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

P. J. Domaille,[1a] **Bruce M. Foxman,***[1b] **T. J. McNeese,**[1c] **and S. S. Wreford***[1d]

Contribution No. 2747 from the Central Research and Development Department,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898,
the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254,
the Department of Chemistry, Loyola College, Baltimore, Maryland 21210,
and the Department of Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 1A1. *Received December 10, 1979*

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, $\alpha = 76.00$ (3)°, $\beta = 74.48$ (3)°, $\gamma = 66.60$ (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 $R_W = 0.093$. 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 0. Although $(\eta\text{-}C_5H_5)_2V$,[2] $V(CO)_6$,[3] and other V(0) compounds[4] are well known, Ta and Nb analogues 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(dimethylphosphino)ethane) with particular nucleophilic reagents 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 disproportionation 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 $TaH[PPh_2]_2(dmpe)_2$ 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. $TaCl_2(dmpe)_2$[12] and $K[PPh_2]\cdot 2$dioxane[20] were prepared by literature procedures. ^1H (100 MHz) and ^{31}P NMR (40.5 MHz) 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-MHz ^{31}P noise decoupling was introduced onto a separate crossed coil. The elemental analysis was by Dornis and Kolbe, Mülheim, West Germany.

$TaH(PPh_2)_2(dmpe)_2$. Dry THF (250 mL) was added to 7.0 g (0.012 mol) of $TaCl_2(dmpe)_2$ and 9.6 g (0.024 mol) of $KPPh_2\cdot 2$dioxane contained in a flask, cooled in an ice bath. A deep purple color developed instantly. The reaction was allowed to proceed for 2 h at 0 °C 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: mol wt (cryoscopic in benzene) 820 ± 30 (calcd, 852); IR (Nujol mull) ν(Ta–H) 1648 cm^{-1}; ^{31}P NMR (toluene-d_8) 20.52 (s), 10.11 (d, $J_{PH} = 83$ Hz), −3.85 ppm (s); $^1H\{^{31}P\}$ NMR (toluene-d_8) δ 8.05 and 7.43 (aryl, 20 H), 1.72 and 1.32 (dmpe methyls, singlets, 24 H), 1.51 (dmpe methylenes, br, 8 H).

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.

Degradation of $TaH(PPh_2)_2(dmpe)$. A. Reaction with DCl and D_2O. 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 $[{}^{12}C_{12}{}^1H_{10}{}^2D_1{}^{31}P_1]^+$ (*m/e* 187) and $[{}^{12}C_{12}{}^1H_{11}{}^{31}P_1]^+$ (*m/e* 186) in the ratio of 1.00:0.95. A similar experiment with D_2O showed the presence of $[{}^{12}C_{12}{}^1H_{10}{}^2D_1{}^{31}P_1]^+$ and $[{}^{12}C_{12}{}^1H_{11}{}^{31}P_1]^+$ 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 ^1H NMR spectrum indicated the presence of diphenylphosphine: HPPh$_2$ at δ 5.17, $J_{PH} = 219$ Hz (lit.[21] HPPh$_2$ δ 5.14, $J_{PH} = 216$ Hz). Integration of the phenyl region vs. HPPh$_2$ 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

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slowly, and were mounted in capillary tubes sealed under N_2. Several batches of crystals were examined, and about 20 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 crystals were transferred sequentially to a Syntex $P2_1$ diffractometer. Unfortunately, two of these decomposed during the first 4-6 h, and it was suspected that a structure determination would be impossible because of 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 (24K Nova configuration).[24] Within minutes of the end of data collection, the crystal suddenly 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 (½, ½, ½), 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 chemical and spectroscopic data suggested that the molecule was seven coordinate; hence it was decided to place the Ta atom at (¼, ¼, ¼) rather than on two independent centers of symmetry. The structure was solved with some difficulty by "manual trial and error" shifting of the Ta atom away from that position 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 ($\Delta/\sigma \leqslant 0.01$), a weighting scheme analysis revealed large discrepancies for reflections (mainly $0kl$) measured between 18.5 and 22.5 h 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 ($F_o \simeq 1.3F_c$) led, apparently, to five large peaks of height ~2.5 e/Å^3. These were near the Ta and P atoms, but all had locations of the type (X, ~¼, ~¼). The effect of omitting the reflections with the largest discrepancies (~130) was tested 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/Å^3 were still present, but with heights of 0.9-1.2 e/Å^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/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.

Table I. 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]	V = 1923.8 Å^3
space group: $P\bar{1}$ [C_i^1; no. 2]	Z = 2
a = 10.556 (3) Å	formula wt = 852.7
b = 11.175 (3) Å	ρ(calcd) = 1.47 g cm^{-3}
c = 18.663 (5) Å	ρ(obsd)[c] = 1.51 (2) g cm^{-3}
α = 76.00 (3)°	μ(calcd) = 79.1 cm^{-1}
β = 74.48 (3)°	(Cu Kα)
γ = 66.60 (3)°	

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

B. Collection of Intensity Data

radiation	Cu Kα, Ni β filter
reflections measured	$\pm h$, $\pm k$, $\pm l$ (to 2θ = 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 $< \pm 3\sigma(I)$ for each
automatic recentering of crystal	every 800 reflections

C. Treatment of Intensity of Data[d]

data reduction	intensities as before;[22] esd's of $\lvert F_o \rvert$ 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	$w = [\sigma^2(\lvert F_o \rvert + (\rho \lvert F_o \rvert)^2)]^{-1}$; ρ = 0.040
Patterson solution	Ta,6P; R = 0.204
isotropic refinement, all nonhydrogen atoms	R = 0.094; R_w = 0.114
anisotropic refinements: Ta, 6P, dmpe C atoms[f]	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 following tables. [b] The dimensions of the corresponding Delaunay reduced cell are a = 10.556 Å, b = 11.175 Å, c = 17.362 Å, α = 91.06°, β = 91.83°, γ = 113.38°. [c] Measured by flotation in 1,2-dibromoethane/hexane. [d] $R_s = \sum\sigma(|F_o|)/\sum|F_o|$; $R_{av} = [(\sum||I| - |I_{av}||)/\sum|I|]$. [e] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. Standard deviation of an observation of unit weight $= \{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (=2942) is the number of observations and n (=263) is the number of parameters varied. [f] Except C33, which would not refine anisotropically; other atoms isotropic; H atoms on phenyl rings included as fixed contributions with $r_{C\text{-}H}$ = 0.95 Å.

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).

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

The ^{31}P NMR (toluene-d_8) of the complex exhibited three broad resonances at 20.52, 10.11, and −3.85 ppm (presumably

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

atom	x	y	z	U_{iso}[a]
Ta	0.231 37(11)	0.269 04(10)	0.250 77 (6)	
P1	0.228 06(66)	0.397 48(56)	0.125 57(33)	
P2	0.255 87(64)	0.110 35(55)	0.363 83(33)	
P3	0.069 94(65)	0.167 80(62)	0.226 18(35)	
P4	−0.024 80(65)	0.406 97(61)	0.311 86(36)	
P5	0.498 77(62)	0.202 10(61)	0.214 81(35)	
P6	0.283 53(69)	0.439 57(59)	0.300 39(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)

[a] $U_{iso} = B_{iso}/8\pi^2$.

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	0.042 59 (71)	0.031 97 (64)	0.024 74 (58)	−0.015 80 (48)	−0.007 88 (45)	0.000 90 (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 $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2b^*c^*U_{23}kl)]$.

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 ($J_{P_B\text{-}H}$ = 83 Hz); similar J_{PH} values have been reported for a large number of seven-coordinate metal hydride complexes[13] of the type $MH(CO)_2(\text{bidentate phosphine})_2{}^{n+}$. Slight broadening of the A_2B_2 reso-

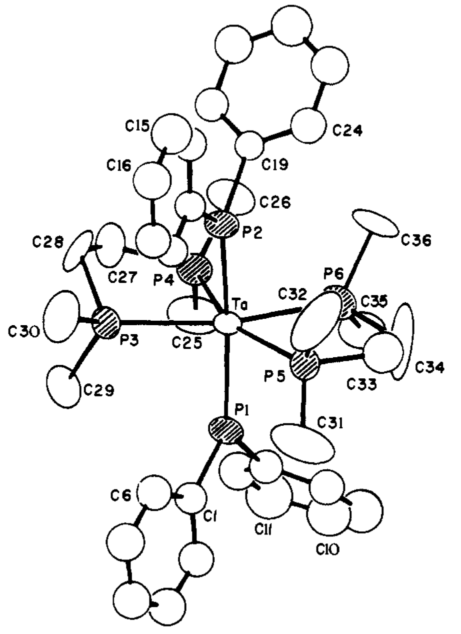


Figure 1. Molecular structure of $TaH(PPh_2)_2(dmpe)_2$. For clarity only two of each of the phenyl carbon atoms are labeled.

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)		

nances occurs at 80 °C, 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 temperature the $^1H\{^3P\}$ NMR showed two distinct dmpe methyl resonances. Above ambient temperature, these resonances broadened and coalesced; the coalescence point was reached at 80 °C. 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/mol.

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 $\mathit{H}PPh_2$ 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 $\mathit{H}PPh_2$ to the aryl hydrogen atoms was observed, consistent with the formation of equimolar amounts of $HPPh_2$ and $DPPh_2$.

Table V. Bond Angles (deg) for $TaH(PPh_2)_2(dmpe)_2$

P1-Ta-P2	170.36(22)	P3-C28-C27	110.5(21)
P3-Ta-P4	74.13(21)	C28-P3-Ta	108.5(10)
P5-Ta-P6	76.02(21)	C28-P3-C29	103.6(14)
P1-Ta-P3	89.06(22)	C28-P3-C30	100.7(13)
P1-Ta-P4	96.45(22)	C29-P3—Ta	119.4(10)
P1-Ta-P5	85.87(22)	C29-P3-C30	101.9(13)
P1-Ta-P6	92.44(22)	C30-P3-Ta	120.2(10)
P2-Ta-P3	87.15(22)	P4-C27-C28	110.3(23)
P2-Ta-P4	91.04(22)	C25-P4-C26	98.2(13)
P2-Ta-P5	89.73(22)	C25-P4-C27	97.0(15)
P2-Ta-P6	94.82(22)	C25-P4-Ta	119.7(10)
P3-Ta-P5	129.70(22)	C26-P4-C27	99.4(15)
P3-Ta-P6	154.26(22)	C26-P4-Ta	123.1 (9)
P4-Ta-P5	156.16(22)	C27-P4-Ta	114.6(12)
P4-Ta-P6	80.17(21)	P5-C33-C34	118.0(24)
C1-P1-C7	100.7 (11)	C31-P5-C32	104.5(18)
C1-P1-Ta	128.3 (8)	C31-P5-C33	103.1(17)
C7-P1-Ta	130.8 (8)	C31-P5-Ta	120.8(14)
C13-P2-C19	98.9 (10)	C32-P5-C33	87.6(16)
C13-P2-Ta	130.1 (8)	C32-P5-Ta	120.2(13)
C19-P2-Ta	131.0 (8)	C33—P5-Ta	114.7(11)
P1-C1-C2	124.7 (18)	P6-C34-C33	114.1(25)
P1-C1-C6	120.8 (18)	C34-P6-C35	99.5(15)
P1-C7-C8	119.0 (19)	C34-P6-C36	96.6(16)
P1-C7-C12	121.4 (20)	C34-P6-Ta	110.4(12)
P2-C13-C14	121.6 (18)	C35-P6-C36	99.8(14)
P2-C13-C18	121.5 (18)	C35-P6-Ta	122.8(9)
P2-C19-C20	121.0 (18)	C36-P6-Ta	122.6(11)
P2-C19-C24	120.2 (18)		

Molecular Structure of $TaH(PPh_2)_2(dmpe)_2$. The molecular structure of the complex and the atom labeling 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 toward 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 minor deviations (<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/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 (η-$C_5H_5)_2TaH_3$ 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

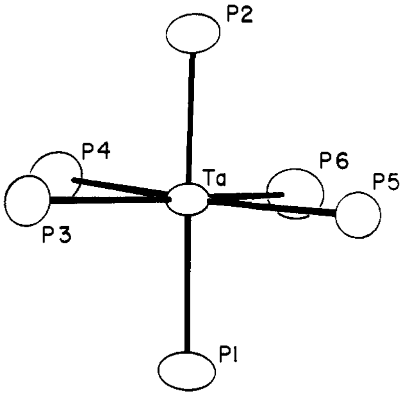


Figure 2. Skeletal geometry of $TaH(PPh_2)_2(dmpe)_2$, showing the expanded P3-Ta-P5 angle.

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: $0.933X - 0.094Y - 0.075Z - 4.196 = 0$
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 ref 33.

(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 because of 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 to 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) Å) are 0.13-0.22 Å shorter than the bond distances between Ta and the equatorial tertiary phosphines.

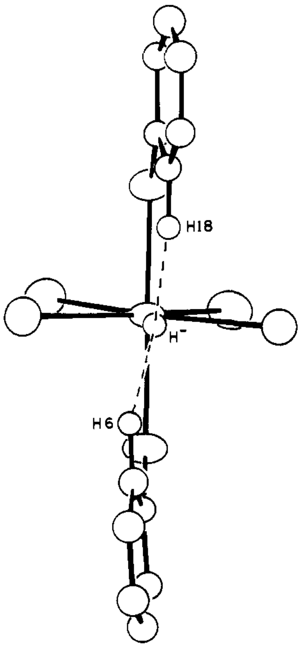


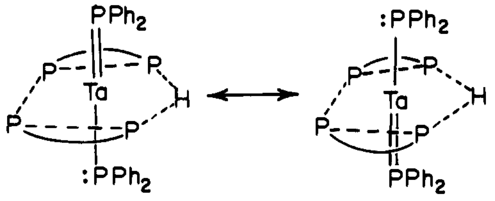
Figure 3. Illustration of H···H contacts in $TaH(PPh_2)_2(dmpe)_2$.

Discussion

Nature of the Ta-PPh₂ 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, $M-P(R)_2-M$, 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.

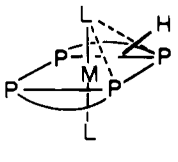
The only other structurally characterized R_2P-metal complexes are those having a phosphide bridge.[42] No structural reports of compounds containing terminal phosphide groups, $M{=}PR_2$, have appeared. Such compounds have been suggested as reaction intermediates[43] and are probably capable of existence, since nitrogen analogues 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:

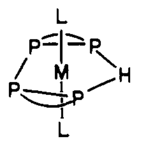


The approximate trigonal-planar arrangement of the diphenylphosphide ligands is consistent with this description. The trans-eclipsed geometry found for the $Ph_2P-Ta-PPh_2$ unit is required to attain an 18-electron configuration about Ta. For instance, compare $Ta(NMe_2)_2(O_2CNMe_2)_3$,[46] which has cis dialkylamide groups.

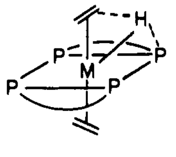
Relationship to Other Seven-Coordinate Hydrides. Hydrides of the general formula $MH(\pi \text{ acceptor})_2(\text{bidentate phosphine})_2{}^{n+}$ (M = Nb, Ta, n = 0; M = Cr, Mo, W, n = 1)[15-19] are well known. Three structural reports have appeared for examples with monodentate π-accepting ligands. The complex $TaH(CO)_2(dmpe)_2$ is reported to have monocapped 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 $TaH[PPh_2]_2(dmpe)_2$, 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.



I

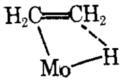


II



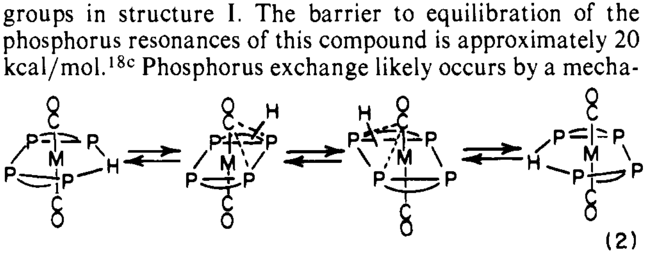
III

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



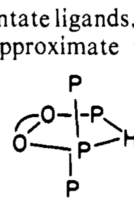
However, in this example C_1 and C_2 are not symmetrically bound to Mo; the $Mo(H)(C_2H_4)$ group approaches an $Mo-C_2H_5$ unit.[18b] The implied C_2-H interaction may be responsible for the location of the hydride.

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 $^{13}C\{^{31}P, {}^1H\}$ NMR spectrum. In contrast to an earlier study,[18c] which reported a broadened ^{13}C resonance at −70 °C in $(CD_3)_2CO$,[47] we find no evidence for chemical inequivalence of the carbonyl groups. Nonexchanging 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/mol 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 for exchange between upper and lower faces would be significantly less.



(2)

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.[48]

The approximate C_{2v} sturcture 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 adjacents to the hydride and those opposite the hydride. The observed exchange between these sites is accommodated 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 $HOsCl_2(PBu_2Ph)_3$,[49] $Pt(H)_2(diphos)_2$,[50] $HM(N(SiMe_3)_2)_3$ (M = Th, U),[51] and $HMn(CO)_3(PBu_3)_2$.[52] 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.

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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (Table VII) and hydrogen atom positions (Table VIII) (11 pages). Ordering information is given on any current masthead page.

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The Solvent as H-Atom Donor in Organic Electrochemical Reactions. Reduction of Aromatic Halides

F. M'Halla, J. Pinson, and J. M. Savéant*

Contribution from the Laboratoire d'Electrochimie de l'Université de Paris 7, 2, place Jussieu, 75221 Paris Cedex 05, France.

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Abstract: The first step following the initial formation of the anion radical in the electrochemical reduction of aromatic halides is the cleavage of the C–X bond leading to the neutral Ar· radical. The latter species undergoes three concurrent reactions: H-atom abstraction from the solvent and electron transfer at the electrode and/or from the initial anion radical. The quantitative analysis of this threefold competition allows one to predict the effect of the intrinsic (rate constants) and operational (concentration, stirring rate, cell geometry) parameters. It is the basis on which the results of deuterium incorporation by deuterated water or solvent can be used as a tool to investigate the reaction mechanism and to determine the characteristic rate constants. This is illustrated by the study of the chloro, bromo, and iodo derivatives of three aromatic residues (9-anthryl, 1-naphthyl, and 4-cyanophenyl) in Me_2SO and acetonitrile. It is shown that the proposed reduction mechanism is indeed followed in each case and the degree of competition between the three concurrent steps can be evaluated. Using the values obtained independently (by cyclic voltammetry or redox catalysis) for the cleavage rate of the anion radicals of the chloro compounds, the corresponding rates for the bromo and iodo derivatives are determined as well as the rates of H-atom transfer to the three aromatic radicals and the magnitude of the corresponding deuterium isotope effects.

Introduction

The chemical interference of the solvent in the mechanisms of organic electrochemical reactions is classically thought to involve its acid–base and/or nucleophile–electrophile properties.

The anion radicals and species formed upon further reduction may abstract protons from the solvent or react on it insofar as it possesses an electrophilic character. Conversely, the cation radicals and further oxidized species formed upon oxidation may transfer a proton to the solvent or add a solvent molecule if it possesses a sufficient nucleophilic character. There has been consequently a continuous effort in the development of organic electrochemistry to select solvents of low acidity and electrophilicity for reductions and low basicity and nucleophilicity for oxidations. A first interest of this is the stabilization of the ion radicals resulting in a more facile approach of the reaction mechanisms. On the other hand, the use of an inert solvent with purposely designed addition of a nucleophile or an electrophile has opened up synthetic routes of great interest (e.g., reductive alkylation and carboxylation, anodic substitution).

The role of the solvent as H-atom donor has been considerably less investigated in the context of organic electrochemical reactions carried out in organic solvents. It is, however, anticipated that as soon as a neutral carbon radical is

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