$Cl_2(bpy)\overline{PtCH_2CH_2CH_2}$. Nearly all crystals obtained were either twinned or split. A single crystal (0.02 × 0.04 × 0.20 mm) was finally obtained by a crystallization from CH_3CN, in which only extremely thin needles were present. An orthorhombic cell of space group *Amma* (nonstandard setting of *Cmcm*) was characterized with cell dimensions at −162 °C of a = 12.414 (12), b = 7.683 (7), and c = 14.583 (15) Å. The cell volume of 1390.8 (6) $Å^3$ gives a density of 2.217 g cm^{-3} for Z = 4, indicating the molecule must possess *mm* or $2/m$ symmetry. A total of 790 reflections were collected in the range $5° \le 2\theta \le 45°$ and reduced to 517 unique intensities. A scan speed of 2.0° min^{-1} and 10-s stationary background counts were used because of the low scattering of the crystal. The data were corrected for absorption (μ = 105.7 cm^{-1}), and the minimum and maximum transmission coefficients were 0.253 and 0.811, respectively.

The structure was solved by direct methods and Fourier techniques and possesses *mm* crystallographic symmetry. Full-matrix refinement using anisotropic thermal parameters converged to $R(F)$ = 0.078 and $R_w(F)$ = 0.065. A difference Fourier synthesis indicated several peaks of density 4.0–5.0 e $Å^{-3}$ near the platinum, and the random distribution of numerous peaks of density 0.6–1.0 e $Å^{-3}$ precluded the unequivocal assignment of hydrogen atoms. The refinement was concluded when the maximum shift/error was less than 0.10 and the goodness of fit for the first cycle was 2.105.

$(bpy)Pt(COCH_2CH_2CH_3)_2$. A suitable crystal was obtained by cleaving the bright red needles to obtain an irregularly shaped crystal of 0.06-mm maximum dimension. The selected crystal was thermochromic, changing from red to orange as it was cooled to −168 °C. The space group was determined to be $P2_1/a$ (nonstandard setting of $P2_1/c$) with cell dimensions at −168 °C of a = 16.195 (7) Å, b = 14.775 (6) Å, c = 7.085 (2) Å, and β = 93.31 (2)°. The density is calculated as 1.937 g cm^{-3} assuming Z = 4 for a volume of 1692.5 (1) $Å^3$. Data collection parameters were identical with those of $(bpy)PtC_3H_6$ presented above. A total of 2611 intensities were collected for $5° \le 2\theta \le 50°$ and reduced to 2229 unique data, of which 1649 had $F_o \ge 2.33\sigma(F_o)$. Manual ψ scans and an examination of symmetry-related intensity indicated a maximum absorption of ca. 10%. Due to the irregular shape of the sample, no attempt was made to perform this correction.

The structure was solved by a combination of Patterson and Fourier techniques. A difference Fourier synthesis phased on the refined nonhydrogen parameters located all but two hydrogen atoms. Attempts to include hydrogen parameters in the refinement were unsuccessful, since several refused to converge. In the final cycles of full-matrix refinement, hydrogen contributions were included as fixed atom contributors with d(C–H) = 0.95 Å, and all angles fixed as sp_3 or sp_2 coordination. Final residuals were $R(F)$ = 0.057 and $R_w(F)$ = 0.054, and the goodness of fit for the last cycle was 1.293. The maximum shift/error for the final cycle was 0.05.

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Supplementary Material Available: Complete listing of anisotropic thermal parameters (Table X), observed and calculated structure factors (Table XI), hydrogen bond distances and angles (Table XII), and hydrogen fractional coordinates and isotropic thermal parameters (Table XIII) (36 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of New Polyhydride Compounds of Tantalum(V)

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Abstract: A series of (pentamethylcyclopentadienyl)tantalum bis(phosphine) polyhydride complexes, $(\eta^5\text{-}C_5Me_5)TaL_2H_{4-n}Cl_n$ (n = 0, L = PMe_3, $PMe_2(C_6H_5)$, $P(OMe)_3$, and $Me_2PCH_2CH_2PMe_2$; n = 1, L = PMe_3), have been prepared by high-pressure hydrogenation of $(\eta^5\text{-}C_5Me_5)TaMe_4$ or $(\eta^5\text{-}C_5Me_5)TaMe_3Cl$ in the presence of L. The hydride ligands are more hydridic than protic in character. All of the compounds react with acetone and methanol to afford isopropoxide and methoxide complexes, respectively. Reactions with carbon monoxide yield carbonyl hydride and dicarbonyl compounds resulting from sequential reductive elimination of dihydrogen. Hydrogenation of ethylene is observed as well as catalytic dimerization of ethylene to 1-butene. Most reactions of these 18-electron polyhydride complexes are thought to involve rate-determining loss of a phosphine ligand. Evidence is presented in support of coordination of acetone to tantalum prior to its reduction to isopropoxide. By contrast, methanol can react directly with the coordinatively saturated tantalum hydride species to generate H_2.

Polyhydride complexes have been isolated for most of the transition metals, often with phosphines as the only other ligands.[3] The primary focus of this research has been the definition of the solid-state structures and the fluxional processes that are very common for these molecules.[3,4] Polyhydride compounds have high coordination numbers (6–9) and are among the least sterically crowded examples of these coordination geometries. The formal oxidation states for the metal center in early and middle transition-metal polyhydrides are often high, with d^2 and d^0 configurations quite common. The chemistry of transition-metal polyhydride complexes, especially those with formal d^0 configurations, has not yet been systematically examined. This may be due to the fact that these compounds are nearly always coordinatively saturated and thus relatively inert.[5] Lower valent "hydrides" are generally chemically more protic than hydridic: they are stable to alcohols, can often be deprotonated with strong bases, and can usually be protonated by strong acids without loss of dihydrogen.

Our interest in d^0 transition-metal hydride complexes was stimulated by the wealth of chemistry we found for bis(pentamethylcyclopentadienyl)zirconium dihydride, $Cp^*{}_2ZrH_2$ (1) (Cp* = $\eta^5\text{-}C_5(CH_3)_5$).[6] 1 is unusual both because its zirconium–hydride

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(1) National Science Foundation Predoctoral Fellow, 1978–1981.

(2) Camille and Henry Dreyfus Teacher-Scholar, 1977–1982.

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bonds are chemically like those of boron, aluminum, or alkali metal hydrides and because it is coordinatively unsaturated. Both of these properties are thought to be important in its stoichiometric reduction of carbon monoxide.[7] In this light we set out to prepare some new d^0 hydride complexes of tantalum. The following is a report on the synthesis, characterization, and reaction chemistry of a series of tantalum(V) polyhydrides of the general formula $Cp^*TaL_2H_{4-n}Cl_n$.

Results

1. Synthesis and Characterization. The general synthetic strategy for the hydrides reported here is based on hydrogenation of a corresponding alkyl compound. High-yield synthetic routes to (pentamethylcyclopentadienyl)trimethyltantalum chloride, Cp^*TaMe_3Cl (**2**), and (pentamethylcyclopentadienyl)tetramethyltantalum, Cp^*TaMe_4 (**3**), have been described by Schrock and co-workers.[8] Treatment of these alkyls with hydrogen under normal conditions yields intractable mixtures; even in the presence of added phosphines, hydrogenation at 1 atm does not give identifiable products. We find that under 100 atm of H_2 in the presence of phosphorus donor ligands, however, polyhydride complexes are formed in high yields. Thus $Cp^*TaL_2H_4$ (L = PMe_3 (**4**), $PMe_2(C_6H_5)$ (**5**), $P(OMe)_3$ (**6**); L_2 = $Me_2PCH_2CH_2PMe_2$ (≡dmpe) (**7**)) were obtained by treatment of **3** with 100 atm of H_2 and 2–3 equiv of L in petroleum ether for 1 day at room temperature (eq 1). $Cp^*Ta(PMe_3)_2H_3Cl$ (**8**)

$$\underset{\mathbf{3}}{Cp^*TaMe_4} + 4H_2\ (100\text{ atm}) + 2L \xrightarrow{25\ ^\circ C} Cp^*TaL_2H_4 + 4CH_4 \quad (1)$$

$$\begin{aligned} &\mathbf{4},\ L = PMe_3\\ &\mathbf{5},\ L = PMe_2(C_6H_5)\\ &\mathbf{6},\ L = P(OMe)_3\\ &\mathbf{7},\ L_2 = \text{dmpe}\end{aligned}$$

can be prepared similarly from hydrogenation of **2** in the presence of PMe_3 (eq 2). In all cases white crystalline materials can be

$$\underset{\mathbf{2}}{Cp^*TaMe_3Cl} + 3H_2\ (100\text{ atm}) + 2PMe_3 \xrightarrow{25\ ^\circ C} \underset{\mathbf{8}}{Cp^*Ta(PMe_3)_2H_3Cl} + 3CH_4 \quad (2)$$

obtained, although the very high solubility of these compounds in hydrocarbon solvents does present some difficulty in their isolation.

Thus far the success of the method has been restricted to the use of phosphorus donors as auxiliary ligands. With trimethylamine, pyridine, tetrahydrofuran, ethylenediamine, and dimethoxyethane, intractable mixtures have been obtained. In the absence of an added ligand, a black solid is obtained which is difficult to purify and has yet to be identified.

Hydrogenation of **3** in the presence of bipyridine (bpy) affords a black crystalline solid, **9**, in high yield. This reaction (eq 3),

$$\underset{\mathbf{3}}{Cp^*TaMe_4} + H_2\ (1\text{ atm}) + \text{bpy} \rightarrow \underset{\mathbf{9}}{Cp^*TaMe_2(\text{bpy})} + 2CH_4 \quad (3)$$

unlike those above, proceeds smoothly at 1 atm of hydrogen. The stoichiometry of eq 3 has been confirmed by Toepler pump measurements of the hydrogen absorbed and the methane produced. In addition, spectroscopic, analytical, and molecular weight data support the formulation of **9** as $Cp^*TaMe_2(\text{bpy})$. Treatment of **3** with deuterium gas and bpy produced **9** and a mixture of methanes, roughly 80% CH_3D and 20% CH_4. Surprisingly, **9** can be treated with 100 atm of hydrogen at room temperature for a week without change. Reaction does occur at 80 °C, but a mixture of products is obtained. **9** reacts rapidly with 2 equiv of carbon monoxide to give a bright blue compound, $Cp^*Ta(\eta^2\text{-}OCMe_2)(CO)(\text{bpy})$ (**10**) (eq 4).

$$\underset{\mathbf{9}}{Cp^*TaMe_2(\text{bpy})} + 2CO \rightarrow \underset{\mathbf{10}}{Cp^*Ta(\eta^2\text{-}OCMe_2)(CO)(\text{bpy})} \quad (4)$$

The reaction of **3** with CO has also been reported to yield an η^2-acetone or metallaoxirane complex.[8]

The four tetrahydride complexes **4**–**7** are fluxional on the NMR time scale at ambient temperatures. Thus the hydrides appear as binomial triplets in the proton NMR spectra and in each case the $^{31}P\{^1H\}$ NMR spectrum exhibits only a singlet (NMR and IR data in Table I). The hydride count was established for **7** by integration and by observation of a quintet in the ^{31}P NMR spectrum on selective decoupling of the dmpe protons. By contrast, the ^1H NMR spectrum of **8** at ambient temperatures indicates that the hydrides are not equivalent. The 500-MHz proton spectrum[9] exhibits two broad (30- and 50-Hz fwhm) hydride resonances which unlike **4** show no resolvable P–H coupling. Moreover, the hydrogens of the trimethylphosphine ligands appear as a triplet for **4** but as a doublet for **8**. These observations suggest that the PMe_3 ligands in **8** are labile, undergoing a rapid, reversible dissociation (eq 5). In support of this suggestion, a solution of

$$\underset{\mathbf{8}}{Cp^*TaH_3Cl(PMe_3)_2} \rightleftarrows [Cp^*TaH_3Cl(PMe_3)] + PMe_3 \quad (5)$$

8 with excess trimethylphosphine shows only one signal for PMe_3 in the ^1H NMR spectrum, intermediate between the positions of coordinated and free ligand. This type of NMR behavior for phosphine complexes has been examined in detail by Tolman.[10] The phosphine dissociation from **8** can be slowed sufficiently at low temperatures such that the expected strong P–H coupling may be observed. The low-temperature NMR spectra of all five hydride complexes will be the subject of a future publication.[11]

2. Reactions Involving Hydride Donation. These new hydride complexes react even with weak acids such as methanol to afford H_2 and the corresponding methoxytantalum species (eq 6 and 7).

$$Cp^*TaL_2H_4 + 4CH_3OH \rightarrow \underset{\mathbf{11}}{Cp^*Ta(OCH_3)_4} + 4H_2 + 2L \quad (6)$$

$$L_2 = 2PMe_3\ (\mathbf{4}),\ 2PMe_2(C_6H_5)\ (\mathbf{5}),\ 2P(OMe)_3(\mathbf{6}),\ \text{dmpe}\ (\mathbf{7})$$

$$\underset{\mathbf{8}}{Cp^*Ta(PMe_3)_2H_3Cl} + 3CH_3OH \rightarrow Cp^*Ta(OCH_3)_3Cl + 3H_2 + 2PMe_3 \quad (7)$$

The molecular weights of these alkoxide complexes have not been determined; fluxional, oligomeric structures are entirely possible. Loss of the phosphorus donor ligands accompanies these reactions, presumably due both to the greater steric crowding in the products and to the reduced Lewis acidity of the metal center because of π donation from the methoxy ligands. The π-donor ability of methoxide undoubtedly also contributes to the stability of the (formally) coordinatively unsaturated $Cp^*Ta(OCH_3)_4$ and $Cp^*Ta(OCH_3)_3Cl$. The reaction of **4** with less than 4 equiv of CH_3OH yields only the commensurate amounts of $Cp^*Ta(OCH_3)_4$ (**11**) and unreacted $Cp^*Ta(PMe_3)_2H_4$, suggesting that the intermediate methoxy hydride complexes are more reactive toward methanol than **4**. The reactivity of the hydride complexes varies over a fairly wide range: **8** reacts with methanol rapidly at 25 °C, **4**, **5**, and **7** react over a few hours at 25 °C, and **6** requires hours at 80 °C.

The facile reduction of acetone to the corresponding isopropoxide derivatives provides further evidence for the hydridic character of these compounds (eq 8 and 9). The rates of these

$$Cp^*TaL_2H_4 + 4Me_2CO \rightarrow Cp^*Ta(OCHMe_2)_4 + 2L \quad (8)$$

$$L_2 = 2PMe_3\ (\mathbf{4}),\ 2PMe_2(C_6H_5)\ (\mathbf{5}),\ 2P(OMe)_3\ (\mathbf{6}),\ \text{dmpe}\ (\mathbf{7})$$

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$$\underset{\mathbf{8}}{\mathrm{Cp^*Ta(PMe_3)_2H_3Cl}} + \mathrm{3Me_2CO} \rightarrow \mathrm{Cp^*Ta(OCHMe_2)_3Cl} + \mathrm{2PMe_3} \quad (9)$$

reactions also vary considerably, in the order **8** (seconds at 25 °C) > **5** (hours at 25 °C) > **4** (1 day at 25 °C) > **6** (hours at 80 °C) > **7** (1 week at 80 °C). This order of reactivity, **8** $\gg$ **4** $\gg$ **7**, is also the expected order for the rate of phosphine loss (see Discussion). The phosphine ligands for **8** are very labile (as described above, eq 5), and loss of PMe_3 from **4** should be much more facile than dissociation of one end of the dmpe ligand from **7**. This suggests that the reduction of acetone is proceeding via an initial substitution of Me_2CO for phosphine. In agreement with this hypothesis, added trimethylphosphine was found to greatly inhibit the conversion of $Cp^*Ta(PMe_3)_2H_4$ to $Cp^*Ta(OCHMe_2)_4$.

3. Reactions with Carbon Monoxide. Compounds **4**–**8** react with carbon monoxide to form lower valent carbonyl complexes in which CO displaces two hydride ligands. These reactions proceed cleanly with stoichiometric evolution of dihydrogen. In each case the reaction with CO proceeds at a rate similar to that with acetone. The reaction of **4** with CO yields first $Cp^*Ta(PMe_3)_2H_2(CO)$ (**12**) and finally $Cp^*Ta(PMe_3)_2(CO)_2$ (**13**) (eq 10). Both reactions are strongly inhibited by added phosphine,

$$\underset{\mathbf{4}}{\mathrm{Cp^*Ta(PMe_3)_2H_4}} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{CO,\,-H_2}} \underset{\mathbf{12}}{\mathrm{Cp^*Ta(PMe_3)_2H_2(CO)}} \xrightarrow[80\ ^\circ\mathrm{C}]{\mathrm{+CO,\,-H_2}} \underset{\mathbf{13}}{\mathrm{Cp^*Ta(PMe_3)_2(CO)_2}} \quad (10)$$

especially the final conversion of **12** to **13**. Thus both **12** and **13** can be isolated in good yield; the preparation of **12** requires a large amount of PMe_3. The reaction of **7** with carbon monoxide shows no evidence for a Ta(III) intermediate; the only detectable species during the reaction is the final product, $Cp^*Ta(dmpe)(CO)_2$ (**15**) (eq 11). Despite the vigorous conditions, the reactions proceeds

$$\underset{\mathbf{7}}{\mathrm{Cp^*Ta(dmpe)H_4}} + \mathrm{2CO} \xrightarrow{110\ ^\circ\mathrm{C}} \underset{\mathbf{15}}{\mathrm{Cp^*Ta(dmpe)(CO)_2}} + \mathrm{2H_2} \quad (11)$$

cleanly so that only **7** and **15** were observed by NMR spectroscopy even after 24 h at 110 °C. Equation 11 is analogous to the reaction of $Ta(dmpe)_2H_5$ with 1500 psi of CO at 80 °C reported to give $Ta(dmpe)_2(CO)_2H$.[12] No Ta(III) species was formed from this reaction either. **8** reacts rapidly with CO at 0 °C to afford a mixture of $Cp^*Ta(PMe_3)_2(CO)HCl$ (**16**) and $Cp^*Ta(PMe_3)(CO)_2HCl$ (**17**) (eq 12). Free phosphine inhibits this reaction

$$\underset{\mathbf{8}}{\mathrm{Cp^*Ta(PMe_3)_2H_3Cl}} + \mathrm{CO} \xrightarrow{0\ ^\circ\mathrm{C}} \underset{\mathbf{16}}{\mathrm{Cp^*Ta(PMe_3)_2(CO)HCl}} + \underset{\mathbf{17}}{\mathrm{Cp^*Ta(PMe_3)(CO)_2HCl}} + \mathrm{PMe_3} + \mathrm{H_2} \quad (12)$$

and increases the yield of **16** at the expense of **17**. **17** is favored in more dilute solutions under higher pressures of CO.

Compounds **13** and **15** can be assigned "four-legged piano stool" structures on the basis of equivalent phosphorus nuclei and equivalent carbonyls in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra, respectively. The carbonyl resonance in the spectrum of **15** is a doublet of doublets ($^2J_{PC}$ = 17 and 4 Hz), which indicates a static structure with the CO ligands cis. A triplet is observed for the carbonyl carbons in the $^{13}C\{^1H\}$ NMR spectrum of **13**, which, together with the large phosphorus–phosphorus coupling,[13] suggests a trans geometry for **13**. The extremely low CO stretching frequencies (1840 and 1750 cm^{-1} for **13**, 1830 and 1745 cm^{-1} for **15**) are among the lowest values thus far observed for neutral, monomeric carbonyl complexes. Similarly, the carbonyl resonances in the ^{13}C NMR spectra are observed extremely downfield (δ 278 (**13**) and δ 271 (**15**)).

4. Photochemistry. Irradiation of a benzene-d_6 solution of **7** in an NMR tube under 2 atm of carbon monoxide proceeds in a manner analogous to the thermal reaction of **4** with CO (eq 13).

$$\underset{\mathbf{7}}{\mathrm{Cp^*Ta(dmpe)H_4}} \xrightarrow[-\mathrm{H_2}]{\mathrm{CO},\,h\nu} \underset{\mathbf{14}}{\mathrm{Cp^*Ta(dmpe)(CO)H_2}} \xrightarrow[-\mathrm{H_2}]{\mathrm{CO},\,h\nu} \underset{\mathbf{15}}{\mathrm{Cp^*Ta(dmpe)(CO)_2}} \quad (13)$$

Since $Cp^*Ta(dmpe)(CO)H_2$ (**14**) is as photosensitive as **7**, it has been obtained only in mixtures with **7** and/or **15**. Irradiation under vacuum leaves **7** unchanged except for a small amount of decomposition. No hydrogen/deuterium exchange is observed between solvent C_6D_6 and the hydride ligands of **7**, in contrast to the photolysis of $CpMo(dmpe)H_3$.[14] However, when **7** is irradiated under 3 atm of D_2 exchange is observed with Ta–H ligands.

The absorption spectrum of **7** in petroleum ether shows no bands in the visible region, with a strong absorption centered below 250 nm. Since the tail of this band barely extends past 300 nm, a low-pressure mercury lamp that emits primarily at 254 nm has been used as a light source. While we realize benzene is an unusual solvent for photolyses in the ultraviolet region because it absorbs strongly below 280 nm, irradiation of **7** in a nonabsorbing solvent such as petroleum ether does not accelerate the reaction. Furthermore, in contast with the nearly quantitative conversions observed in benzene or toluene, photolyses in petroleum ether generate a number of side products.

Photolysis of a benzene solution of **7** under 2 atm of ethylene produces $Cp^*Ta(dmpe)H_2(C_2H_4)$ (**18**) and a stoichiometric amount of ethane (eq 14). **18** reacts at 25 °C with 2 equiv of

$$\underset{\mathbf{7}}{\mathrm{Cp^*Ta(dmpe)_2H_4}} + \mathrm{2C_2H_4} \xrightarrow{h\nu} \underset{\mathbf{18}}{\mathrm{Cp^*Ta(dmpe)H_2(C_2H_4)}} + \mathrm{C_2H_6} \quad (14)$$

carbon monoxide to yield **15** and ethane (eq 15). The reaction of **18** with hydrogen at 80 °C or under irradiation also releases ethane and regenerates **7** (eq 16). The $^{13}C\{^1H\}$ NMR spectrum

$$\underset{\mathbf{18}}{\mathrm{Cp^*Ta(dmpe)H_2(C_2H_4)}} + \mathrm{2CO} \xrightarrow{25\ ^\circ\mathrm{C}} \underset{\mathbf{15}}{\mathrm{Cp^*Ta(dmpe)(CO)_2}} + \mathrm{C_2H_6} \quad (15)$$

$$\underset{\mathbf{18}}{\mathrm{Cp^*Ta(dmpe)H_2(C_2H_4)}} + \mathrm{2H_2} \xrightarrow{80\ ^\circ\mathrm{C}} \underset{\mathbf{7}}{\mathrm{Cp^*Ta(dmpe)H_4}} + \mathrm{C_2H_6} \quad (16)$$

of **18** has eight groups of lines all coupled to one or both phosphorus nuclei. The ^{13}P NMR spectrum is a pair of doublets. An unsymmetrical static structure is thus implicated such that the six carbons of the dmpe ligand and the two carbons of the ethylene ligand are inequivalent. In contrast, the isoelectronic $Cp^*Ta(dmpe)H_2(CO)$ (**14**) is either fluxional or symmetrical, since both the hydride ligands and the carbon of the carbonyl appear as triplets in their respective NMR spectra.

5. Thermal Reactions with Ethylene. The reaction of **4**–**8** with ethylene produces a mixture of tantalum-containing products together with ethane, free phosphine, and 1-butene. These reactions proceed at roughly the same rate as the analogous thermal reactions with carbon monoxide or acetone. **7** and ethylene do not yield **18**, the photolytic product. However, **18** is unstable at the high temperatures required for reaction, so that the intermediacy of **18** in these reactions is uncertain. **4** appears to be a precursor for a fairly active ethylene dimerization catalyst: under 1 atm of ethylene the initial turnover rate of 1-butene is approximately one per hour. Since **4** is mostly unreacted after an hour, the turnover per active catalyst is probably much higher, however. Added PMe_3 inhibits the reaction.

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(13) For compounds **10**–**12** the phosphorus–phosphorus and the individual phosphorus–carbon coupling constants can be calculated from the triplet-type pattern for the trimethylphosphine carbons in the $^{13}C\{^1H\}$ NMR spectrum. The following values have been calculated (±5 Hz) following the method in ref 41: **10**, $^2J_{PP'} = 26$ Hz, $J_{CP} = \pm 75$ Hz, $J_{CP'} = \pm 48$ Hz; **11**, $^2J_{PP'} = 28$ Hz, $J_{CP} = \pm 75$ Hz, $J_{CP} = \mp 49$ Hz; **12**, $^2J_{PP'} = 16$ Hz, $J_{CP} = \pm 31$ Hz, $J_{CP'} = \mp 2$ Hz.

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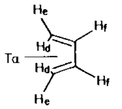
Table I. NMR[a] and IR[b] Data

		NMR			
compound	IR	assignment	type	chemical shift	coupling
$\mathrm{Cp^*Ta(PMe_3)_2H_4}$ (4)	ν(Ta-H) 1725, 1640	$\mathrm{C_5(CH_3)_5}$	^{1}H	2.16 s	
	ν(Ta-D) 1225, 1095	$\mathrm{[P(CH_3)_3]_2}$		1.42 t	$J_{\mathrm{PH}} = 4$
		$\mathrm{TaH_4}$		1.08 t	$J_{\mathrm{PH}} = 52.5$
$\mathrm{Cp^*Ta[PMe_2(C_6H_5)]_2H_4}$ (5)	ν(Ta-H) 1730, 1700, 1655	$\mathrm{C_5(CH_3)_5}$	^{1}H	1.94 s	
		$\mathrm{[P(C\mathit{H}_3)_2(C_6H_5)]_2}$		1.73 m^c	$J_{\mathrm{PH}} = 4^c$
		$\mathrm{[P(CH_3)_2(C_6H_5)]_2}$		7.11 m	
		$\mathrm{[P(CH_3)_2(C_6\mathit{H}_5)]_2}$		7.70 m	
		$\mathrm{TaH_4}$		1.44 t	$^2J_{\mathrm{PH}} = 50$
$\mathrm{Cp^*Ta[P(OMe)_3]_2H_4}$ (6)	ν(Ta-H) 1755, 1715, 1690	$\mathrm{C_5(CH_3)_5}$	^{1}H	2.28 s	
		$\mathrm{[P(OCH_3)_3]_2}$		3.47 m^c	$J_{\mathrm{PH}} = 5^c$
		$\mathrm{TaH_4}$		−1.38 t	$^2J_{\mathrm{PH}} = 58$
$\mathrm{Cp^*Ta(dmpe)H_4}$ (7)	ν(Ta-H) 1715, 1625	$\mathrm{C_5(CH_3)_5}$	^{1}H	2.33 s	
	ν(Ta-D)^d 1250, 1160	$\mathrm{(C\mathit{H}_3)_2PCH_2CH_2P(C\mathit{H}_3)_2}$		1.32 m	
		$\mathrm{(CH_3)_2PC\mathit{H}_2C\mathit{H}_2P(CH_3)_2}$		1.16 d	$J_{\mathrm{PH}} = 15$
		$\mathrm{TaH_4}$		0.19 t	$^2J_{\mathrm{PH}} = 37$
$\mathrm{Cp^*Ta(PMe_3)_2H_3Cl}$ (8)	ν(Ta-H) 1765, 1700	$\mathrm{C_5(CH_3)_5}$	^{1}H	1.96 s	
	ν(Ta-D)^d 1250, 1220	$\mathrm{[P(CH_3)_3]_2}$		1.33 d	$^2J_{\mathrm{PH}} = 7.5$
		$\mathrm{Ta\mathit{H}'H_2}$"		5.2^e broad	
		$\mathrm{TaH'\mathit{H}_2}$"		4.8^e broad	
$\mathrm{Cp^*Ta(OCHMe_2)_4}$	ν(Ta-O) 575	$\mathrm{C_5(CH_3)_5}$	^{1}H	1.91 s	
		$\mathrm{[OC\mathit{H}(CH_3)_2]_4}$		4.58 septet	$^3J_{\mathrm{HH}} = 6$
		$\mathrm{[OCH(C\mathit{H}_3)_2]_4}$		1.17 d	$^3J_{\mathrm{HH}} = 6$
$\mathrm{Cp^*Ta(OCHMe_2)_3Cl}$	ν(Ta-O) 575	$\mathrm{C_5(CH_3)_5}$	^{1}H	2.03 s	
		$\mathrm{[OC\mathit{H}(CH_3)_2]_3}$		4.89 septet	$^3J_{\mathrm{HH}} = 6$
		$\mathrm{[OCH(C\mathit{H}_3)_2]_3}$		1.20 d	$^3J_{\mathrm{HH}} = 6$
$\mathrm{Cp^*Ta(OMe)_4}$ (11)	ν(Ta-O) 535, 480	$\mathrm{[C_5(CH_3)_5}$	^{1}H	2.00 s	
		$\mathrm{(OCH_3)_4}$		4.22 s	
$\mathrm{Cp^*Ta(PMe_3)_2H_2(CO)}$ (12)	ν(CO) 1840	$\mathrm{C_5(CH_3)_5}$	^{1}H	2.01 s	
	ν(Ta-H) 1750, 1590	$\mathrm{[P(CH_3)_3]_2}$		1.36 m^c	$J_{\mathrm{PH}} = 3.5^c$
		$\mathrm{Ta\mathit{H}_2}$		−0.50 t	$^2J_{\mathrm{PH}} = 47$
		$\mathrm{\mathit{C}_5(CH_3)_5}$	$^{13}\mathrm{C}\{^1\mathrm{H}\}$	100.52 s	
		$\mathrm{C_5(\mathit{C}H_3)_5}$		12.06 s	
		$\mathrm{[P(CH_3)_3]_2}$		25.49 t	$J_{\mathrm{PC}} = 14^f$
		$\mathrm{Ta(CO)}$		261.04 t	$^2J_{\mathrm{PC}} = 6$
$\mathrm{Cp^*Ta(PMe_3)_2(CO)_2}$ (13)	ν(CO) 1842, 1750	$\mathrm{C_5(CH_3)_5}$	^{1}H	1.90 s	
		$\mathrm{[P(CH_3)_3]_2}$		1.35 m^c	$J_{\mathrm{PH}} = 8^c$
		$\mathrm{\mathit{C}_5(CH_3)_5}$	$^{13}\mathrm{C}\{^1\mathrm{H}\}$	104.31 s	
		$\mathrm{C_5(\mathit{C}H_3)_5}$		12.44 s	
		$\mathrm{[P(CH_3)_3]_2}$		20.48 t	$J_{\mathrm{PC}} = 14^f$
		$\mathrm{Ta(CO)_2}$		278.11 t	$J_{\mathrm{PC}} = 19.5$
$\mathrm{Cp^*Ta(dmpe)H_2(CO)}$ (14)	ν(CO)^d 1850	$\mathrm{C_5(C\mathit{H}_3)_5}$	^{1}H	2.09 s	
		$\mathrm{(C\mathit{H}_3)_2PC\mathit{H}_2C\mathit{H}_2P(C\mathit{H}_3)_2}$		overlap with 6 and 15	
		$\mathrm{TaH_2}$		−2.30 t	$^2J_{\mathrm{PH}} = 40$
$\mathrm{Cp^*Ta(dmpe)(CO)_2}$ (15)	ν(CO) 1830, 1745	$\mathrm{C_5(CH_3)_5}$	^{1}H	1.97 s	
		$\mathrm{(C\mathit{H}_3)(CH_3)PCH_2CH_2P(C\mathit{H}_3)(CH_3)}$		1.45 d	$J_{\mathrm{PH}} = 7.5$ Hz
		$\mathrm{(CH_3)(C\mathit{H}_3)PC\mathit{H}_aH_bC\mathit{H}_aH_bP(CH_3)(C\mathit{H}_3)}$		0.99 d	$J_{\mathrm{PH}} = 6$ Hz
		$\mathrm{(CH_3)(CH_3)PCH_a\mathit{H}_bCH_a\mathit{H}_bP(CH_3)(CH_3)}$		0.85 m	
		$\mathrm{\mathit{C}_5(CH_3)_5}$	$^{13}\mathrm{C}\{^1\mathrm{H}\}$	104.16 s	
		$\mathrm{C_5(\mathit{C}H_3)_5}$		12.66 s	
		$\mathrm{(\mathit{C}_aH_3)(C_bH_3)PCH_2CH_2P(\mathit{C}_aH_3)(C_bH_3)}$		21.32 dd	$J_{\mathrm{PC}} = 30, 4$

		$(C_aH_3)(\mathit{C}_bH_3)PCH_2CH_2P(C_aH_3)(\mathit{C}_bH_3)$		19.60 d	$J_{PC} = 17$
		$(CH_3)(CH_3)P\mathit{C}H_2\mathit{C}H_2P(CH_3)(CH_3)$		32.95 dd	$J_{PC} = 26, 17.5$
		$Ta(CO)_2$		270.88 dd	$J_{PC} = 17, 4$
$Cp^*Ta(PMe_3)_2(CO)HCl$ (16)	ν(CO) 1820	$C_5(CH_3)_5$	^1H	1.83 s	
		$[P(CH_3)_3]_2$		1.26 m[c]	$J_{PH} = 4$[c]
		TaH		5.64 t	$^2J_{PH} = 45$
		$\mathit{C}_5(CH_3)_5$	$^{13}C\{^1H\}$	102.10 s	
		$C_5(\mathit{C}H_3)_5$		11.70 s	
		$[P(CH_3)_3]_2$		18.20 t	$J_{PC} = 15$[f]
		Ta(CO)		267.83 t	$^2J_{PC} = 6$
$Cp^*Ta(PMe_3)(CO)_2HCl$ (17)	ν(CO) 1975, 1890 ν(Ta-H) 1645	$C_5(CH_3)_5$	^1H	1.75 s	
		$P(CH_3)_3$		1.05 d	$^2J_{PH} = 8$
		TaH		5.78 d	$^2J_{PH} = 36$
		$\mathit{C}_5(CH_3)_5$	$^{13}C\{^1H\}$	103.57 s	
		$C_5(\mathit{C}H_3)_5$		10.91 s	
		$P(CH_3)_3$		15.65 d	$^2J_{CP} = 26$
		$Ta(CO)_2$		not obsd	
$Cp^*Ta(dmpe)(C_2H_4)H_2$ (18)	ν(Ta-H) 1695, 1590	$C_5(CH_3)_5$	^1H	2.01 s	
		$(\mathit{CH}_3)_2P\mathit{CH}_2\mathit{CH}_2P(\mathit{CH}_3)_2$		1.5-0.5 m	
		$Ta\mathit{H}_2$		−0.4 broad	
			^{31}P	two doublets separated by 9.34 ppm	$^2J_{PP} = 21$
		$\mathit{C}_5(CH_3)_5$	$^{13}C\{^1H\}$	102.6 s	
		$C_5(\mathit{C}H_3)_5$		13.4 s	
		$(CH_3)(CH_3)PCH_2CH_2P(CH_3)(CH_3)$ and CH_2CH_2; each carbon gives rise to one set of resonances		33.4 dd	$J_{PC} = 23, 27$
				31.0 dd	$J_{PC} = 13, 20$
				27.7 dd	$J_{PC} = 7, 50$
				21.2 d	$J_{PC} = 13$
				16.0 dd	$J_{PC} = 4, 11$
				14.5 d	$J_{PC} = 4$
				12.4 d	$J_{PC} = 21$
				9.0 d	$J_{PC} = 3$
$Cp^*TaCH_2CH_2CH_2CH_2(C_4H_6)$ (19)		$C_5(CH_3)_5$	^1H[g]	1.77 s	
		$Ta\mathit{CH}_aH_bC(H_c)_2C(H_c)_2\mathit{CH}_aH_b$		2.15 m	$J_{H_aH_b} = 6$
		$TaCH_a\mathit{H}_bC(H_c)_2C(H_c)_2CH_a\mathit{H}_b$		3.10 m	$J_{H_aH_c} = 5$
		$TaCH_aH_bC(\mathit{H}_c)_2C(\mathit{H}_c)_2CH_aH_b$		0.33 m	$J_{H_bH_e} = 7$
		 H_e H_d H_f		0.24 m −1.64 m 7.00 m	$J_{H_dH_e} = 6$ $J_{H_eH_f} = 10$ $J_{H_dH_f} = 5$
		$\mathit{C}_5(CH_3)_5$	^{13}C	119.49 s	
		$C_5(\mathit{C}H_3)_5$		11.49 q	$^1J_{CH} = 127$
		$Ta\mathit{C}H_2CH_2CH_2\mathit{C}H_2$		54.96 t	$^1J_{CH} = 118$
		$TaCH_2\mathit{C}H_2\mathit{C}H_2CH_2$		36.75 t	$^1J_{CH} = 124$
		$Ta(\mathit{C}H_2{=}CHCH{=}\mathit{C}H_2)$		55.17 t	$^1J_{CH} = 147$
		$Ta(CH_2{=}\mathit{C}H\mathit{C}H{=}CH_2)$		117.06 d	$^1J_{CH} = 160$

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[a] NMR spectra taken in benzene-d_6 solvent at ambient temperature. Chemical shifts in δ measured from internal Me_4Si; coupling constants reported in hertz. All phosphine complexes show one singlet in the $^{31}P\{^1H\}$ NMR except 18 as noted. Spectroscopic data for Cp^*TaMe_2(bpy) (9) and $Cp^*Ta(\eta^2\text{-}OCMe_2)$(CO)bpy (10) are listed in the Experimental Section. [b] IR spectra obtained as Nujol mulls except where indicated. Values given in cm^{-1}. The complete spectra are detailed in the Experimental Section. [c] Non-first-order NMR pattern intermediate between a doublet and triplet; coupling constants are those that best describe the pattern. See ref 38. [d] IR spectrum taken in benzene-d_6 solvent. [e] See ref 9. [f] See ref 13. [g] Spectrum interpretable only at 500 MHz; see Figure 1. Tentative assignments made by selective decoupling experiments and by analogy to ref 39 and 40: coupling constants ± 3 Hz.

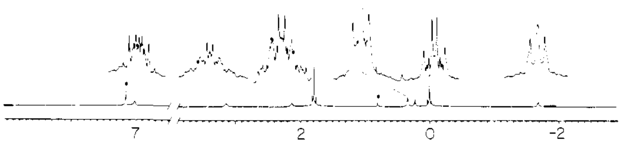
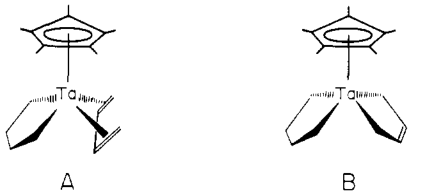


Figure 1. 500-MHz ^1H NMR spectrum of $Cp^*\overline{TaCH_2CH_2CH_2CH_2}$-$(C_4H_6)$ (**19**), benzene-d_6 solvent, $SiMe_4$ internal standard. Inserts are expanded by a factor of 10. Asterisks denote solvent and impurity resonances.

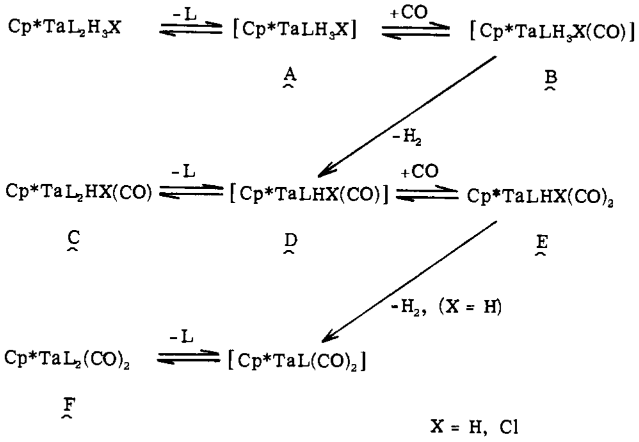
One of the products of the reaction of **4** with ethylene has been isolated and characterized as a metallacyclopentane–butadiene complex, $Cp^*\overline{TaCH_2CH_2CH_2CH_2}(C_4H_6)$ (**19**). **19** is also formed in higher yields in the reactions of ethylene with **5** and **6**. The 500-MHz ^1H NMR spectrum of **19** is shown in Figure 1; Table I contains tentative assignments based on selective decoupling experiments. The disparity in the ^{13}C–H coupling constants for the butadiene ligand ($^1J_{C_\alpha H}$ = 147 Hz, $^1J_{C_\beta H}$ = 160 Hz) suggests some contribution of the canonical form B shown below. In light of the observation that solutions of **19** do not react with ethylene, the catalytic dimerization was not pursued further. Schrock and co-workers have examined several systems that are olefin dimerization catalysts.[15,16] One based on a Cp^*TaCl_2(olefin)–Cp^*TaCl_2(metallacyclopentane) cycle[16] appears to be similar to the system reported here.



Discussion

Hydrogenation of alkyl complexes has proven to be a powerful synthetic route to polyhydride compounds, especially for the early transition metals. In addition to the syntheses described above, other examples include the reaction of hexamethyltungsten with high pressures of hydrogen in the presence of phosphine to give WH_6L_3, WH_4L_4, or WH_2L_5, depending on the size of the ligand L,[17a] and the preparation of $Ta(dmpe)_2H_5$ from $TaMe_5(dmpe)$[17b] or $Ta(C_6H_5)_6^-$ with dmpe and hydrogen.[12] This procedure has a number of advantages over the more common synthetic routes using boron or aluminum hydride reagents: usually nonforcing conditions and nonpolar media are used, and the problems of the boron or aluminum complexing with the transition-metal hydride are avoided. The mechanism of the reaction is a matter of debate,[18] since the alkyl starting materials used are often formally d^0 (as are **2** and **3**) and therefore cannot react with dihydrogen by a conventional oxidative addition/reductive elimination pathway. High pressures are usually required when the product is a polyhydride, presumably because a high concentration of dihydrogen is required to trap reactive, coordinatively unsaturated intermediates.

Scheme I



It is not clear why the hydrogenation of **3** is successful only in the presence of phosphine or phosphite ligands and not with oxygen or nitrogen donors. The sole exception occurs with bipyridine as the added ligand. In this case the reaction proceeds smoothly even at only 1 atm of hydrogen to yield $Cp^*TaMe_2(bpy)$ (**9**). Curiously, the reaction stops at **9**, a d^2 16-electron complex that seems ideally suited to oxidatively add H_2.

The five new polyhydride complexes reported here are formally 18-electron compounds and thus coordinatively saturated. Each compound reacts with carbon monoxide, acetone, and ethylene at roughly similar rates, suggesting a common pathway. The strong inhibition of these reactions by excess phosphine suggests that dissociation of a phosphine ligand is a prerequisite for reaction with these substrates. This conclusion is also consistent with the relative reactivities of the polyhydride complexes. $Cp^*Ta(PMe_3)_2H_3Cl$ (**8**) is the most reactive of the group—reactions with the above substrates are rapid at 0 °C. Furthermore, **8** is the only compound for which phosphine dissociation is rapid at room temperature on the NMR time scale. **4** and **7** should be electronically quite similar, but the reactions of **4** proceed at room temperature while **7** requires heating to 100 °C to achieve comparable rates. Dissociation of one end of the bidentate dmpe ligand is expected to be more difficult than loss of one or two PMe_3 ligands. This anticipated difference in phosphine dissociation rate has also been observed for the reaction of $Ta(CHCMe_3)L_2Cl_3$ (L_2 = $2PMe_3$, dmpe) with ethylene. Displacement of the phosphine occurs rapidly at room temperature for the bis(trimethylphosphine) derivative; the dmpe complex requires heating to 80–100 °C for several hours.[19]

The variation in the rate of phosphine loss from the bis(phosphine) compounds appears to be due to both electronic and steric factors. These complexes are formally nine-coordinate, if the bulky η^5-C_5Me_5 ligand is considered to occupy three sites, and thus are sterically quite crowded. Since a chloride ligand is larger than a hydride, **8** is more crowded than **4**; phosphine dissociation should therefore be more favored in **8** than in **4** on steric grounds. Chloride can also act as a weak π donor and hence can serve as a potential three-electron donor. As such Cl^- is expected to better stabilize the product of ligand loss relative to H^-. A similar trend has been reported in the dissociation of triphenylphosphine from $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$.[20] **5** is slightly more reactive than **4**, presumably because PMe_2Ph is larger than PMe_3.[21] The low reactivity of **6** indicates that trimethyl phosphite dissociates much more slowly than the ligands in **4** and **5**, probably due to

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the small size of $P(OMe)_3$.[21] Other workers have noted that, at least for later transition-metal complexes, phosphite ligands are less labile than phosphine ligands. Tolman observed that phosphite ligands dissociate from Ni(0) much more slowly than phosphines of similar size.[10] Reactions of the iron and ruthenium hydrides H_2ML_4 (L = PR_3, $P(OR)_3$) require conditions where ligand dissociation is facile. $H_2M(PPh_2Me)_4$ (M = Fe, Ru) substitute CO or benzonitrile for phosphine at 30–60 °C, while the phosphite derivatives $H_2M[P(OC_2H_5)_3]_4$ do not react with CO at temperatures exceeding 100 °C and at pressures up to 100 atm.[22]

The reactions of the polyhydride compounds with carbon monoxide can be accommodated by the mechanism shown in Scheme I. For **4** and **7** the compounds C and F (X = H) have been isolated; for **8** the reaction produces a mixture of C and E (X = Cl). Dissociation of a phosphine ligand generates coordinatively unsaturated species A. A can add a CO ligand, which is expected to better stabilize the incipient Ta(III) d^2 species accompanying reductive elimination of H_2. Indeed, d^0 carbonyl complexes such as intermediate B are unstable because the metal has no filled nonbonding orbitals available for π bonding with the CO. The complexes $Cp_2{}^*MH_2(CO)$ (M = Zr, Hf)[23] are unstable above −10 °C; under most conditions these compounds form products based on the reduction of carbon monoxide.[5] In the presence of excess CO, however, the predominant pathway can be reductive elimination of dihydrogen.[24] Similarly, $Cp_2NbH_2(CO)^+$ (Cp = η^5-C_5H_5), proposed as an intermediate in the protonation of $Cp_2Nb(H)CO$, eliminates H_2 above −30 °C.[25] Thus it is not surprising to find that for these tantalum systems reductive elimination of H_2 is a very facile process. It is interesting that the reduction from Ta(III) to Ta(I) is finely tuned: $Cp^*Ta(PMe_3)_2H_2(CO)$ (**12**) is stable while $Cp^*Ta(PMe_3)H_2(CO)_2$ is not observed. $Cp^*Ta(PMe_3)H_2(CO)_2$ would be analogous to **17** and presumably is an intermediate on the path from **12** to **13** (see Scheme I).

These new tantalum polyhydrides are clearly hydridic rather than protic; that is, they behave formally as sources of H^- like boron or aluminum hydride reagents. In contrast, most transition-metal hydrides either are acidic or are radical precursors—the hydrogen ligands react either as H^+ or in an increasing number of examples as sources of $H\cdot$.[26] There is a rough correlation of chemical properties with position in the periodic table; the most acidic compounds are found for the later transition metals and the hydridic complexes on the far left.[3] Although this general trend is clear, obtaining a measure of the hydridic character of a specific transition-metal hydride is difficult. There have been some attempts to construct a scale of hydridic character based on certain test reactions with common substrates; however, these reactions may require an open coordination site, so that a comparison of a series of hydrides may be dominated by the accessibility of a coordinatively unsaturated intermediate. One study has compared a number of cyclopentadienylmetal hydride complexes in their reactions with acetone and trifluoroacetone.[27] While compounds **4**–**8** react with acetone to yield isopropoxide complexes, the available evidence indicates that phosphine dissociation is required for this process. Thus the relative reactivity of the hydride complexes is dominated by the rate of phosphine loss, not the hydridic character of the hydride ligands. Presumably, acetone, like ethylene, must coordinate before a hydrogen is transferred to the unsaturated carbon. It is also conceivable that this process closely resembles borane reductions of ketones and aldehydes, where coordination of the carbonyl oxygen accelerates H^- transfer.[28]

The hydride compounds all react at −80 °C with anhydrous HCl to generate a stoichiometric amount of dihydrogen. Since phosphine dissociation is very slow at low temperature, this reaction does not appear to require an open coordination site. Here the mechanism probably involves direct protonation of a metal–hydride bond. A weak acid such as methanol can react either by direct protonation, if the hydride ligands are sufficiently reactive, or by coordinating to the metal prior to elimination of H_2. The latter is probably the more facile process if an open site is available in view of the enhanced acidity of ligated MeOH. The tantalum–oxygen interaction should also stabilize the transition state for hydrogen production by this mechanism. Compounds **4**, **5**, **6**, and **8** react with methanol at roughly the same rate as they react with acetone or CO, consistent with phosphine loss and prior coordination of MeOH for these reactions. The reaction of **7** with MeOH, however, is 3 or 4 orders of magnitude faster than its reactions with acetone, CO, or ethylene (hours at room temperature vs. days at 100 °C), implicating a direct electrophilic attack of methanol at the Ta–H bonds of coordinatively saturated **7**.

Under conditions where a coordination site is not available, the rate of reaction with weak protic acids could thus be used as a rough measure of the hydridic character of a transition-metal hydride. The rates of reaction of the series of tantalum hydrides reported herein with CH_3OH compare qualitatively as follows: $Cp^*Ta(PMe_3)_2H_3Cl$ (**8**) (seconds, 25 °C) > $Cp^*Ta(PMe_2Ph)_2H_4$ (**5**) ~ $Cp^*Ta(PMe_3)_2H_4$ (**4**) ~ $Cp^*Ta(dmpe)H_4$ (**7**) > $Cp^*Ta[P(OMe)_3]_2H_4$ (**6**) (hours, 80 °C). Since **6** reacts (regardless of mechanism) with methanol more slowly than **7**, **7** is more hydridic than **6** by this criterion. This order could reasonably be attributed to the greater σ donation from a phosphine vs. a phosphite. Unfortunately, the situation is muddled for **4**, **5**, and **8**, since the mechanism could involve prior loss of a phosphine ligand. **7** seems to fall on this scale between $Ta(dmpe)_2H_5$, which rapidly reacts with ethanol at 25 °C,[12] and Cp_2TaH_3, which is decomposed only by aqueous acids.[29] By contrast, d^2 group 6 hydrides show no hydridic character by the above criterion. Cp_2WH_2, Cp_2MoH_2, and $CpMo(dmpe)H_3$, like the d^2 group 5 species $Cp_2Nb(PR_3)H$, are all protonated by aqueous acid to give stable cations.[29-31] We tentatively conclude therefore that d^0 transition-metal hydrides are more hydridic than d^2 species bearing the same auxiliary ligands.

Experimental Section

General Considerations. All manipulations were carried out by using either high-vacuum line or glovebox techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$ and then from titanocene prepared as described earlier.[32] Hydrogen and deuterium (Matheson) were purified by passage over MnO on vermiculite[33] and activated 4-Å molecular sieves. Reactions at high pressure of hydrogen were performed in a Parr stirred "minireactor" no. 4561 using UHP hydrogen (Matheson) of minimum purity 99.999%. Carbon monoxide (Matheson) was used directly from the cylinder. Ethylene (Matheson) was condensed at −196 °C and evaporated at −78 °C. Photolyses were performed with a low-pressure mercury lamp. Elemental analyses and molecular weights were determined by Alfred Berhardt Analytical Laboratory.

Trimethylphosphine (Strem) was stored under vacuum and vacuum transferred prior to use. Trimethyl phosphite was fractionally distilled and stored over 4-Å molecular sieves, acetone was stored over 4-Å molecular sieves, and methanol was stored over freshly made sodium methoxide; all were vacuum transferred prior to use. bpy (MCB) was sublimed prior to use.

^1H NMR spectra were recorded with Varian EM390, JEOL FX90Q, or Bruker WM500 spectrometers. ^{13}C and ^{31}P NMR spectra were ob-

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tained by using a JEOL FX90Q spectrometer. Infrared spectra were measured on a Beckman 4240 spectrometer as Nujol mulls and are reported in cm^{-1}.

Many reactions were carried out in sealed NMR tubes and monitored by NMR spectrosocpy. Most of the information on rates of reactions has been obtained in this manner. A typical example is the reaction of Cp*Ta(PMe$_3$)$_2$H$_4$ (**4**) with CO: 30 mg (0.07 mmol) of **4** was transferred to an NMR tube sealed to a ground-glass joint and fitted with a Teflon needle valve adapter. Benzene-d_6 was vacuum transfered into the tube at -78 °C, 1 atm of CO introduced, the Teflon needle valve closed, the lower portion of the tube cooled to −196 °C, and the tube sealed with a torch.

Procedures. Cp*Ta(PMe$_3$)$_2$H$_4$ (4). A high-pressure reactor, charged with 1.8 g of Cp*TaMe$_4$[8] (**3**), 60 mL of petroleum ether, and 1.8 mL of PMe$_3$, was pressured to 1700 psi of hydrogen and stirred for 5 days. White Cp*Ta(PMe$_3$)$_2$H$_4$ (1.75 g, 77%) was crystallized from this solution, washed with petroleum ether, and dried in vacuo: dec 75 °C under vacuum; IR 1725–1640, 1300, 1280, 1125, 1030, 955, 935, 905, 855, 720, 660. Cp*Ta(PMe$_3$)$_2$D$_4$ was prepared by exchange of **4** with D$_2$ in C$_6$D$_6$ at room temperature for 2 days. Anal. Calcd for C$_{16}$H$_{37}$P$_2$Ta: C, 40.68; H, 7.90; Ta, 38.31. Found: C, 40.51; H, 7.74; Ta, 38.14.

Cp*Ta[PMe$_2$(C$_6$H$_5$)]$_2$H$_4$ (5). A high-pressure reactor, charged with 1.39 g of **3**,[8] 1.3 mL of PMe$_2$(C$_6$H$_5$) (Strem), and 100 mL of petroleum ether, was pressured to 1560 psi of hydrogen and stirred for 2 days. White Cp*Ta[PMe$_2$(C$_6$H$_5$)]$_2$H$_4$ (1.83 g, 88%) was crystallized from this solution, washed with petroleum ether, and dried in vacuo; IR 1730, 1700, 1655, 1290, 1270, 1110, 1025, 940, 915, 895, 740, 720, 700, 690, 490, 390.

Cp*Ta[P(OMe)$_3$]$_2$H$_4$ (6). A high-pressure reactor, charged with 2.2 g of Cp*TaMe$_4$[8] (**3**), 80 mL of petroleum ether, and 1.5 mL of P(OMe)$_3$, was pressured to 1600 psi of hydrogen and stirred for 1.5 days. White Cp*Ta[P(OMe)$_3$]$_2$H$_4$ (1.9 g, 57%) was crystallized from this solution, washed with petroleum ether, and dried in vacuo; IR 1755, 1715, 1690, 1180, 1070, 1030, 755, 740, 710, 510, 480. Anal. Calcd for C$_{16}$H$_{37}$O$_6$P$_2$Ta: C, 33.81; H, 6.56; Ta, 31.84. Found: C, 33.76; H, 6.47; Ta, 32.08.

Cp*Ta(dmpe)H$_4$ (7). A high-pressure reactor, charged with 3.56 g of Cp*TaMe$_4$[8] (**3**), 125 mL of petroleum ether, and 1.8 mL of dmpe,[34] was pressured to 1300 psi of hydrogen and stirred for 1 day. The solvent was removed and the product (3.35 g, 75%) recrystallized from petroleum ether. **7** sublimes with decomposition at 110 °C; IR 1715, 1625, 1295, 1280, 1035, 935, 895, 845, 805, 740, 725, 655. Cp*Ta(dmpe)D$_4$ was prepared by photolysis of a C$_6$D$_6$ solution of **7** under D$_2$ for 36 h. Anal. Calcd for C$_{16}$H$_{35}$P$_2$Ta: C, 40.86; H, 7.50; Ta, 38.47. Found: C, 40.71; H, 7.39; Ta, 38.21.

Cp*Ta(PMe$_3$)$_2$H$_3$Cl (8). A high-pressure reactor, charged with 6.03 g of Cp*TaMe$_3$Cl[8] (**2**), 100 mL of petroleum ether, and 4 mL of PMe$_3$, was pressured to 1650 psi of hydrogen and stirred for 5 days. Blue-green **7** (5.73 g, 74%) was crystallized from this solution. **8** can be recrystallized from petroleum ether to give a white solid identical by NMR spectroscopy; IR 1765, 1700, 1300, 1200, 950, 720, 340. Cp*Ta(PMe$_3$)$_2$D$_3$Cl was prepared from a solution of **8** in C$_6$D$_6$ under D$_2$ for 2 days at 25 °C. Anal. Calcd for C$_{16}$H$_{36}$ClP$_2$Ta: C, 37.92; H, 7.16; Ta, 35.70. Found: C, 37.88; H, 6.95; Ta, 35.82.

Cp*TaMe$_2$(bpy) (9). A solution of 1.15 g of **3**,[8] and 0.63 g of bpy in 60 mL of petroleum ether was stirred under an atmosphere of hydrogen for 4 days. A black solid (0.55 g, 36%) was crystallized from this solution, washed with cold petroleum ether, and dried in vacuo. A separate reaction using D$_2$ was examined with a Toepler pump.[34] D$_2$ (0.92 equiv) was taken up and 1.75 equiv of methane was produced, roughly 80% CH$_3$D and 20% CH$_4$ (by ^{1}H NMR): ^{1}H NMR (C$_6$D$_6$) δ 1.57 (s, C$_5$(CH_3)$_5$), 0.13 (s, Ta(CH_3)$_2$), 6.29 (m, 4 H, bpy), 7.08 (d, J_{HH} = 7 Hz, 2 H, bpy), 7.77 (d, J_{HH} = 9 Hz, 2 H, bpy); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 10.46 (C$_5$(CH$_3$)$_5$), 60.30 (Ta(CH$_3$)$_2$), 113.01, 115.07, 118.43, 122.43, 137.87, 139.60 (C_5(CH$_3$)$_5$ and bpy); IR 1575, 1560, 1300, 760, 725; UV–vis (petroleum ether) 452, 545 nm ($\epsilon \sim 10^4$ M^{-1} cm^{-1}). Cyclic voltammetry in THF shows a reversible one-electron reduction at −2.2 V (vs. SCE, referenced to internal ferrocene). No oxidation wave was observed to +1.4 V. Anal. Calcd for C$_{22}$H$_{29}$N$_2$Ta: C, 52.29; H, 5.82; Ta, 36.01. Found: C, 52.33; H, 5.61; Ta, 36.25. Mol wt (C$_6$H$_6$) calcd 502, found 491.

Cp*Ta(η^2-OCMe$_2$)(CO)(bpy) (10). A solution of 0.16 g of **9** in 10 mL of benzene was stirred under an atmosphere of carbon monoxide for 20 min, the benzene and residual CO were removed, and the bright blue solid (0.06 g, 35%) was washed with cold petroleum ether and dried in vacuo. A separate experiment using a Toepler pump indicated that 1.77 equiv of CO was absorbed in this reaction. Treatment of **10** with anhydrous HCl produces no methane (by NMR): ^{1}H NMR (C$_6$D$_6$) δ 1.47 (s, C$_5$(CH_3)$_5$), 2.15 (s, η^2-OC(CH_3)(CH$_3$)), 1.34 (s, η^2-OC(CH$_3$)(CH_3)), 6.30 (m, 4 H, bpy), 7.50 (d, J_{HH} = 9 Hz, 2 H, bpy), 9.00 (d, J_{HH} = 7 Hz, 1 H, bpy), 9.53 (d, J_{HH} = 7 Hz, 1 H, bpy); ^{13}C NMR (C$_6$D$_6$, chemical shifts obtained from a ^{1}H-decoupled spectrum; only nine of ten bpy carbons were observed (multiplicities were obtained from an off-resonance ^{1}H-decoupled spectrum; due to the complexity of the spectrum multiplicities could not be assigned to all peaks)) δ 9.86 (q, C$_5$(CH$_3$)$_5$), 30.10 (q, η^2-OC(CH$_3$)(CH$_3$)), 30.78 (q, η^2-OC(CH$_3$)(CH$_3$)), 87.46 (s, η^2-OC(CH$_3$)(CH$_3$)), 111.67, 113.26, 114.40, 120.77, 121.91, 122.12, 124.14, 138.54 (s), 144.65 (d), 149.35 (d) (C_5(CH$_3$)$_5$ and bpy), 257.41 (s, Ta(CO)); IR 1775, 1580 (w, bpy), 1520 (w, bpy), 1160, 1080, 1030, 985, 720. Anal. Calcd for C$_{24}$H$_{29}$N$_2$O$_2$Ta: C, 51.62; H, 5.23; Ta, 32.40. Found: C, 51.48; H, 5.17; Ta, 32.33.

Cp*Ta(OCHMe$_2$)$_4$. **4** (0.49 g) was dissolved in 10 mL of toluene with 0.6 mL of acetone and stirred for 2 days at 25 °C. The solution was filtered, reduced to 5 mL, and cooled to −78 °C, yielding a white crystalline solid, 0.15 g, 25%. The product is air sensitive and can be sublimed at room temperature at 10^{-4} mmHg; IR 1170, 1120, 980 (OCHMe$_2$), 1015 (Cp*), 575 (Ta–O).[35] Anal. Calcd for C$_{22}$H$_{43}$O$_4$Ta: C, 47.82; H, 7.94; Ta, 32.75. Found: C, 47.58; H, 7.60; Ta, 32.87.

Cp*Ta(OCHMe$_2$)$_3$Cl. Acetone (80 mmHg in 108 mL, 8 equiv) was condensed into a solution of **8** (30 mg) in 0.3 mL of C$_6$D$_6$; after 1 h at 25 °C, solvent was removed to leave white Cp*Ta(OCHMe$_2$)$_3$Cl, 20 mg, 60%; IR 1165, 1120, 995 (OCHMe$_2$), 1015 (Cp*), 575 (Ta–O).[35]

Cp*Ta(OCH$_3$)$_4$ (11). Methanol (330 torr in 56.7 mL, 1.01 mmol) was condensed into a solution of **4** (0.1 g, 0.212 mmol) in 10 mL of petroleum ether. After the solution was stirred at 25 °C for 8 h, the solvent and residual gas were removed to leave a white solid (0.06 g, 65%). H$_2$ (0.840 mmol, 3.97 equiv) was produced in the reaction, as measured by a Toepler pump. IR 1155, 1115, 655, 535, 480.

Cp*Ta(PMe$_3$)$_2$H$_2$(CO) (12). A thick-walled glass reaction vessel with a Teflon needle valve, charged with 0.51 g of **4**, 0.5 mL of PMe$_3$, 10 mL of toluene, and 5 mmol of carbon monoxide (2 atm), was stirred at 25 °C for 24 days. The solvent and residual gas were removed, and the light brown solid (0.30 g, 56%) was washed with cold petroleum ether and dried in vacuo. Toepler pump analysis of the residual gas[36] showed 1.04 equiv of dihydrogen produced. IR 1840, 1750, 1690, 1300, 1280, 1030, 945, 845, 720, 710, 665. Anal. Calcd for C$_{17}$H$_{35}$OP$_2$Ta: C, 40.97; H, 7.08; Ta, 36.31. Found: C, 40.92; H, 6.98; Ta, 36.19.

Cp*Ta(PMe$_3$)$_2$(CO)$_2$ (13). A thick-walled glass reaction vessel with a Teflon needle valve, charged with 0.49 g of **4**, 0.4 mL of PMe$_3$, 5 mL of toluene, and 2.7 mmol of carbon monoxide (loaded by a Toepler pump), was stirred for 2.5 days at 70 °C. The solvent and residual gas were removed, and the red solid (0.15 g, 28%) was recrystallized from petroleum ether. Toepler pump analysis of the gas present[36] after reaction showed 1.92 equiv of H$_2$ given off and 1.92 equiv of CO taken up. IR 1842, 1750, 1300, 1280, 1125, 1030, 940, 715, 660. Anal. Calcd for C$_{18}$H$_{33}$O$_2$P$_2$Ta: C, 41.23; H, 6.34; Ta, 34.51. Found: C, 41.41; H, 6.30; Ta, 34.38.

Cp*Ta(dmpe)H$_2$(CO) (14). **14** has only been prepared in a mixture with **7** and **15**. In a typical reaction, 40 mg of **7**, 0.3 mL of C$_6$D$_6$, and 1 atm of CO were placed in an NMR tube which was then sealed with a torch. The solution was photolyzed for 24 h to give 50% **7**, 40% **14**, and 10% **15**. An IR spectrum of this solution showed a band at 1850 cm^{-1} assignable to **14**.

Cp*Ta(dmpe)(CO)$_2$ (15). A thick-walled glass reaction vesssel with a Teflon needle valve, charged with 0.90 g of **7**, 15 mL of toluene, and 10 mmol of CO (4 atm), was stirred at 130 °C for 1 week. Bright red **15** (0.68 g, 68%) was crystallized from this solution, washed with cold petroleum ether, and dried in vacuo. A separate experiment using a Toepler pump[36] showed that 1.88 equiv of CO was taken up and 1.88 equiv of H$_2$ was given off. IR 1830, 1750, 1300, 1280, 1090, 1030, 940, 920, 900, 635. Anal. Calcd for C$_{18}$H$_{31}$O$_2$P$_2$Ta: C, 41.39; H, 5.98; Ta, 34.64. Found: C, 41.17; H, 5.91; Ta, 34.78.

Cp*Ta(PMe$_3$)$_2$(CO)HCl (16). A solution of **8** (0.79 g), 2 mL of PMe$_3$, and 20 mL of petroleum ether was stirred under 150 torr of CO for 26 h. The CO was removed and a pink-purple solid (0.24 g, 29%) was crystallized from the solution, washed, and dried in vacuo; IR 1820, 1420, 1300, 1280, 1030, 950, 725, 665, 340. Anal. Calcd for C$_{17}$H$_{34}$ClOP$_2$Ta: C, 38.32; H, 6.43; Ta, 33.96. Found: C, 38.47; H, 6.28; Ta, 34.20.

Cp*Ta(PMe$_3$)(CO)$_2$HCl (17). A solution of **8** (0.50 g) in 60 mL of petroleum ether was stirred under 1 atm of carbon monoxide at -80 °C for 1 h and then warmed to room temperature. The residual CO was

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removed and the solution filtered, reduced in volume, and cooled to give a pink-purple solid (0.115 g, 24%), which was washed and dried in vacuo; IR 1975, 1890, 1645, 1030, 960, 750, 395. Anal. Calcd for $C_{15}H_{25}ClO_2PTa$: C, 27.17; H, 5.20; Ta, 37.33. Found: C, 26.97; H, 5.22; Ta, 37.50.

$Cp^*Ta(dmpe)H_2(C_2H_4)$ (18). A thick-walled quartz reaction vessel with a Teflon needle valve, charged with 0.90 g of **7**, 15 mL of benzene, and 5 mmol of ethylene (2 atm), was photolyzed while stirring for 3 days. A light yellow solid (0.50 g, 53%) was crystallized from benzene, washed with cold petroleum ether, and dried in vacuo; IR 1695, 1590, 1290, 1280, 1090, 1030, 940, 925, 892, 840, 790, 740, 720, 695, 650. Anal. Calcd for $C_{18}H_{37}P_2Ta$: C, 43.55; H, 7.51; Ta, 36.45. Found: C, 43.34; H, 7.32; Ta, 36.74.

$Cp^*\overline{TaCH_2CH_2CH_2CH_2}(C_4H_6)$ (19). **19** has been prepared by another route and characterized by Schrock and co-workers.[37] A thick-walled glass reaction vessel with a Teflon needle valve, charged with 0.83 g of **4**, 30 mL of petroleum ether, and 25 mmol of ethylene, was stirred for 6 h. **19** (0.12 g, 16%) was crystallized from the solution and dried in vacuo; IR 1040, 1030, 950, 845, 720.

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Registry No. 2, 69302-75-6; **3,** 71763-35-4; **4,** 80964-80-3; **5,** 80964-81-4; **6,** 80964-82-5; **7,** 80964-83-6; **8,** 80964-84-7; **9,** 80964-85-8; **10,** 80975-59-3; **11,** 80964-86-9; **12,** 80964-87-0; **13,** 80964-88-1; **14,** 80964-89-2; **15,** 80964-90-5; **16,** 80964-91-6; **17,** 80964-92-7; **18,** 80964-93-8; **19,** 71860-93-0; $Cp^*Ta(OCHMe_2)_4$, 80964-94-9; $Cp^*Ta(OCHMe_2)_3Cl$, 80964-95-0; acetone, 67-64-1.

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Synthesis, Crystal Structure and Molecular Conformations, and Magnetic Properties of a Cu^{II}–VO^{II} Heterobinuclear Complex: Interaction between Orthogonal Magnetic Orbitals

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Abstract: The complex $CuVO(fsa)_2en{\cdot}CH_3OH$, where $(fsa)_2en^{4-}$ denotes the binucleating ligand derived from the Schiff base *N,N′*-(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane, has been synthesized and its crystal structure solved at room temperature. It crystallizes in the monoclinic system, space group $P2_1/n$. The lattice constants are a = 11.636 (3) Å, b = 13.612 (3) Å, c = 12.426 (3) Å, and β = 100.8 (4)° with Z = 4. Least-squares refinement of the structure led to a conventional weighted R factor of 0.082. The structure is made of heterobinuclear units, in which a copper atom is fivefold coordinated to two nitrogens, two phenolic oxygens, and the oxygen of a methanol molecule, and a vanadium atom is also fivefold coordinated to two phenolic and two carboxylic oxygens and the oxygen of the vanadyl group. At the accuracy of the experimental results, the metallic atoms and the oxygens of the methanol molecule and of the vanadyl group are in a mirror plane σ for the two square-pyramids CuN_2O_3 and VO_5. These pyramids point in the same direction. During the crystal growing attempts, in addition to the compound described above (**1**), species **2** and **3** were detected. **2** is built up from molecules with CuN_2O_3 and VO_5 pyramids orientated up–up and up–down in the respective proportions of 80% and 20% and randomly distributed within the crystal. **3** consists of a random distribution of molecules with conformation close to **1** and molecules of $Cu_2(fsa)_2en{\cdot}CH_3OH$ following the proportion of 85% and 15%, respectively. The magnetic behavior of **1** studied in the temperature range 4–300 K reveals an intramolecular ferromagnetic coupling characterized by a ground triplet state separated by around J = 118 cm^{-1} from the excited singlet state. The EPR spectrum confirms that the triplet state is the lowest and is interpreted with a zero-field splitting characterized by $|D|$ = 0.24 cm^{-1} and E = 0.04 cm^{-1}. The nature of the intramolecular interaction is easily explained by the orthogonality of the magnetic orbitals centered on the Cu(II) and V(IV) metallic ions, antisymmetric and symmetric, respectively, with regard to the mirror plane σ. The magnitude of the ferromagnetic interaction may be interpreted from considerations of overlap density between the magnetic orbitals. In the present case, the overlap density map exhibits two strongly positive lobes around one of the oxygen bridges and two strongly negative lobes around the other oxygen bridge. Finally, a strategy is proposed to obtain new binuclear complexes exhibiting a strong ferromagnetic coupling with binucleating ligands of the same type as $(fsa)_2en^{4-}$.

In a communication published 3 years ago,[2] we described the synthesis and the main structural parameters of the heterobinuclear complex $CuVO(fsa)_2en{\cdot}CH_3OH$, where $(fsa)_2en^{4-}$ stands for the heterobichelating ligand derived from the Schiff base *N,N′*-(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane. The interest of this complex, in our opinion, lies in the fact that the exchange interaction between Cu^{II} and VO^{II} ions is purely ferromagnetic due to the orthogonality of the magnetic orbitals ϕ_{Cu} and ϕ_{VO} centered on the Cu^{II} and V^{IV} ions, respectively. To the best of our knowledge, $CuVO(fsa)_2en{\cdot}CH_3OH$ was one of the first complexes exhibiting this property.[3] Since this communication, the

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