Deprotonation of Uncharged Transition-Metal Dihydrogen Complexes with Copper Alkoxides, Characterization of the Heterometallic Complexes $(PR_3)_xMH_yCu(PR_3)$ (M = Fe, W), and X-ray Crystal Structure of $(PEtPh_2)_3FeH_3Cu(PEtPh_2)$

Lori Stepan Van Der Sluys,[§,‡,⊥] **M. M. Miller,**[†] **Gregory J. Kubas,**[*,§] **and Kenneth G. Caulton**[*,‡]

Contribution from the Inorganic and Structural Chemistry Group (INC-4), Los Alamos National Laboratory, Los Alamos, New Mexico 87545, the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received September 4, 1990*

Abstract: Reaction of $FeH_2(\eta^2\text{-}H_2)(PEtPh_2)_3$ (**1**) or $W(\eta_2\text{-}H_2)(CO)_3(PR_3)_2$ ($PR_3 = P(C_6H_{11})_3$ (**2a**), $P(i\text{-}Pr)_3$ (**2b**), $P(C_5H_9)_3$ (**2c**), $P(i\text{-}Pr)(C_6H_{11})_2$ (**2d**)) with $^1/_4[CuO\text{-}t\text{-}Bu]_4$ or $^1/_2[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$ ($PR_3 = PPh_3$, $P(C_6H_{11})_3$, or PPh_2Et) results in deprotonation and concomitant elimination of HO-*t*-Bu. Characterization and reactivity studies of the bimetallic products $(PEtPh_2)_3Fe(\mu\text{-}H)_3Cu(PEtPh_2)$ (**3**) and $(PR_3)_2(CO)_3W(\mu\text{-}H)Cu(PR_3)$ ($PR_3 = P(C_6H_{11})_3$ (**4a**), $P(i\text{-}Pr)_3$ (**4b**), and $P(C_5H_9)_3$ (**4c**)) are described, including an X-ray crystallographic study of **3**. The latter complex consists of a facial P_3FeH_3 moiety, bridged by three hydrides to a Cu–P fragment with an Fe–Cu distance of 2.319 (1) Å. Crystal data for **3** (233 °K): $a =$ 10.872 (2) Å, $b =$ 18.512 (4) Å, $c =$ 12.647 (3) Å, $\beta =$ 94.10 (3)°, and $Z = 2$ in space group $P2_1$.

Introduction

Metal dihydrogen complexes have been synthesized by a number of different methods,[1] including borohydride reduction of metal chlorides (as in $FeH_2(\eta^2\text{-}H_2)(PEtPh_2)_3$ (**1**)[2] and $RuH_4(PPh_3)_3$[3]), low-temperature matrix isolation (as in $Cr(CO)_5(H_2)$[4]), and addition of H_2 to complexes such as $M(CO)_3(PR_3)_2$ (M = Cr, Mo, W[5–7]). However, by far the most common method for synthesis of metal–dihydrogen complexes is protonation of a neutral metal hydride; the majority of known metal–dihydrogen complexes are cations, all synthesized by this method.[8–10] In many of these cases, the protonation reaction is reversible, and thus the cationic dihydrogen complex is itself a Brønsted acid, with pK_a's measured to be in the range of 7–10 (extrapolated to an aqueous scale).[8f,10a] The question then arises as to whether this is a *general feature* for all metal–dihydrogen complexes: Is a neutral metal–dihydrogen complex easily deprotonated as well?

Crabtree has proposed that a metal–(H_2) interaction can be compared to an agostic metal–(C–H) interaction, which is more readily deprotonated than a simple hydrocarbon ligand. The postulated explanation is that the electron density is delocalized between the metal and ligand, creating a partial positive charge on the proton.[9] It should be possible to remove such an acidic proton with an appropriate base, in both the C–H and H–H cases.

One point of interest in mixed hydride/dihydrogen complexes is whether deprotonation involves the dihydrogen ligand or a hydride ligand. Even in those dihydrogen complexes containing no other classical hydrides, an equilibrium between dihydrogen and dihydride forms may still exist. However, preferential deprotonation of the dihydrogen ligand is indicated in Heinekey's labeling studies of $[CpRu(dmpe)(H_2)]BF_4$ (dmpe = (dimethylphosphino)ethane)[10] and Crabtree's studies of $[IrH(H_2)(bq)(PR_3)_2]^+$ (bq = 7,8-benzoquinolinate).[9] Another factor to be considered is that the highly labile dihydrogen ligand can readily be displaced by a variety of Lewis bases. Thus, substitution rather than deprotonation may occur when a dihydrogen complex encounters the lone pair of a Brønsted base.

We explore here the reaction of H_2 complexes with the strong Brønsted bases $[CuO\text{-}t\text{-}Bu]_4$ and $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$. It will be seen that dinuclear elimination occurs, providing an efficient route to heterobimetallic hydride compounds.

Experimental Section

General. All manipulations were carried out under a pre-purified atmosphere of the indicated gas following standard Schlenk and He atmosphere drybox techniques. Solvents were dried and deoxygenated with conventional procedures.[11] The preparation of $FeH_2(H_2)(PEtPh_2)_3$ (**1**) has been described previously.[2] $[CuO\text{-}t\text{-}Bu]_4$,[12,13] $RuH_4(PPh_3)_3$,[3] and $W(H_2)(CO)_3(PCy_3)_2$ (**2a**)[6] where Cy = C_6H_{11}, $W(H_2)(CO)_3(P\text{-}i\text{-}Pr_3)_2$ (**2b**),[6] $W(H_2)(CO)_3(P(C_5H_9)_3)_2$ (**2c**),[5] $W(H_2)(CO)_3(P\text{-}i\text{-}PrCy_2)_2$ (**2d**),[6] $Mo(H_2)(CO)_3(PCy_3)_2$,[6] $W(CO)_3(PCy_3)_2$,[14] $[CuH(PPh_3)]_6$,[15] and [Cu-

---

[§] Los Alamos National Laboratory.
[†] Colorado State University.
[‡] Indiana University.
[⊥] Current address: 2700 Lyon Creek Rd., Missoula, Montana 59801.

(1) For recent reviews on coordinated dihydrogen chemistry see: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Henderson, R. A. *Transition Met. Chem.* **1988**, *13*, 474. (c) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (d) Ginzburg, A. G.; Bagatur'yants, A. A. *Organomet. Chem. USSR*, **1989**, *2*, 111. (e) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

(2) (a) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831. (b) Aresta, M.; Giannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1971**, *5*, 115.

(3) Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259.

(4) Church, S. P.; Grevels, F.-W.; Hermann, H.; Shaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30.

(5) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855.

(6) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(7) Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-L.; Zhang, K.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419.

(8) See, for example: (a) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. (b) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (c) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (d) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593. (e) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (f) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581. (g) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

(9) Crabtree R. H.; Lavin, M.; Bonnevoit, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(10) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(11) *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*; Gordon, A. J., Ford, R. A., Eds.; John Wiley & Sons: New York, 1972.

(12) (a) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658. (b) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142.

(13) Lemmen, T. H.; Goeden, G. V.; Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680.

0002-7863/91/1513-2513$02.50/0

(O-*t*-Bu)(PPh_3)]$_2$[13] were prepared as described in the literature. $PEtPh_2$, PCy_3, PPh_3, and HO_3SCF_3 were obtained commercially, used without further purification, and stored under Ar or N_2. ^1H NMR spectra were recorded on a Nicolet NT-360 spectrometer or an IBM AF-250 MHz spectrometer and referenced to the proton impurity of toluene-d_8 at 6.98 ppm or benzene-d_6 at 7.15 ppm. ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer (40.5 MHz) or an IBM AF-250 MHz spectrometer (101 MHz) and referenced externally to 85% H_3PO_4 at 0 ppm. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer or a Digilab FTS-40 spectrophotometer with NaCl plates and referenced to polystyrene at 1601 cm^{-1}. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN elemental analyzer or from the University of California Department of Chemistry Microanalysis Laboratory, Berkeley, CA.

Synthesis. Preparation of [Cu(O-*t*-Bu)(PCy_3)]$_2$. [CuO-*t*-Bu]$_4$ (0.050 g, 0.091 mmol) was placed in 5 mL of hexane under He (in a drybox), and PCy_3 (0.097 g, 0.34 mmol) was added to the slurry with stirring. A fine white powder precipitated from the solution within a few minutes, which was isolated after 1 h of stirring by filtration and washed with hexane to yield 0.093 g (60%). Elemental analysis showed that one hexane molecule is present for every two copper atoms in the microcrystalline powder.

^1H NMR (25 °C, benzene-d_6) δ 1.93 (br, 1 H, cyclohexyl C*H*), 1.70–0.89 (br, 10 H, cyclohexyl CH_2), 1.59 (s, 9 H, –O(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 22.00 (br s). Anal. Calcd for $C_{25}H_{48}CuOP$: C, 65.38; H, 10.56. Found: C, 65.17; H, 10.72.

Preparation of [Cu(O-*t*-Bu)(PPh_2Et)]$_2$. [CuO-*t*-Bu]$_4$ (0.055 g, 0.101 mmol) was placed in 10 mL of hexane, and PPh_2Et (0.086 g, 0.067 mL, 0.40 mmol) was added to the slurry with stirring. A pale yellow powder precipitated from the solution within a few minutes. After 1 h of stirring it was isolated by filtration and washed with hexane to give a yield of 80%.

^1H NMR (25 °C, benzene-d_6) δ 7.52 (m, 4 H, *o*-phenyl), 7.05 (m, 6 H, *m*- and *p*-phenyl), 1.92 (m, 2 H, CH_2CH$_3$), 1.46 (s, 9 H, –O(CH_3)$_3$), 1.05 (m, 3 H, CH$_2$CH_3). $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ –8.0 (br s). Anal. Calcd for $C_{18}H_{24}CuOP$: C, 61.62; H, 6.91. Found: C, 61.34; H, 6.81.

($PEtPh_2$)$_3$FeH$_3$Cu($PEtPh_2$) (3). (A) $FeH_2(H_2)(PEtPh_2)_3$ (**1**) (1.09 g, 1.55 mmol) was dissolved in 50 mL of toluene under H_2, and [CuO-*t*-Bu]$_4$ (0.212 g, 0.388 mmol) was added with stirring at 0 °C. An immediate color change from yellow to dark red-orange was observed. After the mixture was stirred for 10 min the toluene was removed, 50 mL of pentane was added, and the solution was heated gently in a water bath until most of the red oil had dissolved. After 1 week at –40 °C small clusters of red plates had formed, which were isolated by removal of the mother liquor.

(B) **1** (0.253 g, 0.360 mmol) was partially dissolved in 50 mL of hexane under H_2, and [Cu(O-*t*-Bu)(PPh_2Et)]$_2$ (0.128 g, 0.182 mmol) was added with stirring at 0 °C. An immediate color change from yellow to orange was observed, and precipitation of an orange powder began. After removal of the ice bath and stirring for 2 h the slurry was placed in the freezer at –40 °C to encourage precipitation; the orange product was isolated by filtration to give a yield of 90%. Recrystallization was accomplished through gentle warming of a hexane solution, filtration of insoluble material, cooling to room temperature, and slow evaporation of the solvent.

(C) An NMR scale reaction in benzene-d_6 (analogous to method A) showed production of HO-*t*-Bu (δ 1.06 and 2.11 ppm).

^1H NMR (25 °C, benzene-d_6) δ –15.02 (m), 1.02 (m, Fe–P–CH$_2$CH_3, 9 H), 1.28 (dt, J_{PH} = 19.6 Hz, J_{HH} = 7.5 Hz, Cu–P–CH$_2$CH_3, 3 H), 1.99 (m, Cu-P-CH_2CH$_3$, 2 H), 2.16 (m, Fe–P–CH_2CH$_3$, 6 H). ^1H NMR (–80 °C, toluene-d_8) coalescence. $^{31}P\{^1H\}$ NMR (–50 °C, toluene-d_8) δ 77.1 (d, J_{PP} = 12.6 Hz, Fe–*P*, 3P), –5.3 (q, Cu–*P*, 1 P). ^1H NMR {selective phosphorus coupling}: ^1H NMR (25 °C, benzene-d_6, Fe–P signal at 77.1 ppm decoupled) δ –15.02 (d, J_{PH} = 24.3 Hz), 1.02 (t, J_{HH} = 7.0 Hz, Fe–P–CH$_2$CH_3, 9 H), 1.28 (dt, H_{PH} = 19.6 Hz, J_{HH} = 7.5 Hz, Cu–P–CH$_2$CH_3, 3 H), 1.99 (m, Cu–P–CH_2CH$_3$, 2 H), 2.16 (q, J_{HH} = 6.8 Hz, Fe–P–CH_2CH$_3$, 6 H); ^1H NMR (25 °C, benzene-d_6, Cu–P signal at –5.3 ppm decoupled) δ –15.02 (m), 1.02 (m, Fe–P–CH$_2$CH_3, 9 H), 1.28 (t, J_{HH} = 6.4 Hz, Cu–P–CH$_2$CH_3, 3 H), 1.99 (q, J_{HH} = 6.8 Hz, Cu–P–CH_2CH$_3$, 2 H), 2.16 (m, Fe–P–CH_2CH$_3$, 6 H). IR (25 °C, Nujol, cm^{-1}) ν(M–H) = 1725, 1650. IR (25 °C, benzene-d_6, cm^{-1}) ν(M–H) = 1680, 1653. Anal. (recrystallized sample) Calcd for $C_{56}H_{63}FeCuP_4$: C, 68.67; H, 6.49. Found: C, 68.11; H, 6.49. Found: C, 68.11; H, 6.49.

Table I. X-ray Data for ($PEtPh_2$)$_3$Fe(μ-H)$_3$Cu($PEtPh_2$)

mol wt	979.3
cryst system	monoclinic
space group	$P2_1$
a (Å)	10.872 (2)
b (Å)	18.512 (4)
c (Å)	12.647 (3)
β (deg)	94.10 (3)
V (Å^3)	2538.9 (9)
Z	2
density (calc, Mg/m^3)	1.281
λ (Mo Kα) (Å)	0.71069
temp (K)	233
cryst color, habit	red-orange, sealed capillary under He
cryst size (mm)	0.35 × 0.40 × 0.40
absorption coeff (mm^{-1})	0.864
scan range (ω)	0.8 + 0.35(tan θ)°
scan type	$2\theta-\theta$
scan speed	variable; 1.30 to 16.48°/min in ω
index ranges	$-11 \leq h \leq 11, 0 \leq k \leq 19, -13 \leq l \leq 11$
reflcns collected	6654
independent reflcns	3434 (R_{int} = 4.93%)
obs reflcns	3220 ($F > 2.5\sigma(F)$)
final *R* indices (obs data)	*R* = 3.18%, *wR* = 3.63%
R indices (all data)	*R* = 3.57%, *wR* = 3.72%
goodness of fit	1.10
data-to-parameter ratio	5.7:1
absolute config	η = 1.02 (7)

Table II. Selected Distances and Angles of ($PEtPh_2$)$_3$Fe(μ-H)$_3$Cu($PEtPh_2$)

atom 1	atom 2	X-ray dist, Å	atom 1	atom 2	X-ray dist, Å
Cu1	Fe1	2.319 (2)	Fe1	P2	2.181 (1)
	P1	2.152 (1)		P3	2.182 (1)
	H1a	1.59		P4	2.184 (3)
	H1b	1.89		H1a	1.58
	H1c	1.61		H1b	1.64
				H1c	1.37

atom 1	atom 2	atom 3	angle (1–2–3), deg
Fe1	Cu1	P1	174.3 (1)
P2	Fe1	Cu1	115.9 (1)
P3	Fe1	Cu1	115.9 (1)
P4	Fe1	Cu1	109.5 (1)
P2	Fe1	P3	100.8 (1)
P2	Fe1	P4	107.6 (1)
P3	Fe1	P4	106.4 (1)
Cu1	H1a	Fe1	94.3
Cu1	H1b	Fe1	81.9
Cu1	H1c	Fe1	102.2

X-ray Structure Determination of ($PEtPh_2$)$_3$Fe(μ-H)$_3$Cu($PEtPh_2$) (3). A suitable crystal of **3** was grown from a concentrated hexane solution at 25 °C and mounted in a glass capillary sealed under He. Unit cell parameters were derived from a least-squares analysis of 25 reflections (graphite monochromated Mo Kα radiation, λ = 0.71069 Å, range 2.0° < θ < 45.0°) automatically centered on an Enraf Nonius CAD-4 diffractometer. The intensities and orientation of 2 standard reflections were monitored every 150 reflections; the standard reflections showed no significant intensity fluctuations. All calculations were performed with the SHELXTL PLUS program library. Further details of data collection for **3** and final refinement parameters for the structure are presented in Table I. Intensity data were corrected for Lorentz and polarization factors. The Fe, Cu, and P atoms were located via Patterson methods; the rest of the structure was solved by difference Fourier methods. The hydrogen atoms H1a, H1b, and H1c were located in the difference map and placed in those locations; all other hydrogen atoms were included in calculated positions with a fixed isotropic *U*. The refinements involved anisotropic thermal parameters for all non-hydrogen atoms. The structure was refined with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.[16] The function

---

(14) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.

(15) Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818.

(16) *International Tables for Crystallography*; Hahn, T., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland; Boston, 1983; Vol. A.

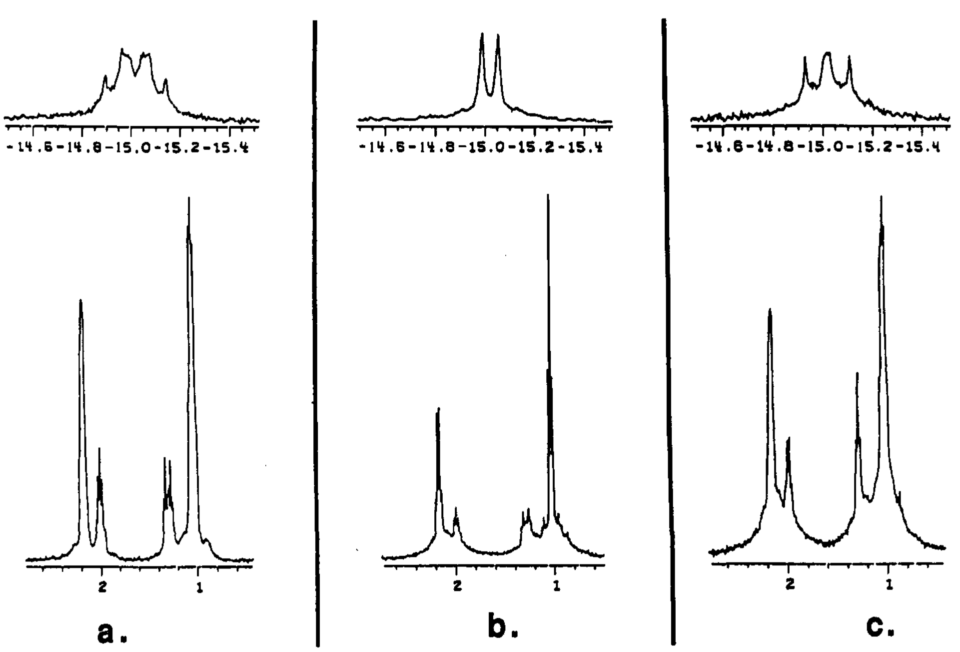


Figure 1. ^1H NMR of $(PEtPh_2)_3Fe(\mu\text{-}H)_3Cu(PEtPh_2)$ (**3**); selective coupling to phosphines (25 °C, benzene-d_6): (a) Fully coupled to all phosphorus atoms (hydride region on top, alkyl region below); (b) ^{31}P doublet at 77.1 ppm (Fe–P) decoupled ($J_{P\text{-}Cu\text{-}H}$ = 24.3 Hz); (c) ^{31}P quartet at −5.3 ppm (Cu–P) decoupled.

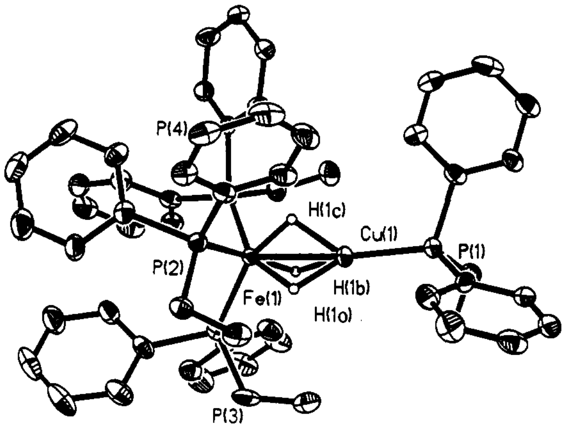


Figure 2. ORTEP view of $(PEtPh_2)_3Fe(\mu\text{-}H)_3Cu(PEtPh_2)$ (**3**), omitting hydrogen atoms on carbon. Ellipsoids are drawn at a 50% probability level.

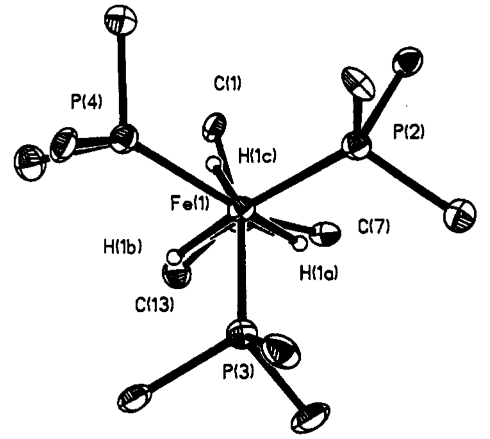


Figure 3. ORTEP view of **3**, viewed along the Fe–Cu vector.

minimized was $R = \sum w^2[F_o - F_c]^2$; the weighted least-squares refinements converged (weights refined by fitting $[F_o - F_c]^2$ to $(\sigma^2(F) + 0.0009F_o^2)^{-1}$). A final difference Fourier map for this structure indicated that the minimum and maximum electron densities were −0.50 and 0.39 $e^-/Å^3$. Since the crystal was small and nearly spherical in shape, no absorption correction was deemed necessary.

The results of the structure determination are shown in Table II and Figures 2 and 3. Atomic coordinates for the atoms are given in the supplementary material. Tables of anisotropic thermal parameters, observed and calculated structure factor amplitudes, and H atom coordinates and isotropic thermal parameters are available as supplementary material.

Protonation of 3. A benzene-d_6 solution of **3** was reacted with either 1 equiv or a 10:1 excess of triflic acid under Ar or H_2 at 0 °C, resulting in an immediate color change from red to yellow. ^1H and ^{31}P NMR data showed the presence of **1**.[17]

Reaction of 3 with CO_2. A benzene-d_6 solution of **3** was reacted with an excess (1 atm) of CO_2 at 0 °C. ^1H NMR data after 15 min of reaction time showed the presence of **3** and a new resonance in the formate region at 9.54 ppm. A slow color change from red-orange to pale yellow occurred over 5 h, and a beige precipitate formed. The ^1H NMR spectrum of this reaction mixture contained no hydride resonances, and the ^{31}P NMR spectrum contained only one resonance. The precipitate was also insoluble in THF and toluene. Analogous observations were made in the reaction of **3** with 1 atm of $^{13}CO_2$.

^1H NMR (25 °C, toluene-d_6) δ 0.95 (m, P–CH_2CH_3, 3 H), 2.04 (m, Cu–P–CH_2CH_3, 2 H), 7.03 (m, 6 H), 7.37 (m, 4 H), 9.54 (s, CO_2H). ^1H NMR (25 °C, $^{13}CO_2$, toluene-d_8) δ 9.54 (d, J_{CH} = 187.4 Hz, HCO_2). $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8) δ −2.0 (s). ^{13}C NMR (25 °C, $^{13}CO_2$ atmosphere, toluene-d_8) δ 168.2 (d, J_{CH} = 186.2 Hz).

$(PCy_3)_2(CO)_3WHCu(PCy_3)$ (4a). (A) $W(H_2)(CO)_3(PCy_3)_2$ (**2a**) (0.061 g, 0.074 mmol) and $[CuO\text{-}t\text{-}Bu]_4$ (0.01 g, 0.018 mmol) were placed in an NMR tube under H_2, brought to 0 °C in an ice bath, and toluene-d_8 was added. An immediate color change from yellow to yellow-orange was observed.

(B) $[CuO\text{-}t\text{-}Bu]_4$ (0.016 g, 0.029 mmol) and PCy_3 (0.12 mmol, 0.034 g) were mixed in hexane and cooled to 0 °C, and a toluene solution of **2a** (0.100 g, 0.12 mmol) was added under H_2. A color change to yellow-orange was observed upon warming. Removal of the solvent produced a yellow-orange oil which was analyzed by NMR.

^1H NMR (25 °C, toluene-d_8) δ −5.11 (dt, J_{PH} = 46.5, 17.3 Hz, with 14% ^{183}W satellites where J_{WH} = 53.46 Hz). $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8) δ 27.15 (d, J_{PP} = 5.5 Hz, 2 P, ^{183}W satellites where J_{WP} = 199.8 Hz), 24.55 (br m, 1 P).

Selectively phosphorus coupled ^1H NMR (25 °C, toluene-d_8): W–P signal at 27.15 ppm decoupled, δ −5.11 (d, J_{HP} = 23.69 Hz); Cu–P signal at 24.55 ppm decoupled, δ −5.11 (t, J_{HP} = 8.7 Hz). Note that these coupling constants are not accurate because the ^{31}P signals are too close

---

[17] Characterization of $FeH_2(H_2)(PEtPh_2)_3$; ^1H NMR (25 °C, benzene-d_6) δ −11.7 (q, J_{HP} = 26.9 Hz, FeH), 0.95 (m, CH_2CH_3), 1.89 (m, CH_2CH_3), 7.00 (m, *m*- and *p*-phenyl), 7.52 (m, *o*-phenyl); hydride-coupled ^{31}P NMR (25 °C, benzene-d_6) δ 73.92 (quint, J_{PH} = 20.6 Hz); IR (25 °C, Fluorolube, cm^{-1}) $\nu(FeH_2)$ = 2380 (m), ν(FeH) = 1930 (m), 1865 (m).

to each other to be exclusively decoupled.

Selectively hydride coupled $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8) δ 27.15 (br m), 24.55 (br d, J_{PH} = 49.9 Hz).

$(P\text{-}i\text{-}Pr_3)_2(CO)_3WHCu(P\text{-}i\text{-}Pr_3)$ (4b). Solid **2b** (0.020 g, 0.048 mmol) and $[CuO\text{-}t\text{-}Bu]_4$ (0.006 g, 0.011 mmol) were placed in an NMR tube under H_2, and toluene-d_8 was added. An immediate color change from yellow to red-orange was observed, and NMR data taken after 15 min were similar to the cyclohexylphosphine analogue **4a**.

^1H NMR (25 °C, toluene-d_8) δ 2.08 (HO-t-Bu), 1.05 ($HOC(CH_3)_3$), −5.46 (dt, J_{PH} = 47.4, 18.2 Hz, WHCu). $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8) δ 37.04 (d, J_{PP} = 5.6 Hz, 2 P), 33.21 (br m, 1 P).

$(P(C_5H_9)_3)_2(CO)_3WHCu(P(C_5H_9)_3)$ (4c). Solid **2c** (0.089 g, 0.12 mmol) and $[CuO\text{-}t\text{-}Bu]_4$ (0.02 g, 0.036 mmol) were placed in an NMR tube under H_2, and benzene-d_6 was added. A color change from yellow to orange-brown was observed, and NMR data taken after 15 min were similar to the cyclohexylphosphine analogue **4a**.

^1H NMR (25 °C, benzene-d_6) δ −5.03 (dt, J_{PH} = 45.6, 17.1 Hz, WHCu).

Results

Synthesis of $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$ (PR_3 = PCy_3, PPh_2Et). Reaction of $^1/_4[CuO\text{-}t\text{-}Bu]_4$ with PR_3 (PR_3 = PCy_3 or PPh_2Et) in hexane results in precipitation of the complexes $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$. Elemental analysis and ^{31}P NMR are consistent with the formulae $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_n$; by analogy with the well-characterized $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$,[13] these complexes are postulated to be dimers. X-ray diffraction has established that $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$ consists of a butterfly structure, with the alkyl groups of the two bridging alkoxides bending *toward* the Cu–PPh_3 wingtips. This leaves one side of the $Cu_2(\mu\text{-}O)_2$ unit "open" and accessible for reaction with a substrate.[13]

Synthesis and Characterization of $(PEtPh_2)_3FeH_3Cu(PEtPh_2)$ (3). The reaction of **1** with 0.5 mol of $[Cu(O\text{-}t\text{-}Bu)(PEtPh_2)]_2$ proceeds quickly at room temperature, resulting in a color change from yellow to dark red-orange; no gas evolution is evident, and no H_2 is detected when the reaction is run in benzene-d_6 and monitored by ^1H NMR. The ^1H NMR of the postreaction mixture shows peaks (1.06 and 2.11 ppm) assigned to free HO-t-Bu (confirmed by observation of an increase in intensity upon addition of HO-t-Bu to the volatiles isolated from the reaction). The yields are higher when the reaction is run under H_2 than under Ar (due to the instability of **1**); N_2 may not be used since it rapidly converts **1** to $FeH_2(N_2)(PEtPh_2)_3$.[2] The reaction product **3** is stable under Ar or N_2, unstable under vacuum in solution, soluble in toluene, benzene, and acetone, and slightly soluble in alkanes and EtOH and it decomposes within 1 h in i-PrOH, MeCN, and pyridine. An elemental analysis of recrystallized **3** is consistent with the formula $[(PEtPh_2)_3FeH_nCu(PEtPh_2)]_x$.

1 also quickly reacts with 0.25 mol of $[Cu(O\text{-}t\text{-}Bu)]_4$ under similar conditions to give the same product **3**, resulting from partial decomposition of **1** and liberation of free phosphine.

Compound **3** shows two $^{31}P\{^1H\}$ multiplets at −50 °C in toluene-d_8: an intensity three doublet at 77.1 ppm, and an intensity one quartet at −5.3 ppm, J_{PP} = 12.6 Hz. The difference of 82.4 ppm between the ^{31}P chemical shifts is extremely large; this influence of the distinct metals is remarkable. This spectrum changes reversibly with temperature to broad singlets of intensity 3:1 at +25 °C. Addition of dppm ((diphenylphosphino)methane) or PPh_3 resulted in partial replacement of the phosphine on Cu as shown by ^{31}P NMR, resulting in a mixture of products. The loss of spin–spin coupling and the reaction with free phosphine suggests a minute amount of dissociation of phosphine as shown in eq 1. Even use of $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$ as the copper reagent results in a mixture of $(PEtPh_2)_3FeH_nCu(PEtPh_2)$ and $(PEtPh_2)_3FeH_nCu(PPh_3)$, the preferred $PEtPh_2$ becoming available from slight decomposition of the tetrahydride starting material.

$$(PEtPh_2)_3FeH_nCu(PEtPh_2) \rightleftharpoons (PEtPh_2)_3FeH_nCu + PEtPh_2 \qquad (1)$$

Given the general lability of phosphine on Cu(I) we propose that it is the unique phosphine in the product which dissociates slightly at 25 °C but negligibly at −50 °C. In this formulation of the product, the 12.6 Hz J_{PP} is an end-to-end coupling from the P on Cu to the three symmetry-equivalent phosphorus atoms on iron. A structure with 3-fold rotational symmetry is suggested.

Consistent with this, the hydride ligands show a single ^1H NMR chemical shift at both 25 and −80 °C (see Figure 1). The 3-fold symmetry (as well as the elimination of 1 mol of HO-t-Bu in the synthesis) suggests that there are three hydride ligands (n = 3 in eq 1). The multiplet pattern of the hydrides is best discussed by first considering its appearance under conditions of selective ^{31}P decoupling. If the phosphorus atoms on Fe (77.1 ppm) are decoupled, the hydride is a doublet with $J_{H\text{-}Cu\text{-}P}$ = 24.3 Hz. (The more intense ethyl peaks become a simple A_2X_3 pattern with this decoupling.) If the phosphorus on Cu (−5.3 ppm) is decoupled, the hydride is a non-first-order multiplet consisting of two sharp outer lines symmetrically flanking a central peak which is composed of several poorly resolved lines. (The less intense ethyl peaks become a simple A_2X_3 pattern with this decoupling.) This latter pattern is consistent with the AA′A″XX′X″ pattern of a stereochemically rigid *facial* P_3FeH_3 unit. The completely phosphorus coupled ^1H NMR pattern for the hydrides is a doubled (24.3 Hz) version of the AA′A″XX′X″ pattern of the P_3FeH_3 component of the molecule.

The metal hydride vibrations at 1655 and 1725 cm^{-1} (in Nujol) are indicative of bridging hydrides. For comparison, the ν(M–H) values in **1**[17] are 1930 and 1865 cm^{-1}; the energy of these hydride vibrations has been lowered significantly.

Solid-State Structure of $(PPh_2Et)_3Fe(\mu\text{-}H)_3Cu(PPh_2Et)$ (3). Crystals of **3** grown from slow evaporation of a saturated hexane solution contain molecules of the formula $(PPh_2Et)_3Fe(\mu\text{-}H)_3Cu(PPh_2Et)$ as shown by X-ray crystallography (see Figure 2 and Tables I and II). The phosphines coordinated to iron adopt a *fac* stereochemistry with similar P–Fe–P angles of 100.8, 107.6, and 106.4° and Cu–Fe–P angles of 115.9, 115.9, and 109.5°. The phosphine on copper is trans to the Fe–Cu vector (Fe–Cu–P = 174.3°), and the distance between Fe and Cu is 2.319 Å. This distance is short compared to the nonbridged Fe–Cu bond distances in $Cu_3Fe_3(CO)_{12}^{3-}$ (ranging from 2.404 to 2.442 Å),[18] $Cu_5Fe_4(CO)_{16}^{3-}$ (2.426, 2.394, and 2.491 Å),[18] $Cu_6Fe_4(CO)_{16}^{2-}$ (2.463 and 2.469 Å),[19] and $[(PPh_3)_2Cu]_2Fe(CO)_4$ (2.499 and 2.522 Å).[19] However, it is comparable to the triply hydride-bridged Fe–Fe distance of 2.332 Å in $[LFe(\mu\text{-}H)_3FeL]PF_6$ (L = 1,1,1-tris((diphenylphosphino)methyl)ethane).[20] Therefore, we believe the short Fe–Cu distance arises primarily from the influence of three bridging hydrides rather than from an Fe–Cu bond.

The three hydrides were located in a difference map based on low-temperature diffraction data and were shown to bridge iron and copper with each hydride approximately trans to one phosphorus (see Figure 3). The local stereochemistry at iron is thus confirmed to be *fac* octahedral H_3FeP_3. The rotational conformations about the Fe–P and P–CH_2 bonds direct the ethyl groups toward the copper, removing the larger phenyl rings from the more congested FeH_3Cu region of the molecule.

Reactivity of $(PPh_2Et)_3Fe(\mu\text{-}H)_3Cu(PPh_2Et)$ (3). **3** reacted immediately with 1 equiv or an excess of triflic acid at 0 °C, with a color change from orange to yellow and eventual decomposition to intractable solids. **1** was identified by ^1H and ^{31}P NMR after 5 min, showing that the original deprotonation is reversible.

The reaction of **3** with CO_2 in benzene or toluene produces a pale yellow solution and a beige precipitate over several hours. A ^1H NMR spectrum of the reaction mixture reveals full conversion to only one soluble product, with signals corresponding to the alkyl groups of coordinated $PEtPh_2$, a formate resonance at 9.5 ppm, free H_2, and no hydrides. $^{31}P\{^1H\}$ NMR shows one broad peak with a shift close to that of free phosphine. Reaction with $^{13}CO_2$ results in a doublet in the formate region of the ^1H NMR (J_{CH} = 187.4 Hz) and a doublet at 168.2 ppm in the ^{13}C NMR assigned to the formate carbon. Since phosphines bound to Cu(I) are often broad and located near the shift of free

---

(18) Doyle, G.; Eriksen, K. A.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 445.

(19) Doyle, G.; Eriksen, K. A.; Van Engen, D. *J. Am. Chem. Soc.* **1985**, *107*, 7914.

(20) Dapporto, P.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1643.

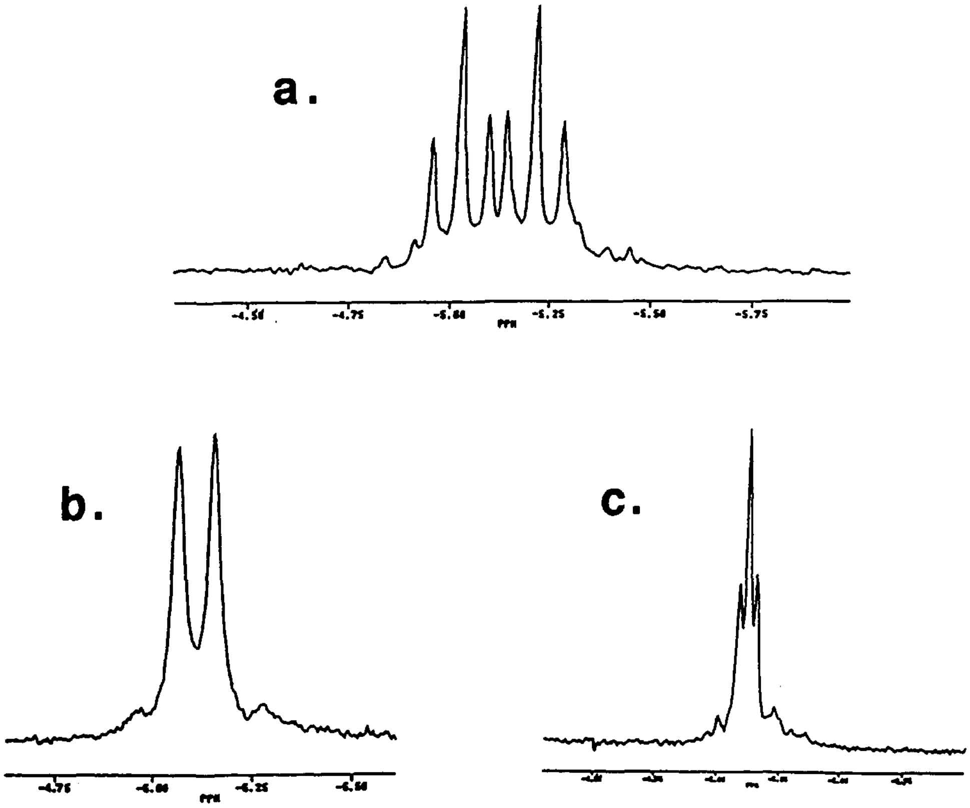


Figure 4. Hydride region of the ^1H NMR of $(PCy_3)_2(CO)_3W(\mu\text{-}H)Cu(PCy_3)$ (**4a**); selective coupling to phosphines (25 °C, toluene-d_8): (a) fully coupled to all phosphorus atoms (δ −5.11, J_{PH} = 46.5, 17.3 Hz); (b) ^{31}P signal at δ 27.2 ppm (W–P) decoupled; (c) ^{31}P signal at δ 24.6 ppm (Cu–P) decoupled.

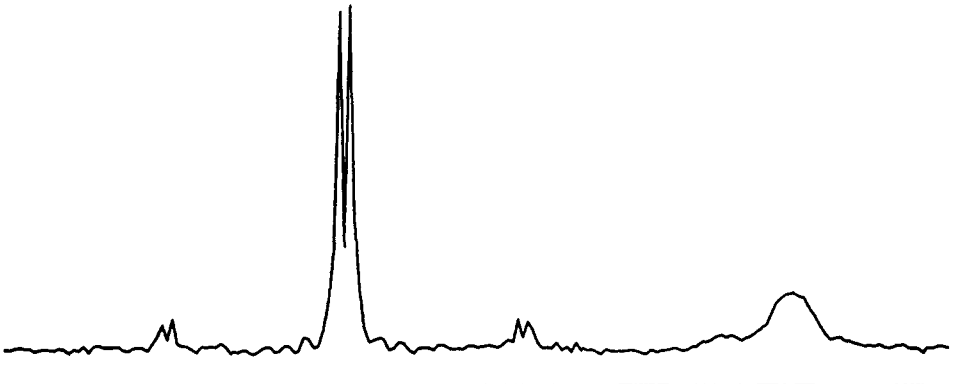


Figure 5. $^{31}P\{^1H\}$ NMR of **4a** (25 °C, toluene-d_8): δ 27.2 (W–P, J_{PP} = 8 Hz, ^{183}W satellites where J_{WP} = 199.8 Hz), δ 24.7 (Cu–P). Selective hydride coupling results in a broadening of the peak at δ 27.2 ppm and a splitting of the peak at δ 24.6 ppm (d, $J_{P\text{-}Cu\text{-}H}$ = 50 Hz).

phosphine, we believe the soluble product to be $[Cu(O_2CH)(PEtPh_2)]_x$. The completely insoluble beige precipitate is incompletely characterized, but possibilities include the known $Fe(\eta^2\text{-}O_2CH)_2(PEtPh_2)_2$[21] or a related species, e.g. $Fe(\eta^2\text{-}O_2CH)(\eta^1\text{-}O_2CH)(PEtPh_2)_3$. The former was reported to be the product of the reaction of **1** with CO_2, and not much characterization was reported because of its insolubility.

Reaction of **3** with H_2, CO, C_2H_4, CH_3CN, *i*-PrOH, pyridine, bipyridine, *cis*-cyclooctene, and cyclooctadiene resulted in slow color changes to brown and produced no identifiable products other than free phosphine.

Synthesis and Characterization of $(PR_3)_2(CO)_3WHCu(PR_3)$ (4). $W(\eta^2\text{-}H_2)(CO)_3(PR_3)_2$[5,6] reacts with 0.25 mol of $[Cu(O\text{-}t\text{-}Bu)]_4$ and PR_3 ($PR_3 = PCy_3$ ($Cy = C_6H_{11}$), P-*i*-Pr_3, P-*i*-$PrCy_2$, or $P(C_5H_9)_3$ (C_5H_9 = cyclopentyl)) or 0.5 mol of $[Cu(O\text{-}t\text{-}Bu)(PR'_3)]_2$ ($PR'_3 = PCy_3$, PPh_2Et) at 0 °C in toluene, resulting in an immediate color change from yellow to orange or red. The reaction must be run under H_2 since the tungsten starting materials dissociate H_2 in solution at room temperature. ^1H NMR for each of these reactions shows conversion to a single hydride-containing product containing a doublet of triplets in the hydride region (see Figure 4; in **4a** δ −5.11, $J_{H\text{-}Cu\text{-}P}$ = 46.5, $J_{H\text{-}W\text{-}P}$ = 17.3 Hz, J_{WH} = 53.46 Hz). Also seen are HO-*t*-Bu at δ 1.05 and 2.08 and alkyl resonances due to coordinated phosphine. This can be compared with NMR data for a related complex, $(CO)_5W(\mu\text{-}H)Au(PPh_3)$, in which $J_{H\text{-}Au\text{-}P}$ = 107 Hz and J_{WH} = 44 Hz.[22] X-ray crystallography of the chromium analogue $(CO)_5Cr(\mu\text{-}H)Au(PPh_3)$ has established that the bridging hydride and the phosphine on gold are in a trans configuration; the structure of the tungsten/gold complex is expected to be similar on the basis of comparable spectroscopic data.[22]

---

(21) $Fe(\eta^2\text{-}O_2CH)_2(PEtPh_2)_2$ was partially characterized as an insoluble beige solid, based on IR and elemental analysis data from the reaction of $FeH_4(PPh_2Et)_3$ with CO_2: Bianco, V. D.; Doronzo, D. S.; Rossi, M. *J. Organomet. Chem.* **1972**, *35*, 337.

The $^{31}P\{^1H\}$ NMR of $(PR_3)_2(CO)_3WHCu(PR_3)$ shows a doublet (with ^{183}W satellites) of intensity two assigned to the phosphines on tungsten and a broad peak of intensity one assigned to the phosphine on Cu (see Figure 5). Selective phosphorus decoupling in the ^1H NMR of **4a** provides more information about the identity of the product (see Figure 4). Decoupling of the ^{31}P doublet at 27.15 ppm (assigned to tungsten phosphines due to the observed W–P coupling) results in a simplification of the hydride signal to a doublet, while decoupling of the ^{31}P doublet at 24.55 ppm (assigned to Cu phosphine due to the broad width and chemical shift) results in a simplification of the hydride signal to a triplet.

The presence of two minor products in the reaction mixture was shown by a small peak in the ^{31}P NMR at 27.6 ppm, and two medium peaks at 35.5 and 9.2 ppm. These products presumably are a result of a hydrogen-loss reaction pathway, rather than deprotonation (vide infra).

Taking into account elimination of HO-*t*-Bu and coupling of the hydride resonance to all phosphines, we propose that the reaction takes place according to eq 2. The reaction is an example of bimolecular reductive elimination, resulting in loss of alcohol by formal deprotonation of the tungsten dihydrogen complex.

$$\underset{\textbf{2}}{W(H_2)(CO)_3(PR_3)_2} + \tfrac{1}{2}[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2 \rightarrow \underset{\textbf{4}}{(PR_3)_2(CO)_3W(\mu\text{-}H)Cu(PR_3)} + HO\text{-}t\text{-}Bu \quad (2)$$

Reaction of $W(H_2)(CO)_3(PR_3)_2$ with $^1/_4[CuO\text{-}t\text{-}Bu]_4$ and free PR'_3 results in formation of $(PR_3)_2(CO)_3W(\mu\text{-}H)Cu(PR'_3)$. However, scrambling of phosphines into the W–P positions complicates the reaction in the presence of other phosphines. Thus, reaction of $W(H_2)(CO)_3(PCy_3)_2$ (**2a**) with $^1/_2[Cu(O\text{-}t\text{-}Bu)(PPh_2Et)]_2$ produces $(PCy_3)(PPh_2Et)(CO)_3W(\mu\text{-}H)Cu(PPh_2Et)$ (recognized by an AMX pattern in the $^{31}P\{^1H\}$ NMR spectrum), as well as $(PCy_3)_2(CO)_3W(\mu\text{-}H)Cu(PPh_2Et)$.

Reaction of $W(CO)_3(PCy_3)_2$ and Cu Reagents. $W(CO)_3(PCy_3)_2$ reacts with $^1/_4[CuO\text{-}t\text{-}Bu]_4$ in benzene-d_6 to give a yellow-orange solution. The ^{31}P NMR spectrum of this product consists of a singlet at 27.6 ppm, and resonances in the ^1H NMR show the presence of a $O\text{-}t\text{-}Bu^-$ moiety. $W(CO)_3(PCy_3)_2$ also reacts with $^1/_2[CuO\text{-}t\text{-}Bu(PCy_3)]_2$ in benzene-d_6 to give a yellow-orange solution. The ^{31}P NMR spectrum of this product consists of product peaks at 35.5 ppm (singlet, ^{138}W satellites, J_{WP} = 214 Hz) and 9.2 ppm (br; consistent with a copper phosphine resonance). Also seen are weak peaks due to the product of reaction of $W(CO)_3(PCy_3)_2$ with $^1/_4[CuO\text{-}t\text{-}Bu]_4$ (above) and due to $W(CO)_4(PCy_3)_2$.[23] Resonances due to the product in the ^1H and $^{13}C\{^1H\}$ NMR spectra (methine resonance at 75.2 ppm) show that the $O\text{-}t\text{-}Bu^-$ ligand is retained. IR spectra of a mineral oil mull provide evidence for both terminal CO ligands (1850 cm^{-1}, br) and a bridging or semibridging CO ligand (1723 cm^{-1}, br).

Discussion

Deprotonation of $FeH_2(\eta^2\text{-}H_2)(PEtPh_2)_3$ (1). **1** has recently been characterized by neutron diffraction; it contains an unprecedented staggered conformation of the dihydrogen ligand (with respect to the P–Fe–P and P–Fe–H axes) which is proposed in part to result from a stabilizing interaction between the H_2 and the adjacent hydride ligand.[2] In this complex, as in its ruthenium analogue, the dominant reactivity pattern is dissociation of H_2 and its replacement by Lewis bases. The H_2 ligand is very loosely bound in this complex, which decomposes in the absence of an H_2 atmosphere.

However, another reaction pathway is available in the reaction of this complex with copper alkoxides. The reaction of **1** with 0.25 mol of $[CuO\text{-}t\text{-}Bu]_4$ (and adventitious phosphine) or 0.5 mol of $[Cu(O\text{-}t\text{-}Bu)(PPh_2Et)]_2$ yields the heterobimetallic polyhydride **3**. The synthetic reaction (eq 3, P = PPh_2Et) is appropriately termed bimolecular reductive elimination. The reaction also

$$\underset{\textbf{1}}{FeH_4P_3} + \tfrac{1}{2}[Cu(O\text{-}t\text{-}Bu)P]_2 \rightarrow \underset{\textbf{3}}{P_3FeH_3CuP} + HO\text{-}t\text{-}Bu \quad (3)$$

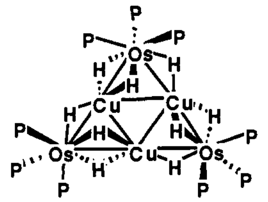
involves a rearrangement from *mer*- to *fac*- FeP_3 stereochemistry. This is presumably driven by the preference for *three* hydride ligands to bridge to the CuP^+ electrophilic center. In effect, deprotonation has taken place, and we have stabilized an $FeH_3(PEtPh_2)_3^-$ fragment with a $Cu–P^+$ cation.

The ruthenium analogue $RuH_4(PPh_3)_3$ (postulated to be $RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$[3,24]) also reacted slowly with $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$ (PR_3 = PPh_3 or PPh_2Et) at 0 °C to result in deprotonation and formation of HO-*t*-Bu. However, the complicated reaction mixture obtained indicated additional reactions were taking place and precluded identification of the products.

We and others have demonstrated the retention of Brønsted basicity of *tert*-butoxide when it is attached to Cu(I).[13,25-30] Since **1** contains an H_2 ligand and since coordinated H_2 has been shown to be more Brønsted acidic than coordinated H^-,[9,10] one mechanism for eq 3 would be bimolecular proton transfer from the $Fe(H_2)$ moiety to $[Cu(O\text{-}t\text{-}Bu)P]_2$. However, since $[Cu(O\text{-}t\text{-}Bu)P]_2$ has less than an 18 valence electron count at copper, the elimination of HO-*t*-Bu could also occur from a preformed "$P_3FeH_4Cu(O\text{-}t\text{-}Bu)P$" adduct. This adduct can be envisioned as an interaction between the electrophilic Cu and either the hydrides or the dihydrogen ligand. It is known that addition of H_2 to $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$ results in elimination of HO-*t*-Bu and formation of $Cu_6H_6(PPh_3)_6$, presumably through coordination of H_2 to the "open" $Cu_2(\mu\text{-}O)_2$ side of $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$.[27] It is interesting to speculate that a metal-bound H_2 may interact with the Cu dimer in a similar manner, also resulting in elimination of alcohol. This speculation is supported by the fact that **1** does not react with LiO-*t*-Bu in benzene-d_6 under H_2 overnight. Therefore, elimination from a heterobimetallic adduct is more likely to be the mechanism of this reaction.

In contrast to the classical polyhydride $OsH_4(PMe_2Ph)_3$, which reacts with $^1/_4[Cu(O\text{-}t\text{-}Bu)]_4$ according to eq 4,[30] **1** does not form a planar six-metal cluster (I) in its reaction with $[Cu(O\text{-}t\text{-}Bu)]_4$. In the Os case, deprotonation presumably initially results in extreme electron deficiency at the copper end of the "P_3OsH_3Cu" adduct, and cluster formation may be the best way to satisfy the coordination preferences of copper.

$$OsH_4(PMe_2Ph)_3 + \tfrac{1}{4}[Cu(O\text{-}t\text{-}Bu)]_4 \rightarrow \tfrac{1}{3}[(PMe_2Ph)_3Os(\mu\text{-}H)_3Cu]_3 + HO\text{-}t\text{-}Bu \quad (4)$$



I

However, it has been reported that use of $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$ in a similar reaction with $Re_2H_8(PMePh_2)_4$ (eq 5) does *not* result in retention of the phosphine on copper.[25] A six-metal planar

---

[22] (a) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 813. (b) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2497.

[23] $W(CO)_4(PR_3)_2$ (PR_3 = $P(C_5H_9)_3$, P-*i*-Pr_3, P-*i*-$PrCy_2$, PCy_3) is a thermodynamic "sink" in this reaction system due to release of CO on decomposition. The amount formed increases after long reaction times. For PR_3 = PCy_3, X-ray structure was done by: Huffman, J. C.; Van Der Sluys, L. S. Unpublished results. $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8) δ 31.5 (s), ^{183}W satellites where J_{WP} = 260 Hz. ^{13}C NMR (25 °C, toluene-d_8) δ 209.9 (t, J_{PC} = 6.10 Hz), 209.9 (d, J_{WC} = 128.18 Hz). IR (25 °C, benzene-d_6, cm^{-1}) $\nu(CO)$ = 1920 (wk), 1870 (s).

[24] Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 706.

[25] Sutherland, B. R.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 135.

[26] Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658.

[27] Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

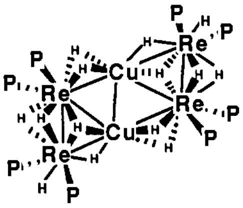
[28] Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

[29] Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774.

[30] Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 262.

cluster is formed (II), along with HO-*t*-Bu and free phosphine.

$$Re_2H_8(PMePh_2)_4 + \tfrac{1}{2}[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2 \rightarrow \tfrac{1}{2}[Re_2H_7Cu(PMePh_2)_4]_2 + HO\text{-}t\text{-}Bu + PPh_3 \quad (5)$$



II

When **3** is synthesized from $[Cu(O\text{-}t\text{-}Bu)]_4$ and *no* added phosphine, no evidence for Fe/Cu cluster formation has been seen by NMR, and heating of **3** causes quick decomposition to an insoluble brown precipitate along with production of free phosphine.

$OsH_4(PMe_2Ph)_3$ has also been shown to react with $Cu_6H_6(PPh_3)_6$ to form the same Os/Cu cluster I, as shown in eq 6,[30] but **1** reacts only slowly with $Cu_6H_6(PPh_3)_6$ to give no single well-defined product.

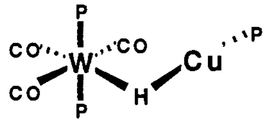
$$OsH_4(PMe_2Ph)_3 + \tfrac{1}{6}[Cu_6H_6(PPh_3)_6] \rightarrow \tfrac{1}{3}[(PMe_2Ph)_3Os(\mu\text{-}H)_3Cu]_3 + H_2 + PPh_3 \quad (6)$$

In the Os case hydrogen gas and PPh_3 are eliminated; one might expect the free phosphine to trap the initial "P_3OsH_3Cu" intermediate and allow isolation of "P_3OsH_3CuP". However, this product is not observed, and we can conclude that cluster formation is favored over coordination of PPh_3 to Cu.

In the Fe case, it is reasonable to propose that PPh_3 is not basic enough to stabilize the desired product "$(PEtPh_2)_3FeH_3Cu(PPh_3)$". This is supported by the fact that reaction of **1** with 0.5 mol of $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$ results in mixtures which include **3**, identified by the ethyl resonances of copper-bound phosphine in the ^1H NMR spectrum. This demonstrates that the more basic $PEtPh_2$ is preferred over PPh_3 if available (in this case by slight decomposition of the starting material).

Reactivity of $(PPh_2Et)_3Fe(\mu\text{-}H)_3Cu(PPh_2Et)$ (3). **3** reacts with a host of reagents, but most produce no single well-defined product. Successful protonation with triflic acid demonstrates the reversibility of the deprotonation reaction, with generation of **1**. Reaction of **3** with an excess of CO_2 appears to have disrupted the Cu–Fe interaction, resulting in a soluble copper product formulated as $[Cu(O_2CH)(PEtPh_2)]_x$ and a second insoluble product, possibly "$Fe(\eta^2\text{-}O_2CH)(\eta^1\text{-}O_2CH)(PEtPh_2)_3$" or $Fe(\eta^2\text{-}O_2CH)_2(PEtPh_2)_2$. The latter is reported to be the product of the reaction of **1** with CO_2, but little in the way of characterization is available because of insolubility problems.[21] Reaction with $^{13}CO_2$ has confirmed that the source of the formate moiety is the added CO_2 and provided a value for J_{CH} for 187 Hz.

Deprotonation of $W(\eta^2\text{-}H_2)(CO)_3(PR_3)_2$ (2). The tungsten dihydrogen complexes are similar to **1** in that the H_2 ligand dissociates unless the complex is kept under an H_2 atmosphere. These complexes also undergo a well-characterized equilibrium in solution between the dihydrogen and seven-coordinate dihydride forms (approximate 7:3 ratio).[5,6] The tungsten complexes **2** reacted smoothly with 0.5 mol of $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$ or 0.25 mol of $[CuO\text{-}t\text{-}Bu]_4$ and adventitious PR_3 to produce $(PR_3)_2(CO)_3WHCu(PR_3)$ (**4**) and HO-*t*-Bu. Again we suspect the PR_3 is present from slight decomposition of **2**. In these complexes, as in the Fe/Cu complexes, we see formal deprotonation of the H_2 ligand, resulting in a hydride-bridged tungsten–copper complex. The phosphine on Cu is labile, as are the W phosphines, as shown by formation of mixtures of the formulae $(PR_3)_2(CO)_3WHCu(PR'_3)$ and $(PR_3)(PR'_3)(CO)_3WHCu(PR'_3)$ in the presence of other phosphines PR'_3. The phosphorus nuclei on tungsten and copper couple weakly to each other, and the bridging hydride couples most strongly to the phosphine on Cu. This suggests a trans orientation of the hydride with respect to this phosphine as shown in III, a structure which is precedented by $(PPh_3)H_2Ir(\mu\text{-}H)Au(PPh_3)^+$,[31] $(PEt_3)_2(C_6F_5)Pt(\mu\text{-}H)Au(PPh_3)^+$,[32] and $(CO)_5Cr(\mu\text{-}H)Au(PPh_3)$.[22] The complexes **4** are not thermally stable, however, and tend to form $W(CO)_4(PR_3)_2$ along with other decomposition products in solution after several days.[23]

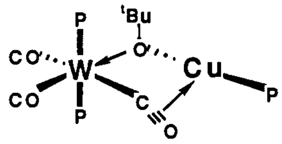


III

The W/Cu complexes are remarkably similar to **3**, in sharp contrast to the Os/Cu cluster $[P_3OsH_3Cu]_3$.[30] Third-row metals should be more likely to cluster, but we have not yet identified such a product in the tungsten case. It is true that in $W(CO)_3(H_2)(PR_3)_2$ the coordination geometry about tungsten is more rigid in the Fe or Os cases; five coordination sites are already occupied by ligands unlikely to interact with Cu^+. However, the lability of both the W and Cu phosphines in **4** provides plenty of opportunity for cluster formation, and we expected such a reaction to take place.

We cannot rule out the possibility of a bridging or semibridging carbonyl interaction in **4**. IR spectra of a mineral oil mull of the crude reaction product reveal 5 bands in the region 1750–1908 cm^{-1}.

Reaction of $W(CO)_3(PCy_3)_2$ and Copper Alkoxides. We propose that the product of the reaction of coordinatively unsaturated $W(CO)_3(PCy_3)_2$ and $[Cu(O\text{-}t\text{-}Bu)]_4$ is the adduct $[W(CO)_3(PCy_3)_2(O\text{-}t\text{-}Bu)Cu]_x$, as is consistent with NMR data. Similarly, we propose that the product of reaction with $[Cu(O\text{-}t\text{-}Bu)(PCy_3)]_2$ is the alkoxide and carbonyl bridged adduct IV, $[W(CO)_2(PCy_3)_2(\mu\text{-}CO)(\mu\text{-}O\text{-}t\text{-}Bu)Cu(PCy_3)]_x$. This carbonyl-bridged formulation for IV is supported by the presence of a band in the IR at 1723 cm^{-1}, although bands as low as 1705 cm^{-1} are observed in the monomeric, *non*-carbonyl-bridged complexes $W(CO)_3(PCy_3)_2(L)$ (L = H_2O, MeOH, and EtOH).[14] Precedence for a W–Cu interaction supported by semibridging CO ligands is found in the structurally characterized complexes $[W(CO)_2(\mu\text{-}dppm)_2(\mu\text{-}Cl)(\mu\text{-}CO)Cu]$ (dppm = Ph_2PCH_2, $\nu(CO)$ = 1784 cm^{-1})[33] and $(\eta^5\text{-}C_5H_5)W(CO)(\mu\text{-}CO)_2Cu(PPh_3)_2$ ($\nu(CO)$ = 1731 cm^{-1}).[34] The presence of minor amounts of the above adducts in the products obtained on reaction of **4** with copper reagents indicates that loss of H_2 was a competing reaction pathway to deprotonation of the dihydrogen ligand, even under an H_2 atmosphere.



IV

Conclusion

We have found that neutral metal–dihydrogen complexes are easily deprotonated by copper alkoxides, which extends the principle that deprotonation is a general feature for all metal–dihydrogen complexes. Although reaction with $[Cu(O\text{-}t\text{-}Bu)]_4$ (versus $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$) will deprotonate the dihydrogen ligand, the Cu^+ cation must satisfy its coordination needs with an acceptable ligand (e.g., phosphine) in order for the bimetallic product to be stable. This may occur in several ways, as characterized by the following features:

(1) In the reaction with $FeH_4(PEtPh_2)_3$ (**1**), three hydrides bridge to copper. This requires a *mer* to *fac* rearrangement of

---

[31] Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6825.

[32] Albinati, A.; Lehner, H.; Venanzi, L. M.; Wolfer, M. *Inorg. Chem.* **1987**, *26*, 3933.

[33] Blagg, A.; Hutton, A. T.; Shaw, B. L.; Thornton-Pett, M. *Inorg. Chim. Acta* **1985**, *100*, L33.

[34] Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* **1983**, 216.

the FeH_3P_3 unit, and this octahedral unit then remains stereochemically rigid in the product. The $(H)_3Cu$ ligation of copper in the product represents an unusually high hydride-to-copper ratio among known copper hydrides. Note, for comparison, that the reaction of $Cu(NCMe)_4^+$ with *mer*-$IrH_3(PMe_2Ph)_3$ gives $Cu[H_3Ir(PMe_2Ph)_3]_2^+$ where the *mer* stereochemistry is retained at iridium.[35]

(2) In the reaction with $WH_2(CO)_3(PR_3)_2$ (**2**), only one hydride is available to bridge to copper. Moreover, there is infrared evidence supporting the possibility of a bridging carbonyl ligand, providing a higher coordination number for copper.

(3) In all of the above reactions, if $[Cu(O\text{-}t\text{-}Bu)]_4$ is employed rather than $[Cu(O\text{-}t\text{-}Bu)(PR_3)]_2$, the coordination requirements of Cu^+ are supplemented by one phosphine scavenged from the phosphine/dihydrogen reaction partner. This phosphine scavenging is possible because the dihydrogen reagents are generally fragile molecules, and their concurrent decomposition can release PR_3. The absence of aggregated products of the sort $L_nM_3Cu_3$ (analogous to I) is due at least in part to this availability of phosphine.

The reactions described here are all fast (i.e., time-of-mixing). They are thus unlike substitution reactions on kinetically inert low-spin d^6 species. This suggests either Lewis acid/base or proton transfer mechanisms.

Acknowledgment. This work was supported by the National Science Foundation (at Indiana University) and the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy. We also thank Timothy H. Lemmen and William G. Van Der Sluys for helpful discussion and Stephen W. Hall for skilled technical assistance.

Registry No. 1, 102149-40-6; **2a**, 104198-75-6; **2b**, 125875-90-3; **2c**, 125593-90-0; **2d**, 104198-78-9; **3**, 132233-13-7; **4a**, 132233-14-8; **4b**, 132233-17-1; **4c**, 132233-18-2; IV, 132233-22-8; $W(CO)_3(PCy_3)_2$, 73690-56-9; $[CuH(PPh_3)]_6$, 33636-93-0; $[Cu(O\text{-}t\text{-}Bu)(PPh_3)]_2$, 106761-46-0; $[CuO\text{-}t\text{-}Bu]_4$, 60842-00-4; $[Cu(O\text{-}t\text{-}Bu)(PCy_3)]_2$, 132233-15-9; $[Cu(O\text{-}t\text{-}Bu)(PPhzEt)]_2$, 132233-16-0; $(PCy_3)(PPh_2Et)(CO)_3W(\mu\text{-}H)Cu(PPh_2Et)$, 132233-19-3; $(PCy_3)(CO)_3W(\mu\text{-}H)Cu(PPh_2Et)$, 132233-20-6; $[Cu(O_2CH)(PEtPh_2)]$, 132233-21-7; $[W(CO)_3(PCy_3)_2(O\text{-}t\text{-}Bu)Cu]$, 132233-23-9.

Supplementary Material Available: Tables of anisotropic displacement coefficients for $(PEtPh_2)_3Fe(\mu\text{-}H)_3Cu(PEtPh_2)$, H-atom coordinates ($\times 10^4$) and isotropic displacement coefficients, and atomic coordinates and equivalent isotropic displacement coefficients (6 pages); listing of observed and calculated structure factor amplitudes for $(PEtPh_2)_3Fe(\mu\text{-}H)_3Cu(PEtPh_2)$ (13 pages). Ordering information is given on any current masthead page.

---

[35] Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 6874.

Cone Angles for Amine Ligands. X-ray Crystal Structures and Equilibrium Measurements for Ammonia, Ethylamine, Diethylamine, and Triethylamine Complexes with the (Bis(dimethylphosphino)ethane)methylpalladium(II) Cation

Allen L. Seligson and William C. Trogler*

Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92093-0506. *Received September 12, 1990*

Abstract: The reaction between $Pd(dmpe)Me_2$, where dmpe = 1,2-bis(dimethylphosphino)ethane, and $[NH_4]PF_6$, $[NH_4]BPh_4$, $[NH_3Et]BPh_4$, $[NH_2Et_2]BF_4$, $[NH_2Et_2]BPh_4$, $[NHEt_3]BPh_4$, $[NH_2{}^iPr_2]BPh_4$, and [1-methylimidazolium]BPh_4 in CH_2Cl_2 or CH_3CN solvent rapidly produces CH_4 and the corresponding amine complexes $[Pd(dmpe)CH_3(NRR'R'')]X$, **1**–**8**, respectively. All can be isolated as crystalline solids in 57–87% yield. Crystals of **1** belong to the monoclinic space group $P2_1/c$ with lattice constants $a = 8.378$ (5) Å, $b = 16.696$ (8) Å, $c = 12.024$ (5) Å, $\beta = 103.91$ (4)°, and $Z = 4$. **3** crystallizes in the monoclinic space group $P2_1/c$ with lattice constants $a = 9.986$ (3) Å, $b = 11.024$ (4) Å, $c = 29.601$ (9) Å, $\beta = 92.69$ (2)°, and $Z = 4$. **4** crystallizes in the orthorhombic space group *Pbcn* with lattice constants $a = 13.181$ (4) Å, $b = 23.897$ (7) Å, $c = 24.854$ (9) Å, and $Z = 16$. **6** crystallizes in the monoclinic space group $P2_1/c$ with lattice constants $a = 9.566$ (4) Å, $b = 21.773$ (7) Å, $c = 17.662$ (5) Å, $\beta = 90.62$ (3)°, and $Z = 4$. Least-squares refinement of the structures led to R factors of 0.047, 0.054, 0.055, and 0.054, respectively. All complexes adopt a square-planar geometry with angle distortions in the plane, which parallel the increasing size of the amine. The Pd–N bond lengths of 2.139 (5), 2.174 (6), 2.182 (8), and 2.244 (7) Å in **1**, **3**, **4**, and **6** correlate linearly with the steric cone angle for the amine ligands. The Pd–N bond length in **6** exceeds that of 2.201 (3) Å for the trans Pd–P bond, which reflects severe steric crowding for the triethylamine ligand. Cone angles for these and other amines were determined from geometric measurements of CPK models. Equilibrium binding constants for 16 amine ligands to the $Pd(dmpe)Me^+$ Lewis acid were measured by variable-temperature ^{31}P NMR spectroscopy. Binding constants for amines of similar pK_a correlate well with the amine cone angles, θ; however, a steric threshold was observed when $\theta \leq 120°$. Binding constants, relative to the $NHEt_2$ complex, K, for the ligands obeyed the relationship $\log K = 8.1 + 0.54pK_a - 0.15\theta$, with a correlation coefficient of 0.95. This shows a dependence on both electronic and steric properties of the amine ligands. Of the various amine ligands studied, 1-methylimidazole and ethylamine bind most effectively. This parallels the role of histidine and lysine for binding metals in metalloproteins.

Introduction

The cone angle concept, developed by Tolman,[1] has been widely accepted by organometallic chemists as a quantitative measure of steric effects for trivalent phosphorus ligands.[2] Cone angles have been used not only to explain structural and thermodynamic aspects of metal complexes[3] but also to construct linear free energy

---

[1] Tolman C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956–2965.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.

[3] Tolman, C. A. *Chem. Rev.* **1988**, *77*, 313–348.

0002-7863/91/1513-2520$02.50/0