4}, \sim\frac{1}{4})$. It was decided to test the effect of omitting the reflections wth the largest discrepancies (~ 130) by removing them from the refinement and ΔF-syntheses. When this was done, (a) no significant changes occurred in the refinement and (b) the seven peaks of height $2.5\ e^-/\mathring{A}^3$ were still present, but with heights of 0.9-$1.2\ e^-/\mathring{A}^3$.

The present work is based upon refinement using all data for which $F > 3.92\sigma(F)$, since we have no justifiable basis for excluding any data. However, the omission test supports the hypothesis that, apart from their effect on the precision of the refinement, inclusion of the data will produce no significant inaccuracies in the reported bond lengths and angles. The final R-value, 0.077, is reasonable based on the discrepancies and the relatively high stochastic $R_s = 0.047$ (see Table I).

The "next six highest" peaks on the final difference synthesis had heights of 0.89-1.24 $e^-/\text{Å}^3$. All were very near Ta, P or dmpe C atoms except for a peak at (0.344, 0.156, 0.219), 1.47 Å from Ta *vide infra*.

Table II lists the positional and isotropic temperature factors for all atoms, while anisotropic temperature factors appear in Table III.

Results

Preparation and Chemical Characterization of $TaH(PPh_2)_2(dmpe)_2$.

A THF solution of $TaCl_2(dmpe)_2$ and $KPPh_2 \cdot 2$ dioxane in a 1:2 mole ratio rapidly reacted at 0°C to give an intense purple solution. Paramagnetic species other than the Ta(II) starting material were not observed by ESR during the course of the reaction. A purple crystalline solid was isolated from the reaction mixture, which exhibited an infrared band (nujol mull) at 1645 cm^{-1}, suggestive of the presence of a Ta-H unit[26]. A total analysis established the empirical formula as $C_{36}H_{53}P_6Ta$, implying formulation as $TaH(PPh_2)_2$-$(dmpe)_2$ (eq. 1). A cryoscopic (benzene) molecular weight determination was consistent with a monomeric formulation (calcd. 852, found 820 ± 30).

$$TaCl_2(dmpe)_2 + 2KPPh_2 \cdot 2\ \text{dioxane} \xrightarrow[THF]{} TaH(PPh_2)_2(dmpe)_2 \quad (1)$$

The ^{31}P NMR (toluene-d^8) of the complex exhibited three broad resonances at 20.52, 10.11 and -3.85 ppm (presumably, an unresolved $A_2B_2X_2$ pattern), integrating in the ratio of 1:1:1. The B_2 part of the spectrum is split into a doublet which collapses on proton decoupling (J_{P_B-H} = 83 Hz); similar J_{PH} values have been reported for a large number of seven-coordinate metal hydride complexes[13] of the type $MH(CO)_2$(bidentate $\text{phosphine})_2^{n+}$. Slight broadening of the A_2B_2 resonances occurs at 80°, while the phosphorus atoms constituting the X_2 part remain unchanged.

The $^1H\{^{31}P\}$ NMR (toluene-d^8) of the complex did not show the hydride resonance. At room temperture the $^1H\{^{31}P\}$ NMR showed two distinct dmpe methyl resonances. Above ambient temperature, these resonances broadened and coalesced; the coalescence point was reached at 80°. That is, two equally populated sites for ligand methyl groups exist in the ground state and these sites exchange. An estimate of the activation energy for this process, derived from the Gutowsky-Holm equation[28], gives $\Delta G^{\ddagger}$ = 17.5 kcal/mole.

Although the hydride ligand was not detected by NMR spectroscopy, its presence was confirmed by chemical data. Mass spectral studies following treatment of the complex with DCl or D_2O showed parent ion peaks for $HPPh_2$ and $DPPh_2$ in approximately equal intensity. It appears that reductive elimination of $HPPh_2$ from the metal center (therefore implying the presence of a Ta-H bond) occurs when the complex is oxidized by D_2O or DCl. The other PPh_2 group is then liberated as $DPPh_2$. There are a number of examples of one-electron oxidations promoting reductive elimination[29]. Consistent with this hypothesis was the observation that $\underline{H}PPh_2$ is formed when the complex is decomposed by CD_2Cl_2. A ^1H NMR sample, prepared in CD_2Cl_2, showed the presence of free $HPPh_2$; a ratio of peak areas of 1:20 for $\underline{H}PPh_2$ to the aryl hydrogen atoms was observed, consistent with the formation of equimolar amounts of $HPPh_2$ and $DPPh_2$.

Molecular Structure of $TaH(PPh_2)_2(dmpe)_2$. The molecular structure of the complex, and the atom labelling scheme, are depicted in Figure 1. Tantalum resides in a pentagonal bipyramidal environment, where the bidentate dmpe ligands and the hydride ion form the equatorial ligand set, and the diphenylphosphide ligands occupy the axial sites. Of particular significance in Figure 1 are (i) the unidentate nature of the diphenylphosphide ligands, (ii) the obviously large P3-Ta-P5 angle (and small P4-Ta-P6 angle), and (iii) the apparent tilting of two of the diphenylphosphide phenyl rings towards the hydride ion. These features, as well as other structural parameters, are discussed in detail below. Bond lengths are presented in Table IV, and pertinent bond angles in Table V.

The skeletal geometry for the inner coordination sphere of the complex is shown in Figure 2. The dmpe phosphorus atoms show very minor deivations ($<0.030(6)$ Å, Table VI) from the pentagonal plane. The bite angles of the dmpe ligands are 74.1(2) (P3-Ta-P4) and 76.0(2) (P5-Ta-P6).

Idealized in-plane coordinates for the hydride ion, (0.320, 0.134, 0.202) were calculated[30], assuming it to be located 1.75 Å from tantalum, with the Ta-H vector bisecting the P3-Ta-P5 angle. The coordinates are in agreement with a peak (1.05 $e^-/\text{Å}^3$) on the final difference synthesis ~1.5 Å from tantalum at (0.344, 0.156, 0.219). The above unrefined distance is compatible with the bond length of 1.774 in $(\eta\text{-}C_5H_5)_2TaH_3$ determined by neutron diffraction[31]. Further evidence for placement of the hydride ion in the equatorial plane, bisecting the P3-Ta-P5 angle is provided from a consideration of (a) the distorted geometry of the complex and (b) intramolecular nonbonded contacts. Thus, the P3-Ta-P5 angle is greatly expanded (129.7(2)°), and the P4-Ta-P6 angle (80.2(2)°) is compressed relative to "normal" values found in dmpe complexes (~104°). The axial phosphorus atoms are tipped

6.1°(P1) and 4.3°(P2) from the normal to the equatorial plane toward the hydride ion. This near-equality again supports location of the H atom in the pentagonal plane, rather than, for instance, on an octahedral face above or below that plane. Figure 3 illustrates the H···H contacts between the hydride ion (Ta-H fixed at 1.75 Å) and the H atoms bound to phenyl carbon atoms C18 and C6 (calculated[30] at r_{C-H} = 1.08 Å). The contacts which obtain ($H18-H_{Ta}$:2.28, $H6-H_{Ta}$:2.17 Å) are very nearly double the van der Waals radius for hydrogen, 1.2 Å [32].

The Ta-P distances, as well as P-Ta-P angles and structural parameters of the dmpe ligands compare well with other structurally characterized dmpe complexes[33]. Two of the $Ta-P_{dmpe}$ distances (-P4, 2.623(7); -P6, 2.599(7)Å) are significantly longer than the other two (-P3, 2.568(7); -P5, 2.555(7)Å), presumably due to a slight trans-influence exerted by the hydride ion or steric effects.

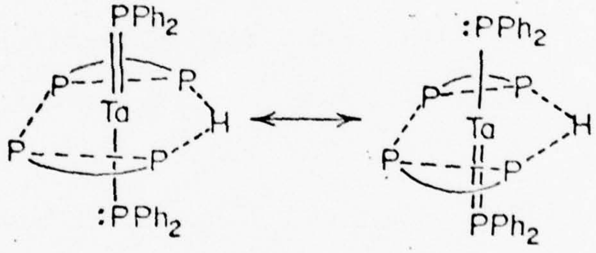
The geometry about the diphenylphosphide centers is very nearly trigonal planar. Thus, the two $TaPC_2$ units are planar within experimental error (Table VI), and the bond angles about the phosphorus atoms vary from 100-130°. Deviations of these angles from 120° are a probable consequence of nonbonded contacts between the phenyl groups and dmpe ligands. Similar patterns are apparent in the structurally-related transition-metal dialkylamide complexes[34]. The $Ta-P_{PPh_2}$ distances (2.404(6), 2.430(6)) are 0.13-0.22 Å shorter than the bond distances between Ta and the equatorial tertiary phosphines.

Discussion

Nature of the Ta-PPh_2 Bond. Dialkyl- and diarylphosphide ions are generally regarded as potent nucleophiles[35]. They are, for instance, capable of effecting nucleophilic substitutions on aryl[36] and acetylenic[37] halides. Further, they are potential four-electron donors to transition metal ions, as two lone pairs are available. There are several examples of reactions of organophosphide salts with transition metal halides. In most cases, phosphide-bridged complexes, $M\text{-}P(R)_2\text{-}M$, are obtained. Examples are $[(C_5H_5)_2M(PR_2)]_2$[38] (M = Ti, Zr), $[Cu(HPR_2)(PR_2)]_2$[39], and $[PdX(PR_2)L]_2$[40] (X = halide, L = tertiary phosphine). The complexes $Ti(PR_2)_2$, $V(PR_2)_3$, and $Cr(PR_2)_3$[41] are obtained as monomers in solution, but may be associated in the solid state.

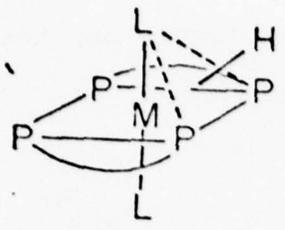
The only other structurally characterized R_2P-metal complexes are those having a phosphide bridge[42]. No structural reports of compounds containing terminal phosphide groups, $M{=}PR_2$, have appeared. Such compounds have been suggested as reaction intermediates[43] and are, likely, capable of existence, since nitrogen analogs are well-known. Numerous examples of terminal dialkylamide complexes are known and evidence for metal-nitrogen multiple bonding has been presented[34].

In transition metal dialkylamide complexes, the ligands are regarded as two-electron σ donors and two-electron π donors. The planarity of the $M-NC_2$ units and the short M-N bond lengths observed for $Nb(NMe_2)_5$[44] and $W(NMe_2)_6$[45] provide an indication of the importance of nitrogen-to-metal π bonding. For example, in $W(NMe_2)_6$ tungsten attains an 18-electron valence shell as a result of forming six N-W σ bonds and three N-W π bonds, leading to an average W-N bond order of 1.5. In $TaH(PPh_2)_2(dmpe)_2$, tantalum achieves a closed-shell electron configuration if the Ta-P(diphenylphosphide) bond orders are 1.5. That is, in valence bond terms, the molecule is best represented as a superposition of the resonance structures shown below:



The approximate trigonal planar arrangement of the diphenylphosphide ligands, as well as their eclipsed configuration relative to one another, is consistent with this description.

<u>Relationship to Other Seven-Coordinate Hydrides.</u> Hydrides of the general formula $MH(\pi\text{-acceptor})_2(\text{bidentate phosphine})_2^{n+}$ (M = Nb, Ta, n = 0; M = Cr, Mo, W, n = 1)[15-19] are well known. Three structural reports have appeared for examples with monodentate π-accepting ligands. The complex $TaH(CO)_2(dmpe)_2$ is reported to have monocapped



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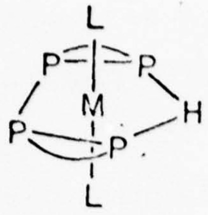

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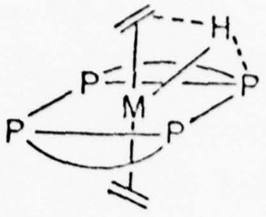
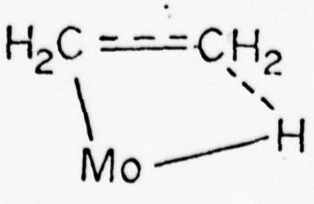


III

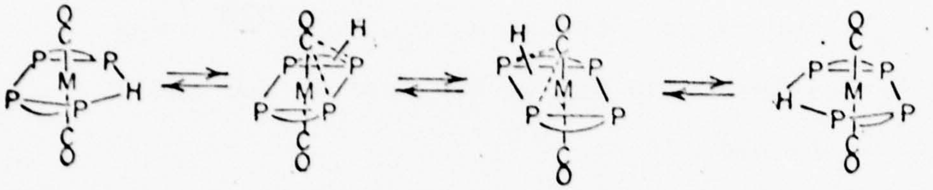
octahedral structure I[16b]; the molecule is, however, severely disordered and the hydride ligand was located on the basis of indirect evidence. Apparently a disordered model based on a pentagonal bipyramid, analogous to $\mathrm{TaH[PPh_2]_2(dmpe)_2}$, was not one of the models tested during the very complicated solution of that structure. Such a model does not appear to be totally inconsistent with the x-ray data, and a reinvestigation of the dicarbonyl structure, e.g., at low temperature, may be worthwhile.

$\mathrm{[WH(N_2)_2(diphos)_2]^+}$ is stated to have the pentagonal bipyramidal structure II, analogous to $\mathrm{TaH(PPh_2)_2(dmpe)_2}$, on the basis of an unpublished structure[19b]. The hydride in $\mathrm{[MoH(C_2H_4)_2(diphos)_2]^+}$ is located on a $\mathrm{C_2H_4}$-P edge, forming an approximate pentagonal bipyramid of type III. However, in this



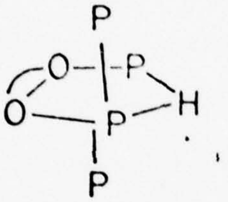
example C_1 and C_2 are not symmetrically bound to Mo; the $Mo(H)(C_2H_4)$ group approaches an $Mo-C_2H_5$ unit[18b]. The implied C_2-H interaction may be responsible for the location of the hydride.

We suggest that pentagonal bipyramidal structure II may be common and present in most hydrides of the type $MH(CO)_2(\text{bidentate phosphine})_2^{n+}$. In this regard we have reexamined the low temperature ^{13}C NMR spectrum of $[MoH(^{13}CO)_2(diphos)_2][SO_3F]$. At -155°C a CD_2Cl_2/Freon 22 solution of $[MoH(^{13}CO)_2(diphos)_2][SO_3F]$ has a single sharp (fwhm 11 Hz) resonance in its $^{13}C\{^{31}P, ^{1}H\}$ NMR spectrum. In contrast to an earlier study[18c], which reported a broadened ^{13}C resonance at -70° in $(CD_3)_2CO$[46], we find no evidence for chemical inequivalence of the carbonyl groups. Non-exchanging sites separated by 0.3 ppm would have been detectable. This suggests that the complex either has structure II or is a monocapped octahedron of type I with the hydride rapidly exchanging between capping sites above and below the P_4 plane. The former is more likely, since a barrier to exchange of less than 6 kcal/mole would be required, assuming a chemical shift difference of 1 ppm between inequivalent carbonyl groups in Structure I. The barrier to equilibration of the phosphorus resonances of this compound is approximately 20 kcal/mol[18c]. Phosphorus exchange likely occurs by a mechanism involving motion of the hydride ligand about the upper faces of the octahedron (eq. 2)[18c]; it is unlikely that the barrier

 (2)

for exchange between upper and lower faces would be significantly less.

Additionally, there are related pentagonal bipyramidal structures with monodentate ligands. Thus, $MoH(CF_3CO_2)[P(OMe)_3]_4$ has an approximate pentagonal bipyramidal structure as shown, although the hydride is



slightly displaced toward one of the axial phosphite groups[47].

The approximate C_{2v} structure of $TaH(PPh_2)_2$-$(dmpe)_2$ is apparently preserved in solution, as shown by the observation of two, equally populated dmpe-methyl resonances - those from the methyl groups attached to the chelate ends adjacent to the hydride and those opposite the hydride. The observed exchange between these sites is accomodated by the process in eq. 2. Indeed the barrier is similar to that found for phosphorus exchange for $MoH(CO)_2(diphos)_2^+$[18c]. The ^{31}P chemical shift separation was too large to allow observation of exchange between phosphorus sites below the decomposition point of the complex.

Implications for Stability of Ta(II) Complexes.

The formation of $TaH(PPh_2)_2(dmpe)_2$ may involve the initial generation of the odd-electron intermediate, $[Ta^{II}(PPh_2)_2(dmpe)_2]$. This 17-electron complex apparently abstracts a hydrogen atom from solvent (THF) or dioxane, thereby attaining an 18-electron valence shell about tantalum. Hydrogen abstraction by metal complexes from solvent has been noted, for example, in the preparation of $HOsCl_2(PBu_2Ph)_3$ [48], $Pt(H)_2(diphos)_2$ [49], $HM(N(SiMe_3)_2)_3$ (M = Th, U) [50], and $HMn(CO)_3(PBu_3)_2$ [51]. The Ta(II) intermediate must be short-lived as it was not detected by static ESR experiments.

On the basis of reactions of $TaCl_2(dmpe)_2$ with $C_5H_5^-$ [13], hydride donors [14], and PPh_2^-, it appears that replacement of halide by stronger field ligands leads to species resembling organic radicals in reactivity, which rapidly disproportionate or abstract hydrogen atoms from solvent.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Office of Naval Research and to the Natural Science and Engineering Research Council of Canada for partial support of this research.

Supplimentary Material Available: Listings of observed and calculated structure factor amplitudes (Table VII), and hydrogen atom positions (Table VIII)(n pages). Ordering information is given on any current masthead page.

References and Notes

1. a) E.I. du Pont de Nemours and Co., contribution No. 0000.
   b) Brandeis University;
   c) Loyola College;
   d) University of Toronto.
2. Fischer, E.O.; Vigoreux, S. Chem. Ber. 1958, 91, 2205.
3. Werner, R.P.M.; Podall, H.E. Chem. Ind. (London) 1961, 144.
4. For example, see Chatt, J.; Watson, H.R. J. Chem. Soc. 1962, 2545.
5. Milne, C.R.; Lappert, M.F. J. Chem. Soc. Chem. Commun. 1978, 925.
6. Manzer, L.E. Inorg. Chem. 1977, 16, 525.
7. a) Elson, I.H.; Kochi, J.K.; Klabunde, U.; Manzer, L.E.; Parshall, G.W.; Tebbe, F.N. J. Am. Chem. Soc. 1974, 96, 7376;
   b) Elson, I.H.; Kochi, J.K. ibid. 1975, 97, 1262.
8. a) Sarry, B.; Dobrusskin, V. J. Organomet. Chem. 1968, 13, 1;
   b) Sarry, B.; Schön, M. ibid. 1968, 13, 9.
9. Sarry, B.; Steinke, J. Abstracts, Fourth International Conference on Organometallic Chemistry, Bristol, 1969, paper C10.
10. Lemenovski, D.A.; Fedin, V.P. J. Organometal. Chem. 1974, 132, C11.

11. a) Guggenberger, L.J.; Tebbe, F.N. J. Am. Chem. Soc. 1971, 93, 5924;

    b) Tebbe, F.N.; Parshall, G.W. ibid., 1971, 93, 3793.

12. Datta, S.; Wreford, S.S. Inorg. Chem. 1977, 16, 1134.

13. Foxman, B.M.; McNeese, T.J.; Wreford, S.S. Inorg. Chem. 1978, 17, 2311.

14. McNeese, T.J.; Wreford, S.S.; Foxman, B.M. J. Chem. Soc. Chem. Commun. 1978, 500.

15. Schrock, R.R. J. Organometal. Chem. 1976, 121, 373.

16. a) Tebbe, F.N. J. Am. Chem. Soc. 1973, 95, 5823;

    b) Meakin, P.; Guggenberger, L.J.; Tebbe, F.N.; Jesson, J.P. Inorg. Chem. 1974, 13, 1025.

17. a) Bond, A.M.; Colton, R.; Jackowski, J.J. Inorg. Chem. 1975, 14, 2526;

    b) Connor, J.A.; Riley, P.I.; Rix, C.J. J. Chem. Soc. Dalton 1977, 1317.

18. a) Datta, S.; McNeese, T.J.; Wreford, S.S. Inorg. Chem. 1977, 16, 2661;

    b) Byrne, J.W.; Kress, J.R.M.; Osborn, J.A.; Ricard, L.; Weiss, R.E. J. Chem. Soc. Chem. Commun. 1977, 662;

    c) Datta, S.; Dezube, B.; Kouba, J.K.; Wreford, S.S. J. Am. Chem. Soc. 1978, 100, 4404.

19. a) Dombeck, B.D.; Angelici, R.J. Inorg. Chem. 1976, 15, 2397;

    b) Heath, G.A.; Mason, R. personal communication cited in Heath, G.A.; Chatt, J.; Richards, R.L. J. Chem. Soc. Dalton 1974, 2074;

19. c) Byrne, J.W.; Blaser, H.U.; Osborn, J.A. J. Am. Chem. Soc. 1975, 97, 3872.

20. Issleib, K.; Tzschach, A. Chem. Ber. 1959, 92, 1118.

21. Olah, G.A.; McFarland, C.W. J. Org. Chem. 1969, 34, 1832.

22. Foxman, B.M. Inorg. Chem. 1978, 17, 1932.

23. Churchill, M.R.; Lashewycz, R.A.; Rotella, F.J. Inorg. Chem. 1977, 16, 265.

24. a) "Syntex $P2_1$ Operations Manual", Syntex Analytical Instruments, Cupertino, Calif., 1973;

    b) "Syntex XTL Operations Manual", Cupertino, Calif., 1974.

25. "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974:

    a) pp. 99-101;

    b) pp. 148-150.

26. Compare ν_{Ta-H} in Cp_2TaH_3 (1735)[27]; $H_5Ta(dmpe)_2$ (1544)[16a]; and $HTa(CO)_2(dmpe)_2$ (1589 cm^{-1})[16a].

27. Green, M.L.H.; McCleverty, J.A.; Pratt, L.; Wilkinson, G. J. Chem. Soc. 1961, 4854.

28. Gutowsky, H.S.; Holm, C.H. J. Chem. Phys. 1956, 25, 1228.

29. a) Morrell, D.G.; Kochi, J.K. J. Am. Chem. Soc. 1975, 97, 7262;

    b) Grubbs, R.H.; Miyashita, A. J. Am. Chem. Soc. 1978, 100, 7416.

30. "Syntex XTL Operations Manual", 2nd ed. Syntex Analytical Instruments, Cupertino, Calif., 1976.

31. Wilson, R.D.; Koetzle, T.F.; Hart, D.W.; Kvick, Å; Tipton, D.L.; Bau, R. *J. Am. Chem. Soc.* 1977, **99**, 1775.

32. Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press, 1960.

33. Albright, J.O.; Datta, S.; Dezube, B.; Kouba, J.K.; Marynick, D.S.; Wreford, S.S.; Foxman, B.M. *J. Am. Chem. Soc.* 1979, **101**, 611

34. Bradley, D.C.; Chisholm, M.H. *Accts. Chem. Res.* 1976, **9**, 273.

35. a) Maier, L. *Prog. Inorg. Chem.* 1963, **5**, 27;
    b) Issleib, K. *Pure Appl. Chem.* 1964, 9, 205;
    c) Davis, D.D.; Gray, C.E. *J. Organometal. Chem. Rev. A* 1970, **6**, 283;
    d) Maier, L. "Organic Phosphorus Compounds", Vol. 1; Kosolapoff, G.M.; Maier, L. Eds.; Wiley: New York, 1972.

36. Bangerter, B.W.; Beatty, R.P.; Kouba, J.K.; Wreford, S.S. *J. Org. Chem.* 1977, **42**, 3247.

37. Miller, S.I.; Dickstein, J.I. *Accts. Chem. Res.* 1976, **9**, 358.

38. Issleib, K. *Pure Appl. Chem.* 1975, **44**, 237.

39. Issleib, K.; Frölich, H.O. *Chem. Ber.* 1962, **95**, 375.

40. Hayter, R.G. *Nature* 1962, **193**, 872.

41. Issleib, K.; Wenschuh, E. *Chem. Ber.* 1964, **97**, 715.

42. Hayter, R.G. "Preparative Inorganic Reactions", Vol. 2; Jolly, W.L., Ed.; 1965, 211.

43. Blickensderfer, J.R.; Kaesz, H.D. J. Am. Chem. Soc. 1975, 97, 2681.

44. Heath, C.; Hursthouse, M.B. J. Chem. Soc. Chem. Commun. 1971, 143.

45. Bradley, D.C.; Chisholm, M.H.; Heath, C.E.; Hursthouse, M.B. J. Chem. Soc. Chem. Comm. 1969, 1261.

46. Broadening is observed in this medium, apparently due to a solvent effect.

47. Wreford, S.S.; Kouba, J.K.; Kirner, J.F.; Muetterties, E.L.; Tavanaiepour, I.; Day, V.W., submitted.

48. Chatt, J.; Leigh, G.J.; Paske, J. J. Chem. Soc. Chem. Commun. 1967, 739.

49. Ibers, J.A. "Transition Metal Hydrides", Adv. in Chem. Ser. No. 167, Bau, R. ed.; Am. Chem. Soc. 1978, 26.

50. Turner, H.W.; Simpson, S.J.; Andersen, R.A. J. Am. Chem. Soc. 1979, 101, 2782.

51. Kidd, D.R.; Cheng, C.P.; Brown, T.L. J. Am. Chem. Soc. 1978, 100, 4103.

Table 1. Data from the X-ray Diffraction Study of $TaH(PPh_2)_2(dmpe)_2$.

(A) Crystal Data at 23(1)°C[a]

crystal system: triclinic[b]

space group: $P\bar{1}[C_i^1;\text{No.}2]$

$a = 10.556(3)$ Å

$b = 11.175(3)$ Å

$c = 18.663(5)$ Å

$\alpha = 76.00(3)°$

$\beta = 74.48(3)°$

$\gamma = 66.60(3)°$

$V = 1923.8$ Å^3

$Z = 2$

formula weight = 852.7

ρ(calculated) = 1.47 g cm^{-3}

ρ(observed)[c] = 1.51(2) g cm^{-3}

μ(calculated) = 79.1 cm^{-1} (CuKα)

Cell constant determination: 9(hkℓ) reflections and refined 2θ, w and χ values in the range $40 < 2\theta < 43°$ (λ(CuK$\bar{\alpha}$) = 1.5418 Å)

(B) Collection of Intensity Data

radiation	CuKα, Ni β-filter
reflections measured	±h,±k,±ℓ (to $2\theta = 101°$)
scan type; speed	θ-2θ; variable, 3.08-6.51°/min
scan range	symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$
background measurement	stationary, for one-fourth of scan time at each of scan limits
number of reflections measured	4351 total; 4050 in unique set
standard reflections	003, 253 measured after every 60 reflections; deviation < ±3σ(I) for each
automatic recentering of crystal	every 800 reflections

Table 1 (continued)

(C) Treatment of Intensity Data[d]

data reduction	intensities at before[22]; esd's of $|F_o|$ values calculated by method of finite differences[23]
statistical information	$R_s = 0.047$; $R_{av} = 0.039$

(D) Refinement[e], with 2942 Data for Which $F > 3.92\sigma(F)$

weighting of reflections	$w = [\sigma^2(|F_o| + (\rho|F_o|)^2)]^{-1}$; $\rho = 0.040$
Patterson solution	Ta,6P; $R = 0.204$
isotropic refinement, all non-hydrogen atoms	$R = .094$; $R_w = .114$
anisotropic refinements; Ta, 6P, dmpe C atoms (except C33, which would not refine anisotropically) only; other atoms isotropic; H atoms on phenyl rings included as fixed contributions with $r_{C-H} = 0.95$ Å.	$R = 0.077$; $R_w = 0.093$
standard deviation of an observation of unit weight	1.522

[a] Estimated standard deviations in the least significant digits are given in parentheses in this and the following tables;

[b] The dimensions of the corresponding Delaunay reduced cell are $a = 10.556$, $b = 11.175$, $c = 17.362$ Å; $\alpha = 91.06$, $\beta = 91.83$, $\gamma = 113.38°$;

[c] measured by flotation in 1,2-dibromoethane/hexane;

[d] $R_s = \Sigma\sigma(|F_o|)/\Sigma|F_o|$; $R_{av} = [(\Sigma||I|-|I_{av}||)/\Sigma|I|]$;

[e] $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o|-|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$. Standard deviation of an observation of unit weight = $\{\Sigma w[|F_o|-|F_c|]^2/(M-n)\}^{1/2}$, where m (= 2942) is the number of observations and n (= 263) is the number of parameters varied.

Table II. Positional and Isotropic Thermal Parameters for $TaH(PPh_2)_2(dmpe)_2$

Atom	x	y	z	U_{iso}
Ta	0.23137(11)	0.26904(10)	0.25077 (6)	
P1	0.22806(66)	0.39748(56)	0.12557(33)	
P2	0.25587(64)	0.11035(55)	0.36383(33)	
P3	0.06994(65)	0.16780(62)	0.22618(35)	
P4	-0.02480(65)	0.40697(61)	0.31186(36)	
P5	0.49877(62)	0.20210(61)	0.21481(35)	
P6	0.28353(69)	0.43957(59)	0.30039(36)	
C25	-0.1213 (29)	0.5702 (27)	0.2607 (15)	
C26	-0.0706 (27)	0.4542 (27)	0.4064 (15)	
C27	-0.1559 (31)	0.3307 (38)	0.3231 (17)	
C28	-0.0793 (27)	0.1809 (29)	0.3070 (16)	
C29	-0.0162 (28)	0.2411 (29)	0.1440 (16)	
C30	0.1351 (28)	-0.0125 (22)	0.2211 (17)	
C31	0.5857 (31)	0.1984 (48)	0.1197 (18)	
C32	0.6075 (31)	0.0603 (31)	0.2650 (23)	
C34	0.4706 (31)	0.4253 (29)	0.2650 (25)	
C35	0.1971 (30)	0.6194 (22)	0.2757 (15)	
C36	0.2823 (39)	0.4293 (26)	0.4012 (14)	
C1	0.2831 (22)	0.3388 (21)	0.0363 (13)	0.0471(5)
C2	0.2875 (24)	0.4193 (22)	-0.0340 (14)	0.0573(5)
C3	0.3258 (25)	0.3681 (24)	-0.0981 (15)	0.0642(6)
C4	0.3633 (26)	0.2386 (25)	-0.1002 (15)	0.0699(6)
C5	0.3630 (27)	0.1555 (25)	-0.0332 (15)	0.0700(6)
C6	0.3247 (24)	0.2027 (23)	0.0330 (14)	0.0584(5)
C7	0.1874 (24)	0.5758 (22)	0.0940 (13)	0.0529(5)
C8	0.2914 (24)	0.6260 (23)	0.0815 (13)	0.0570(5)
C9	0.2552 (31)	0.7703 (28)	0.0627 (17)	0.0839(7)
C10	0.1234 (33)	0.8447 (29)	0.0546 (17)	0.0892(7)
C11	0.0224 (33)	0.7975 (30)	0.0642 (18)	0.0962(8)
C12	0.0569 (27)	0.6575 (25)	0.0851 (15)	0.0674(6)
C13	0.3377 (22)	-0.0714 (20)	0.3760 (13)	0.0451(5)
C14	0.3396 (23)	-0.1490 (22)	0.4485 (13)	0.0535(5)
C15	0.4122 (28)	-0.2816 (26)	0.4545 (16)	0.0746(6)
C16	0.4851 (26)	-0.3483 (24)	0.3933 (15)	0.0668(6)
C17	0.4800 (24)	-0.2690 (23)	0.3229 (14)	0.0596(5)
C18	0.4074 (22)	-0.1356 (21)	0.3172 (12)	0.0467(5)
C19	0.2065 (22)	0.1328 (20)	0.4649 (12)	0.0415(4)
C20	0.0770 (23)	0.1384 (21)	0.5062 (13)	0.0517(5)
C21	0.0422 (27)	0.1546 (25)	0.5820 (15)	0.0716(6)
C22	0.1396 (29)	0.1584 (26)	0.6151 (16)	0.0765(6)
C23	0.2665 (26)	0.1545 (25)	0.5751 (15)	0.0668(6)
C24	0.3025 (25)	0.1375 (23)	0.4997 (14)	0.0616(6)
C33	0.5666 (29)	0.2931 (27)	0.2457 (16)	0.0773(7)

Table III. Anisotropic Thermal Parameters for $TaH(PPh_2)_2(dmpe)_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	0.04259(71)	0.03197(64)	0.02474(58)	-0.01580(48)	-0.00788(45)	0.00090(43)
P1	0.0677 (43)	0.0446 (36)	0.0312 (37)	-0.0211 (34)	-0.0138 (32)	-0.0013 (28)
P2	0.0595 (41)	0.0421 (36)	0.0349 (38)	-0.0200 (33)	-0.0066 (31)	-0.0016 (28)
P3	0.0575 (41)	0.0632 (42)	0.0484 (41)	-0.0335 (36)	-0.0115 (33)	-0.0097 (33)
P4	0.0568 (41)	0.0565 (40)	0.0494 (41)	-0.0202 (34)	-0.0039 (33)	-0.0147 (33)
P5	0.0473 (38)	0.0601 (41)	0.0474 (40)	-0.0247 (33)	-0.0123 (31)	-0.0017 (32)
P6	0.0696 (45)	0.0500 (39)	0.0504 (42)	-0.0231 (36)	-0.0140 (35)	-0.0116 (32)
C25	0.086 (21)	0.077 (18)	0.061 (19)	0.012 (17)	-0.026 (16)	0.007 (15)
C26	0.071 (19)	0.098 (22)	0.054 (18)	-0.011 (17)	-0.002 (15)	-0.032 (16)
C27	0.091 (23)	0.208 (37)	0.090 (25)	-0.112 (25)	0.042 (19)	-0.086 (26)
C28	0.074 (19)	0.122 (24)	0.084 (22)	-0.086 (19)	0.054 (16)	-0.061 (19)
C29	0.073 (19)	0.123 (25)	0.080 (22)	-0.047 (18)	-0.052 (17)	0.004 (18)
C30	0.081 (20)	0.037 (15)	0.126 (27)	-0.023 (14)	-0.026 (18)	-0.009 (16)
C31	0.060 (21)	0.328 (58)	0.056 (22)	-0.045 (28)	0.018 (17)	-0.067 (30)
C32	0.074 (21)	0.104 (25)	0.204 (42)	-0.051 (20)	-0.069 (25)	0.090 (26)
C34	0.071 (21)	0.077 (22)	0.288 (54)	-0.035 (19)	-0.056 (26)	-0.062 (28)
C35	0.115 (23)	0.036 (14)	0.064 (19)	-0.017 (15)	-0.016 (17)	-0.000 (13)
C36	0.222 (37)	0.082 (20)	0.029 (16)	-0.090 (23)	-0.045 (20)	0.009 (14)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \dots + 2b^*c^*U_{23}k\ell)]$.

Table IV. Bond Distances (Å) for $TaH(PPh_2)_2(dmpe)_2$

Ta-P1	2.430 (6)	C1-C2	1.402(33)
Ta-P2	2.404 (6)	C1-C6	1.417(32)
Ta-P3	2.568 (7)	C2-C3	1.347(35)
Ta-P4	2.623 (7)	C3-C4	1.347(37)
Ta-P5	2.555 (7)	C4-C5	1.365(38)
Ta-P6	2.599 (7)	C5-C6	1.359(36)
		C7-C8	1.365(38)
P1-C1	1.803(23)	C7-C12	1.345(39)
P1-C7	1.841(24)	C8-C9	1.477(38)
P2-C13	1.847(22)	C9-C10	1.336(49)
P2-C19	1.868(22)	C10-C11	1.322(53)
P3-C28	1.853(30)	C11-C12	1.435(41)
P3-C29	1.843(31)	C13-C14	1.420(32)
P3-C30	1.871(24)	C13-C18	1.338(31)
P4-C25	1.865(29)	C14-C15	1.363(36)
P4-C26	1.849(27)	C15-C16	1.391(38)
P4-C27	1.839(39)	C16-C17	1.397(36)
P5-C31	1.768(33)	C17-C18	1.371(32)
P5-C32	1.765(36)	C19-C20	1.363(35)
P5-C33	1.720(32)	C19-C24	1.365(37)
P6-C34	1.861(39)	C20-C21	1.401(36)
P6-C35	1.845(24)	C21-C22	1.352(45)
P6-C36	1.854(26)	C22-C23	1.337(44)
C27-C28	1.607(50)	C23-C24	1.395(37)
C33-C34	1.488(43)		

Table V. Bond Angles (deg) for TaH(PPh$_2$)$_2$(dmpe)$_2$

P1-Ta-P2	170.36 (22)
P3-Ta-P4	74.13 (21)
P5-Ta-P6	76.02 (21)
P1-Ta-P3	89.06 (22)
P1-Ta-P4	96.45 (22)
P1-Ta-P5	85.87 (22)
P1-Ta-P6	92.44 (22)
P2-Ta-P3	87.15 (22)
P2-Ta-P4	91.04 (22)
P2-Ta-P5	89.73 (22)
P2-Ta-P6	94.82 (22)
P3-Ta-P5	129.70 (22)
P3-Ta-P6	154.26 (22)
P4-Ta-P5	156.16 (22)
P4-Ta-P6	80.17 (21)
C1-P1-C7	100.65(111)
C1-P1-Ta	128.30 (81)
C7-P1-Ta	130.80 (84)
C13-P2-C19	98.89(104)
C13-P2-Ta	130.05 (78)
C19-P2-Ta	131.00 (76)
P1-C1-C2	124.7 (18)
P1-C1-C6	120.8 (18)
P1-C7-C8	119.0 (19)
P1-C7-C12	121.4 (20)
P2-C13-C14	121.6 (18)
P2-C13-C18	121.5 (18)
P2-C19-C20	121.0 (18)
P2-C19-C24	120.2 (18)
P3-C28-C27	110.5(21)
C28-P3-Ta	108.5(10)
C28-P3-C29	103.6(14)
C28-P3-C30	100.7(13)
C29-P3-Ta	119.4(10)
C29-P3-C30	101.9(13)
C30-P3-Ta	120.2(10)
P4-C27-C28	110.3(23)
C25-P4-C26	98.2(13)
C25-P4-C27	97.0(15)
C25-P4-Ta	119.7(10)
C26-P4-C27	99.4(15)
C26-P4-Ta	123.1 (9)
C27-P4-Ta	114.6(12)
P5-C33-C34	118.0(24)
C31-P5-C32	104.5(18)
C31-P5-C33	103.1(17)
C31-P5-Ta	120.8(14)
C32-P5-C33	87.6(16)
C32-P5-Ta	120.2(13)
C33-P5-Ta	114.7(11)
P6-C34-C33	114.1(25)
C34-P6-C35	99.5(15)
C34-P6-C36	96.6(16)
C34-P6-Ta	110.4(12)
C35-P6-C36	99.8(14)
C35-P6-Ta	122.8 (9)
C36-P6-Ta	122.6(11)

Table VI. Least-Squares Planes[a] for $TaH(PPh_2)_2(dmpe)_2$

(A) Plane equation: $-0.080X + 0.488Y - 0.869Z + 2.580 = 0$

Atoms in plane: Ta, P3, P4, P5, P6

Distances from plane (Å):

Ta	0.000(1)	P5	-0.017 (6)	C28	-0.962(29)
P3	0.022(6)	P6	0.030 (6)	C33	-0.099(29)
P4	-0.027(6)	C27	-0.433(33)	C34	0.318(42)

(B) Plane equation: $0.993X - 0.094Y - 0.075Z - 4.196 = 0$

Atoms in plane: Ta, P1, C1, C7

Distances from plane (Å):

Ta	0.000(1)	C1	0.060(26)
P1	-0.014(8)	C7	0.068(28)

(C) Plane equation: $0.999X + 0.039Y - 0.037Z - 4.851 = 0$

Atoms in plane: Ta, P2, C13, C19

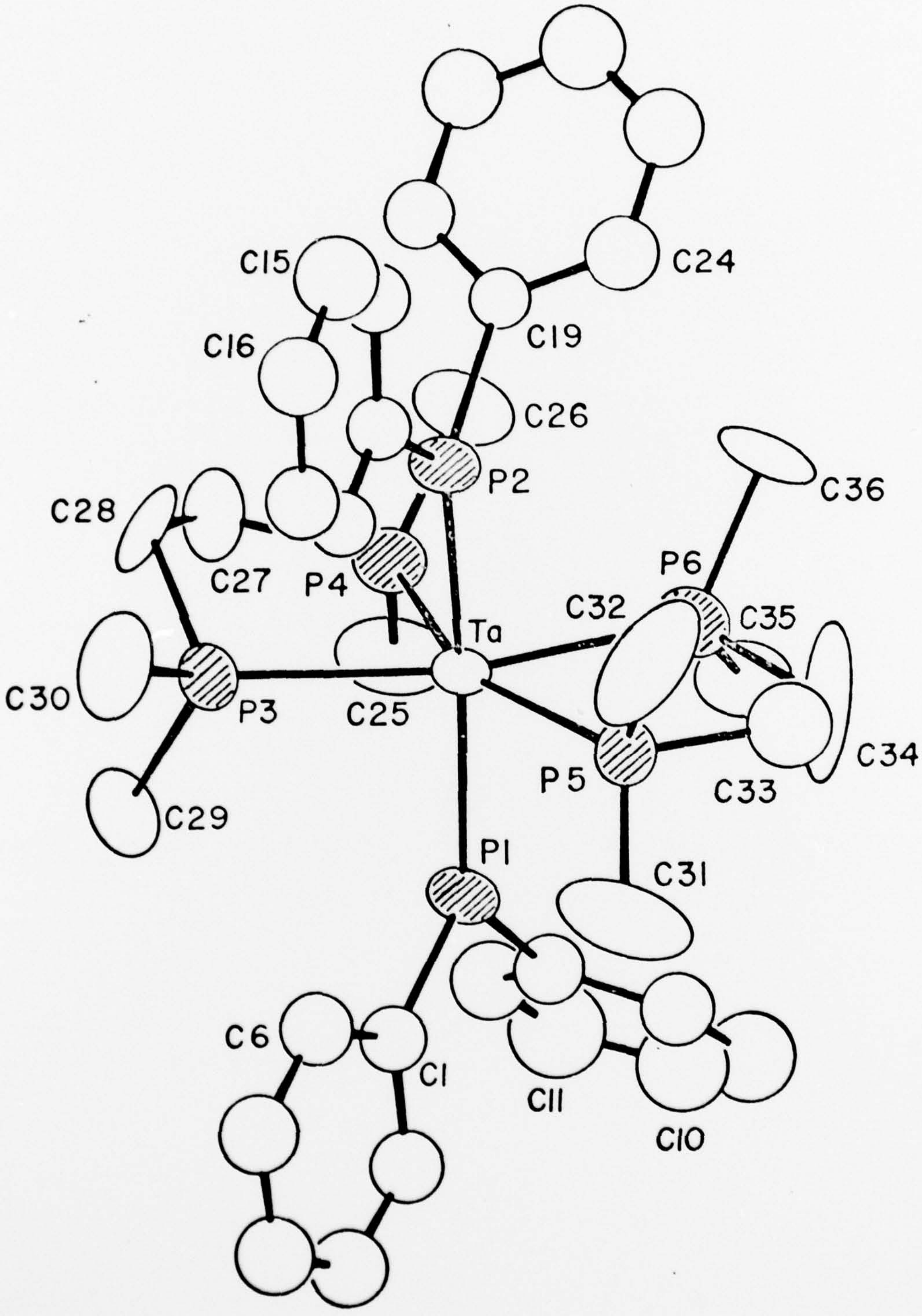
Distances from plane (Å):

Ta	0.000(1)	C13	0.031(25)
P2	-0.007(7)	C19	0.029(25)

---

[a] Orthogonal coordinates X, Y and Z used in these calculations were derived as described in reference 33.

Figure 1. Molecular Structure of $TaH(PPh_2)_2(dmpe)_2$. For clarity only two of each of the phenyl carbon atoms are labelled.



C15
C24
C16
C19
C26
P2
C36
C28
C27
P4
P6
C32
C35
Ta
C30
P3
C25
C34
P5
C33
C29
P1
C31
C6
C1
C11
C10

Figure 2. Skeletal Geometry of $TaH(PPh_2)_2(dmpe)_2$, showing the expanded P3-Ta-P5 angle.

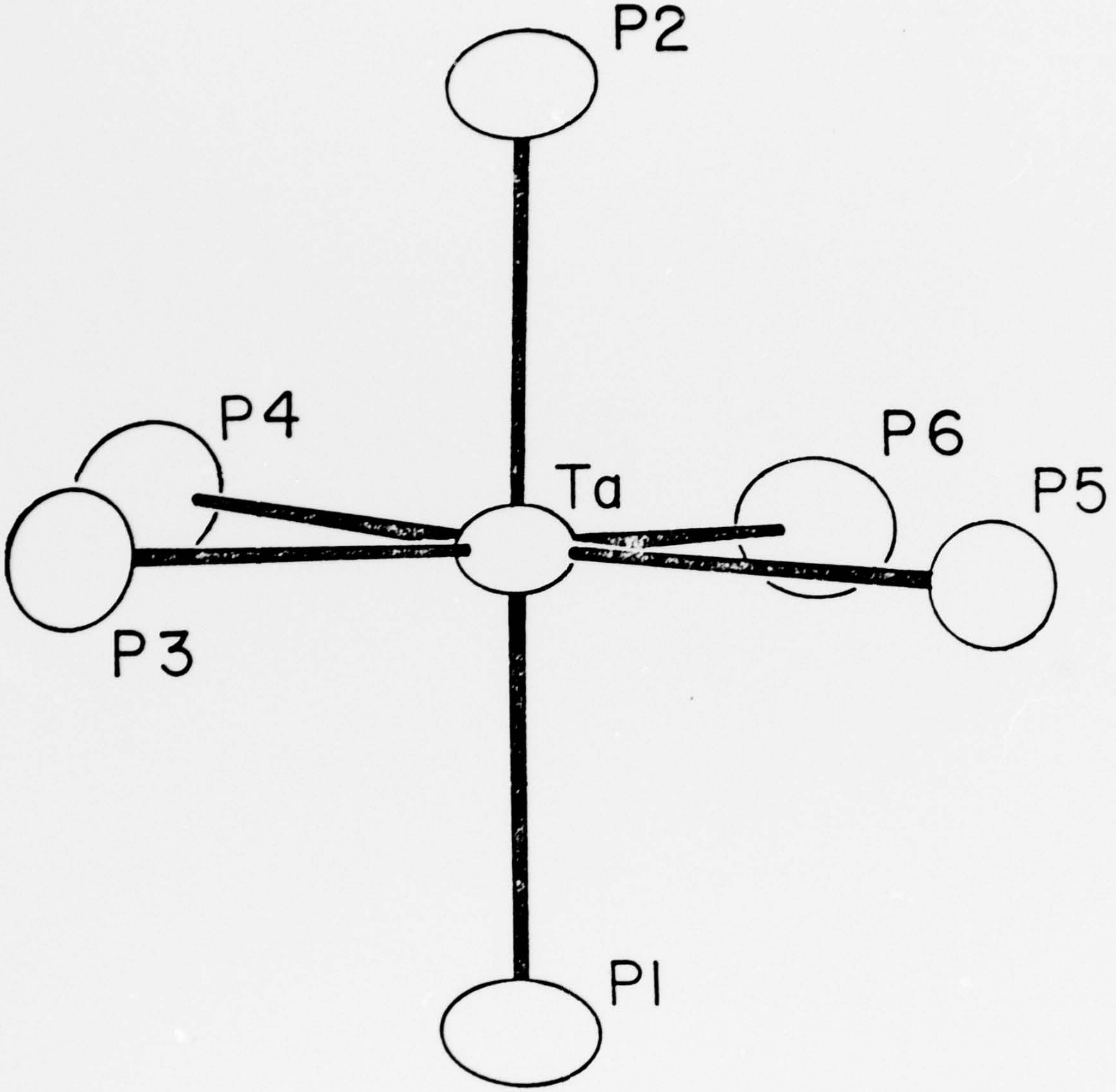
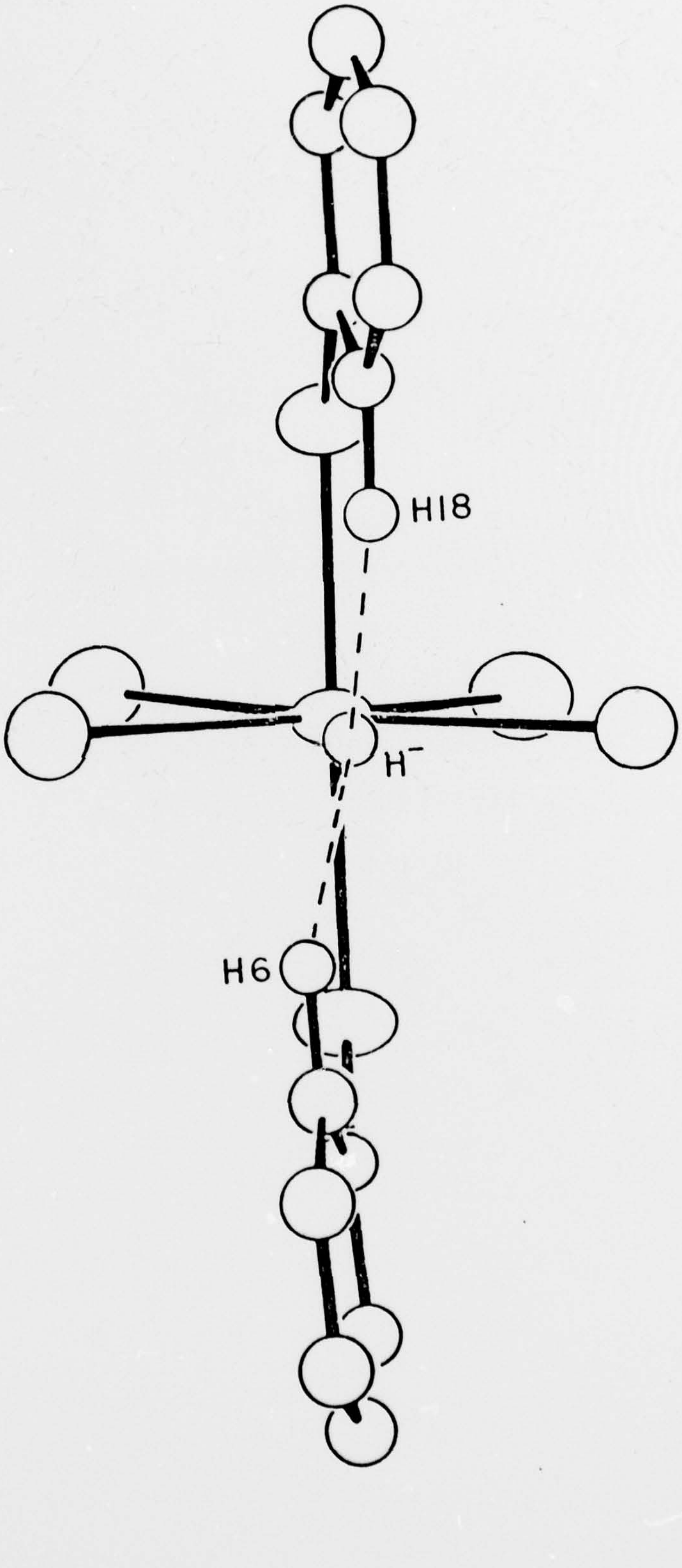

P2
P4
Ta
P6
P5
P3
P1

Figure 3. Illustration of H···H Contacts in $TaH(PPh_2)_2(dmpe)_2$


H18
H⁻
H6

Supplementary
Information
for
Referees and Deposition

1. Table VII. Observed and Calculated Structure Factor Amplitudes

2. Table VIII. Hydrogen atom positions

Table VIII. Derived Hydrogen Atom Positions for Phenyl Rings in $TaH(PPh_2)_2(dmpe)_2$

Atom	x	y	z	U_{iso}
H2	0.2630	0.5115	-0.0364	0.0630
H3	0.3264	0.4265	-0.1446	0.0707
H4	0.3892	0.2063	-0.1466	0.0769
H5	0.3898	0.0635	-0.0329	0.0771
H6	0.3259	0.1424	0.0786	0.0642
H8	0.3852	0.5691	0.0849	0.0626
H9	0.3236	0.8091	0.0567	0.0923
H10	0.1009	0.9374	0.0409	0.0982
H11	-0.0699	0.8542	0.0576	0.1059
H12	-0.0144	0.6216	0.0929	0.0741
H14	0.2910	-0.1091	0.4924	0.0589
H15	0.4131	-0.3316	0.5035	0.0821
H16	0.5346	-0.4410	0.3990	0.0735
H17	0.5274	-0.3078	0.2786	0.0655
H18	0.4064	-0.0854	0.2682	0.0514
H20	0.0103	0.1312	0.4835	0.0568
H21	-0.0496	0.1629	0.6101	0.0787
H22	0.1177	0.1640	0.6673	0.0841
H23	0.3320	0.1632	0.5980	0.0735
H24	0.3948	0.1291	0.4723	0.0677

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