ORGANOMETALLICS

Generation of metal formyl complexes using nickel and platinum hydrides as reducing agents

Alex Miedaner, Daniel L. DuBois, Calvin J. Curtis, and R. Curtis Haltiwanger

Organometallics, **1993**, 12 (2), 299-303• DOI: 10.1021/om00026a014 • Publication Date (Web): 01 May 2002

Organometallics 1993, *12*, 299–303

Generation of Metal Formyl Complexes Using Nickel and Platinum Hydrides as Reducing Agents

Alex Miedaner, Daniel L. DuBois,* and Calvin J. Curtis*

Basic Sciences Division, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

R. Curtis Haltiwanger

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Received June 30, 1992

The five-coordinate nickel hydride complex $[Ni(dmpe)_2H]PF_6$ (**1**) [dmpe = 1,2-bis(dimethylphosphino)ethane] was synthesized by protonation of $Ni(dmpe)_2$ with NH_4PF_6. The platinum analog, $[Pt(dmpe)_2H]PF_6$ (**2**), and $[Pt(depe)_2H]PF_6$ (**3**) [depe = 1,2-bis(diethylphosphino)ethane] were synthesized by reduction of the corresponding Pt(II) complexes with $NaBH_4$ on alumina. Complexes **1** and **3** can also be synthesized electrochemically. Reduction of $Ni(dmpe)_2^{2+}$ by two electrons in the presence of ammonium ion generates **1**, and reduction of $Pt(depe)_2^{2+}$ in methanol or wet acetonitrile produces **3**. These hydrides react with a variety of cationic metal carbonyl complexes to produce known metal formyl complexes. The structure of **3** was determined by X-ray diffraction. Complex **3** crystallizes in a monoclinic unit cell with $P2_1/c$ symmetry with a = 14.258 (4) Å, b = 9.648 (3) Å, c = 21.898 (5) Å, β = 91.17 (2)°, V = 3011.7 (14) Å^3, Z = 4, and d_{calcd} = 1.662 g/cm^3. Full-matrix least-squares refinement converged with residuals R = 4.52% and R_w = 5.90%.

Introduction

A number of research groups have recently described the electrochemical reduction of CO_2 to CO catalyzed by various homogeneous catalysts.[1] Direct reduction of CO at various electrodes has also been reported,[2] but there are no known homogeneous catalysts for electrochemical CO reduction. The transfer of a hydride ligand from a metal to coordinated carbon monoxide is thought to be an important step in the reduction of carbon monoxide by hydrogen,[3] and the intermolecular transfer of a hydride ligand from various borohydride reagents to coordinated carbon monoxide is a general route to metal formyl complexes.[4] However, in a catalytic reaction it must be possible to regenerate the hydride species. The stoichiometric nature of the borohydride reagents makes the use of transition metal hydrides with their potential for regeneration attractive. Although early transition metal hydrides readily transfer hydride ligands to CO to form metal formyl and metal oxycarbene complexes,[5] it seems unlikely that regeneration of these hydrides will occur due to the formation of strong M–O bonds in the products. The use of iron,[4i] copper,[6] molybdenum,[4i] rhodium,[7] and ruthenium[8] hydrides to generate formyl complexes suggests that late transition metals are also capable of transferring hydride ligands to coordinated CO. Metal carbonyl hydride anions have also been shown to promote formyl formation.[9] Although hydride regeneration using hydrogen would appear plausible for some of these complexes, it has not been demonstrated.

An electrochemical system that generates formyl complexes by reduction of metal carbonyls in the presence of hydrogen atom donors such as trialkyltin hydrides has been developed by Kochi and co-workers.[10] In these systems, the metal carbonyl complex is reduced by one electron to form a 19e$^-$ radical species, which then abstracts a hydrogen from the trialkyltin hydride to produce a formyl complex. These systems suffer from the low stability of the formyls produced under the reaction conditions and

---

[1] (a) DuBois, D. L.; Miedaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113. (b) Collin, J.-P.; Sauvage, J.-P. *Coord. Chem. Rev.* **1989**, *93*, 245. (c) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1974**, 158. (d) Fischer, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7363. (e) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153. (f) Beley, M.; Collin, J.-P.; Ruppert, R.; Sausage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461. (g) Hawecker, J.; Lehn, J. M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (h) Ishida, H.; Tanaka, T. *Organometallics* **1987**, *6*, 181.

[2] (a) Uribe, F. A.; Sharp, P. R.; Bard, A. J. *J. Electroanal. Chem.* **1983**, *152*, 173. (b) Silvestri, G.; Gambino, S.; Filardo, G.; Sparado, G.; Palmisano, L. *Electrochim. Acta* **1978**, *23*, 413. (c) Ogura, K.; Yamasaki, S. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 267. (d) Hori, Y.; Murata, A.; Takahashi, R.; Suzuki, S. *J. Am. Chem. Soc.* **1987**, *109*, 5022. (e) Ogura, K.; Yamasaki, S. *J. Chem. Soc., Dalton Trans.* **1985**, 2499.

[3] (a) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325. (b) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (c) Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3623.

[4] (a) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (c) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (d) Sontag, C.; Drama, O.; Berke, H. *Chem. Ber.* **1987**, *120*, 559. (e) Johnston, G. G.; Hommeltoft, S. I.; Baird, M. C. *Organometallics* **1989**, *8*, 1904. (f) Leoni, P.; Aquilini, E.; Pasquali, M.; Marchetti, F.; Sabat, M. *J. Chem. Soc., Dalton Trans.* **1988**, 329. (g) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498. (h) Smith, G.; Cole-Hamilton, D. J.; Thoronton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 387. (i) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1988**, *7*, 1683. (j) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

[5] (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Labinger, J. A.; Wong, K. A.; Sheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3254. (c) Fagan, P.; Moloy, K.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

[6] Nelson, G. O.; Sumner, C. E. *Organometallics* **1986**, *5*, 1983.

[7] Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.

[8] (a) Dombek, B. D.; Harrison, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 2485. (b) Dombek, B. D. *Organometallics* **1985**, *4*, 1707.

[9] Darensbourg, M. Y.; Ash, C. E.; Arndt, L. W.; Janzen, C. P.; Youngdahl, K. A.; Park, Y. K. *J. Organomet. Chem.* **1990**, *383*, 191.

[10] (a) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926. (b) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1987**, *6*, 129.

0276-7333/93/2312-0299$04.00/0

from the very negative potentials required to generate the metal carbonyl radicals.

In an electrochemical cycle for CO reduction, the metal hydride could be generated in the electrochemical step. This electrochemically generated hydride complex could then transfer its hydride ligand to an electrophilic carbonyl ligand on a second complex. Subsequent protonation and hydride transfer reactions of the formyl formed could then lead to reduced carbon products and an electrocatalytic system for CO reduction. Group 8 metal phosphine complexes would seem to be well suited for this purpose. The M(II) complexes are stable and easy to prepare, and they undergo reduction to yield stable M(0) complexes. The five-coordinate hydride complexes are also stable and can be prepared either by sodium borohydride reduction of the M(II) complexes or by protonation of the M(0) complexes,[11] and hydride transfer from these hydrides returns the very-stable M(II) complexes and completes the cycle. We report here the electrochemical generation of $[Ni(dmpe)_2H]^+$ (1) (dmpe = 1,2-bis(dimethylphosphino)ethane) and $[Pt(depe)_2H]^+$ (3) (depe = 1,2-bis(diethylphosphino)ethane) by reduction to the M(0) complex followed by protonation and the reactions of the isolated complexes with a variety of cationic metal carbonyl complexes to produce formyls. The latter reactions have been extended to $[Pt(dmpe)_2H]^+$ (2) as well. The structure of $[Pt(depe)_2H](PF_6)$ was determined using X-ray diffraction.

Experimental Section

General Considerations. Reagent grade tetrahydrofuran (THF) was predried over CaH_2. Diethyl ether, THF, and hexane were purified by distillation from sodium benzophenone ketyl and stored under nitrogen. CH_3CN and CH_2Cl_2 were distilled from CaH_2 under nitrogen. Reagent grade ethanol was deoxygenated by purging with nitrogen prior to use. CD_3CN was purified by vacuum transfer from CaH_2 and stored in an inert atmosphere glovebox.

$Ni(COD)_2$ (COD = cyclooctadiene), $Pt(COD)Cl_2$, and the phosphine ligands dmpe and depe were purchased from Strem. $NaBH_4$ on alumina and NH_4PF_6 were purchased from Aldrich.

Air-sensitive solids were stored and manipulated in a helium-filled Vacuum Atmospheres glovebox equipped with a freezer. Reactions were carried out in dry, deoxygenated solvents using standard cannula and Schlenk techniques.

NMR spectra were obtained using a Varian Unity 300 spectrometer operating at 299.95 MHz for ^1H and 121.42 MHz for ^{31}P. Chemical shifts are reported in parts per million relative to internal tetramethylsilane for ^1H and external H_3PO_4 for ^{31}P. Infrared spectra were obtained using a Perkin-Elmer 599B spectrometer. Coulometric measurements were carried out at 25–30 °C using a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. The working electrode was constructed from reticulated vitreous carbon rod with a diameter of 1 cm and length of 2.5 cm (100 pores/in., The Electrosynthesis Co., Inc.), the counter electrode was a platinum wire, and a silver wire coated with AgCl was used as a pseudoreference electrode. The electrode compartments were separated by porous Vycor disks (7-mm diameter, EG&G Princeton Applied Research). Cyclic voltammetry experiments were carried out using a Cypress Systems computer-aided electrolysis system with a glassy-carbon working electrode and counter and reference electrodes as described above. Ferrocene was used as an internal standard, and all potentials are reported versus the ferrocene/ferrocenium couple. Microanalyses were performed by Huffman Laboratories, Golden, CO. Analyses for both carbon and phosphorus on the reported complexes proved to be difficult. The problem of low carbon analyses was solved by adding V_2O_5 as a combustion aid. However, the values for phosphorus content found were low by 1–2% even when V_2O_5 was added to aid with the oxidation.

[Ni(dmpe)$_2$H](PF$_6$) (1). A solution of dmpe (0.75 g, 5.0 mmol) in THF (50 mL) was cooled to −78 °C, and solid $Ni(COD)_2$ (0.65 g, 2.4 mmol) was added. The resulting suspension was warmed to room temperature and stirred for 16 h to yield a clear yellow solution of $Ni(dmpe)_2$ ($^{31}P\{^1H\}$ NMR, THF, 18.3 ppm). This was then treated with a solution of NH_4PF_6 (0.81 g, 5.0 mmol) in THF (30 mL), which caused a yellow precipitate to form immediately. The volume of this suspension was then reduced under vacuum to 10 mL, and the product was collected by filtration, washed with H_2O (2 × 10 mL) and diethyl ether (2 × 20 mL), and dried under vacuum. It was recrystallized from CH_2Cl_2/hexane to yield 0.52 g of yellow powder (43%). Anal. Calcd for $C_{12}H_{33}P_5F_6Ni$: C, 28.49; H, 6.77. Found: C, 27.72; H, 6.80. ^1H NMR (CD_3CN): δ 1.77 (m, 8 H, PCH_2CH_2P), 1.40 (m, 24 H, CH_3P), −14.02 (quintet, 1 H, $^2J_{P-H} = 8.5$ Hz, Ni–H). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 24.6 (s). IR (Nujol): $\nu_{Ni-H} = 1905\ cm^{-1}$.

Pt(dmpe)$_2$(PF$_6$)$_2$. A suspension of $Pt(COD)Cl_2$ (1.12 g, 3.0 mmol) in CH_3CN (30 mL) was treated with a solution of dmpe (0.90 g, 6.0 mmol) in CH_3CN. The resulting mixture was stirred for 16 h at room temperature, and the volatiles were removed under vacuum, leaving a white solid. This was dissolved in water (30 mL), a solution of NH_4PF_6 (1.50 g, 9.2 mmol) in water (20 mL) was added, and a white precipitate formed immediately. This was collected by filtration, washed with water (10 mL) and then diethyl ether (4 × 10 mL), and dried under vacuum to yield the product as a white powder (2.25 g, 95%). Anal. Calcd for $C_{12}H_{32}P_6F_{12}Pt$: C, 18.35; H, 4.11; P, 23.67. Found: C, 17.74; H, 3.96; P, 22.77. ^1H NMR (CD_3CN): δ 2.10 (m, 4 H, PCH_2CH_2P), 1.79 (m, 12 H, $^3J_{Pt-H} = 13.9$ Hz, P–CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 35.0 (s, $^1J_{Pt-P} = 2169$ Hz).

Pt(depe)$_2$(PF$_6$)$_2$. The procedure above for $Pt(dmpe)_2(PF_6)_2$ was followed by substituting depe (1.24 g, 6.0 mmol) for dmpe. This yielded 1.95 g of product as a white powder (72%). Anal. Calcd for $C_{20}H_{48}P_6F_{12}Pt$: C, 26.77; H, 5.39; P, 20.71. Found: C, 26.69; H, 5.21; P, 20.52. ^1H NMR (CD_3CN): δ 2.38, 2.07 (m, 8 H, PCH_2CH_3), 2.21 (m, 4 H, PCH_2CH_2P), 1.16 (m, 12 H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 58.5 (s, $^1J_{Pt-P} = 2125$ Hz).

[Pt(dmpe)$_2$H](PF$_6$) (2). To a solution of $Pt(dmpe)_2(PF_6)_2$ (1.0 g, 1.27 mmol) in CH_3CN (50 mL) was added solid $NaBH_4$ on alumina (1.0 g of material with 10% $NaBH_4$ content, 2.6 mmol), and the resulting suspension was stirred for 16 h. The alumina was then removed by filtration, and the solvent was removed from the clear solution under vacuum to give a white powder. This was washed with ethanol (3 × 10 mL) to remove excess $NaBH_4$ and then recrystallized from CH_3CN/ethanol to yield 0.58 g of white powder (70%). Anal. Calcd for $C_{12}H_{33}P_5F_6Pt$: C, 22.47; H, 5.19. Found: C, 21.96; H, 5.12. ^1H NMR (CD_3CN): δ 1.79 (m, 8 H, PCH_2CH_2P), 1.60 (m, 24 H, P–CH_3), −11.55 (quintet, 1 H, $^2J_{P-H} = 30$ Hz, $^1J_{Pt-H} = 726$ Hz, Pt–H). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −7.3 (s, $^1J_{Pt-P} = 2184$ Hz). IR (Nujol): $\nu_{Pt-H} = 2015\ cm^{-1}$.

[Pt(depe)$_2$H](PF$_6$) (3). To a solution of $Pt(depe)_2(PF_6)_2$ (1.00 g, 1.11 mmol) in CH_3CN (50 mL) was added solid $NaBH_4$ on alumina (1.2 g of material with 10% $NaBH_4$ content, 3.1 mmol), and the resulting suspension was stirred for 16 h. The alumina was then removed by filtration, and the solvent was removed from the colorless solution under vacuum to give a white powder. This material was dissolved in ethanol (30 mL) and crystallized by cooling the solution to −20 °C. The crystals were collected by decanting the solvent via cannula, washed with cold ethanol (2 × 5 mL), and dried under vacuum to yield 0.66 g of product as colorless crystals (79%). Anal. Calcd for $C_{20}H_{49}P_5F_6Pt$: C, 31.88; H, 6.55; P, 20.55. Found: C, 31.79; H, 6.69; P, 19.51. ^1H NMR (CD_3CN): δ 1.76 (m, 24 H, PCH_2CH_2P and PCH_2CH_3), 1.01 (m, 24 H, PCH_2CH_3), −12.12 (quintet, 1 H, $^2J_{P-H} = 28.8$ Hz, $^1J_{Pt-H} = 650$ Hz, Pt–H). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 22.1 (s, $^1J_{Pt-P} = 2256$ Hz). IR (Nujol): $\nu_{Pt-H} = 2048\ cm^{-1}$.

---

(11) Shunn, R. A. *Inorg. Chem.* **1970**, *9*, 394.

Table I. Products Obtained from Reactions of Hydride Complexes with Cationic Carbonyl Complexes, with Selected Yields in Parentheses

carbonyl/hydride reactants	$[Ni(dmpe)_2H]PF_6$ (**1**)	$[Pt(dmpe)_2H]PF_6$ (**2**)	$[Pt(depe)_2H]PF_6$ (**3**)
$[Cp^*Mo(CO)_3P(OMe)_3]^+$ [a]	*cis*-$Cp^*Mo(CO)_2P(OMe)_3H$ [b]	*cis*-$Cp^*Mo(CO)_2P(OMe)_3(CHO)$ [b]	no reaction
$[Mn(CO)_5PPh_3]^+$	*cis*-$Mn(CO)_4(PPh_3)H$ [c]	*cis*-$Mn(CO)_4(PPh_3)(CHO)$ [c] (52%)	*m*
$[CpRe(CO)_2NO]^+$	$CpRe(CO)(NO)(CHO)$ [d] (75%)	$CpRe(CO)(NO)(CHO)$ [d] (60%)	$CpRe(CO)(NO)(CHO)$ [d] (74%)
$[CpRe(CO)(NO)(CH_3CN)]^+$	$CpRe(CO)(NO)H$ [e]	$CpRe(NO)(CH_3CN)(CHO)$ [f]	*m*
$[CpRe(CO)(NO)(PPh_3)]^+$	no reaction	$CpRe(NO)(PPh_3)(CHO)$ [g] (66%)	$CpRe(NO)(PPh_3)(CHO)$ [g] (5%)
$[CpRe(CO)(NO)(PEt_3)]^+$	no reaction	$CpRe(NO)(PEt_3)(CHO)$ [h] (85%)	no reaction
$[Cp^*Re(CO)_2NO]^+$	$Cp^*Re(CO)(NO)(CHO)$ [i] (50%)	$Cp^*Re(CO)(NO)(CHO)$ [i] (80%)	$Cp^*Re(CO)(NO)(CHO)$ [i] (85%)
$[Cp^*Ru(CO)_3]^+$	$Cp^*Ru(CO)_2(CHO)$ [j]	$Cp^*Ru(CO)_2(CHO)$ [j]	*m*
$[(CP_3)Ru(CO)_3]^{2+}$ [a]	$[(CP_3)Ru(CO)_2H]^+$ [k]	$[(CP_3)Ru(CO)_2(CHO)]^+$ [l]	$[(CP_3)Ru(CO)_2(CHO)]^+$ [l]

[a] $Cp^* = C_5(CH_3)_5$, $Cp = C_5H_5$, $CP_3 = CH_3C(CH_2CH_2PPh_2)_3$. [b] Reference 4f. [c] Reference 4g. [d] Reference 4a,b,j. [e] Reference 17. [f] Reference 18. [g] Reference 4c. [h] Reference 19. [i] Reference 4b. [j] Reference 6. As the reaction proceeds, the formyl decomposes to the hydride, $Cp^*Ru(CO)_2H$. [k] Reference 20. [l] Reference 4e. As the reaction proceeds, the formyl decomposes to the hydride, $[(CP_3)Ru(CO)_2H]^+$. [m] A reaction occurs, but no formyl or hydride products could be identified.

Table II. Crystal Data for $[Pt(depe)_2H]PF_6$

formula	$C_{20}H_{49}F_6P_5Pt$	V, Å^3	3011.7 (14)
fw	753.5	Z	4
space group	$P2_1/c$	d_{calcd}, g/cm^3	1.662
cryst system	monoclinic	$F(000)$, e$^-$	1504
a, Å	14.258 (4)	μ, mm^{-1}	5.014
b, Å	9.648 (3)	radiation (λ, Å)	Mo K$_\alpha$ (0.717 03)
c, Å	21.898 (5)	temp, °C	−100
β, deg	91.17 (2)	R, R_w	0.0452, 0.0590

Reactions of Hydrides with Cationic Carbonyl Complexes. The three hydrides were screened for reactions with all of the cationic carbonyl complexes shown in Table I by carrying out small-scale reactions in NMR tubes and monitoring by ^1H NMR and ^{31}P NMR. This was done by combining 20–30 mg of metal hydride with 1 equiv of cationic carbonyl complex and ~10 mg of ferrocene internal standard in a 5-mm NMR tube and adding 0.7 mL of CD_3CN at room temperature. The spectra were then recorded at intervals and monitored for the formation of new formyl or hydride products. Where reasonably stable formyls were produced, the yields were determined by integration and comparison with the internal standard. These results are summarized in Table I.

X-ray Structure of $[Pt(depe)_2H]PF_6$ (3). Crystals of **3** were grown from ethanol, cleaved and mounted on glass fibers, and coated with grease. Crystal data are shown in Table II. Complete details of the experimental conditions for data collection and structure refinement are given in the supplementary material. The structure was solved by direct methods and refined by using full-matrix least-squares techniques. The orientations of the PF_6^- counterions are disordered. The occupancies of the two observed orientations were determined by least-squares techniques. All non-hydrogen atoms were refined anisotropically. The hydride hydrogen atom was not located. The final model included all other hydrogen atoms in fixed, idealized positions. A perspective view of the platinum hydride cation showing the atom-numbering scheme is shown in Figure 1, with the PF_6^- counterions omitted for clarity. Atomic coordinates and equivalent isotropic displacement parameters are presented in Table III. Selected bond lengths and angles are presented in Table IV. Full tables of derived results are included in the supplementary material.

Results and Discussion

The nickel hydride complex **1** was synthesized from $Ni(COD)_2$ by addition of 2 equiv of dmpe in THF followed by protonation of the intermediate Ni(0) complex with NH_4PF_6. This parallels the work of Shunn[11] in which $Ni(dppe)_2H^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) was prepared by protonation of $Ni(dppe)_2$ with HBF_4. The platinum hydride complexes **2** and **3** were prepared by treatment of the corresponding Pt(II) complexes with sodium borohydride on alumina in acetonitrile. A number of 5-coordinate platinum hydrides have been synthesized in this manner using unsupported $NaBH_4$, including $[(PP_3)PtH]^+$ [12] (PP_3 = tris(2-(diphenylphosphino)ethyl)phospine), $[P_4PtH]^+$ [13] (P_4 = 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane), and $[(PP_2)LPtH]^+$ [14] (PP_2 = bis(2-(diphenylphosphino)ethyl)phenylphosphine, L = PPh_3, PBu_3, PPh_2H, PCy_2H, and $Ph_2PCH_2PPh_2$).

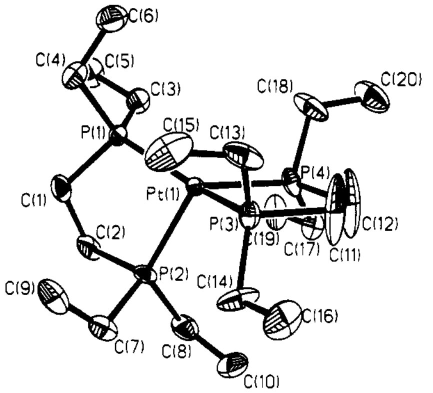

Figure 1. Perspective view of the molecular configuration of $Pt(depe)_2H^+$ (**3**) with the atom-numbering scheme for non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 50% probability.

Complexes **1** and **3** can also be synthesized electrochemically. Controlled-potential electrolysis of $Ni(dmpe)_2(BF_4)_2$ in acetonitrile at -1.36 V vs the ferrocene/ferrocenium couple in the presence of excess NH_4PF_6 results in the passage of 2.0 faradays/mol of complex and the clean formation of **1**, as shown by the ^{31}P NMR spectrum of the electrolysis solution. The same is true for **3** except a much weaker acid is required. Electrolysis of $Pt(depe)_2(PF_6)_2$ in methanol or wet acetonitrile at −1.65 V vs ferrocene/ferrocenium results in the clean formation of **3**. Acids stronger than water, such as NH_4^+, react with **3** to produce H_2 and regenerate $Pt(depe)_2^{2+}$.

The infrared spectra of all three hydride complexes show medium to strong absorptions due to the metal–hydride stretches at the appropriate frequencies (**1**, 1905 cm^{-1}; **2**, 2015 cm^{-1}; **3**, 2048 cm^{-1}). These values agree with those found for the 5-coordinate Ni[11] and Pt[12,13,14] hydrides mentioned earlier and are in the region typical for terminal metal hydride stretching vibrations. The rather high stretching frequencies observed for the platinum complexes, especially **3**, indicate the presence of strong Pt–H

---

(12) Bruggeller, P. *Inorg. Chim. Acta* **1987**, *129*, L27.
(13) Bruggeller, P. *Inorg. Chem.* **1990**, *29*, 1742.
(14) Handler, A.; Peringer, P.; Mueller, E. P. *J. Organomet. Chem.* **1991**, *412*, 451.

Table III. Atomic Coordinates[a] (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10⁴) for [Pt(depe)$_2$H]PF$_6$

	x/a	*y/b*	*z/c*	*U*(eq)[b]
Pt(1)	7579 (1)	2110 (1)	5852 (1)	174 (1)
P(1)	6973 (1)	3006 (2)	4970 (1)	214 (4)
P(2)	6064 (1)	2241 (2)	6216 (1)	227 (4)
P(3)	8568 (1)	2414 (2)	6698 (1)	243 (4)
P(4)	8084 (1)	−272 (2)	5861 (1)	275 (4)
C(1)	5785 (5)	3602 (7)	5104 (3)	330 (19)
C(2)	5295 (4)	2637 (8)	5555 (3)	330 (20)
C(3)	6856 (5)	1787 (7)	4321 (3)	323 (19)
C(4)	7529 (5)	4555 (7)	4651 (3)	350 (20)
C(5)	6407 (6)	2354 (9)	3734 (3)	428 (24)
C(6)	8538 (5)	4366 (8)	4471 (3)	443 (24)
C(7)	5773 (5)	3573 (7)	6782 (3)	327 (20)
C(8)	5482 (5)	704 (8)	6531 (3)	371 (21)
C(9)	6046 (5)	5051 (8)	6615 (3)	453 (24)
C(10)	5894 (5)	221 (9)	7139 (3)	506 (27)
C(11)	9177 (9)	765 (9)	6812 (5)	959 (45)
C(12)	8893 (8)	−397 (9)	6512 (5)	930 (44)
C(13)	9528 (5)	3638 (9)	6605 (3)	429 (24)
C(14)	8083 (6)	2866 (8)	7433 (3)	415 (25)
C(15)	9185 (6)	5115 (9)	6511 (4)	578 (30)
C(16)	8797 (7)	3020 (9)	7965 (3)	505 (29)
C(17)	7343 (6)	−1805 (7)	5957 (3)	359 (21)
C(18)	8777 (6)	−732 (8)	5190 (5)	560 (29)
C(19)	6639 (6)	−1960 (7)	5422 (4)	450 (26)
C(20)	9307 (7)	−2094 (8)	5199 (5)	614 (35)
P(5)	2463 (1)	2691 (2)	1764 (1)	332 (5)
F(1)	2123 (6)	1121 (6)	1830 (3)	960 (28)
F(2)	2780 (6)	4236 (6)	1715 (3)	989 (29)
F(3)*	2988 (13)	2565 (14)	2402 (6)	946 (62)
F(4)*	3333 (8)	1991 (13)	1478 (8)	1000 (59)
F(5)*	1936 (13)	2664 (14)	1129 (6)	971 (65)
F(6)*	1542 (9)	3272 (15)	2060 (9)	1015 (58)
F(3′)*	3450 (18)	2686 (34)	2137 (13)	884 (104)
F(4′)*	3063 (18)	2707 (34)	1168 (10)	972 (126)
F(5′)*	1592 (14)	2936 (47)	1384 (20)	1483 (220)
F(6′)*	2020 (28)	2744 (34)	2390 (11)	1177 (145)

[a] Atoms have occupancies of 1.0 except as marked with asterisks: F(3), 0.66; F(4), 0.66; F(5), 0.66; F(6), 0.66; F(3′), 0.34; F(4′), 0.34; F(5′), 0.34; F(6′), 0.34. [b] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for [Pt(depe)$_2$H]PF$_6$ (3)

Bond Distances			
Pt–P(1)	2.271 (2)	Pt–P(2)	2.321 (2)
Pt–P(3)	2.322 (2)	Pt–P(4)	2.408 (2)
Bond Angles			
P(1)–Pt–P(2)	86.0 (1)	P(1)–Pt–P(3)	147.6 (1)
P(2)–Pt–P(3)	105.9 (1)	P(1)–Pt–P(4)	118.6 (1)
P(2)–Pt–P(4)	109.2 (1)	P(3)–Pt–P(4)	86.4 (1)

bonds and support a structure containing a *trans*-P–Pt–H arrangement.[15]

The ^{1}H and ^{31}P{^{1}H} NMR spectra of the three hydrides are also very similar. The nickel hydride exhibits a hydride resonance at -14.30 ppm (quintet, $^2J_{P-H}$ = 8.5 Hz) in the ^{1}H NMR spectrum and a singlet at 24.6 ppm in the ^{31}P{^{1}H} NMR due to all four phosphorus atoms of the dmpe ligands. The platinum complexes 2 and 3 show hydride resonances at -11.55 ppm (quintet, $^2J_{P-H}$ = 30 Hz) and -12.12 ppm (quintet, $^2J_{P-H}$ = 29 Hz), respectively, in the ^{1}H NMR spectrum with satellites due to ^{195}Pt coupling (J_{Pt-H} = 726, 650 Hz, respectively). The ^{31}P{^{1}H} NMR spectra of 2 and 3 show singlets at −7.3 ppm and +22.1 ppm, respectively, with the appropriate ^{195}Pt satellites (J_{Pt-P} = 2182, 2256 Hz, respectively). These simple NMR spectra, with a single resonance observed for all four phosphorus atoms in the ^{31}P NMR and equivalent coupling of all four phosphorus atoms to the hydride observed in the ^{1}H NMR spectrum, are consistent with two possible structures for these five-coordinate complexes. These are a locked square pyramidal structure with the hydride ligand at the apex or a lower-symmetry structure such as a trigonal bipyramid or a capped tetrahedron that undergoes a rapid fluxional process on the NMR time scale. Variable-temperature NMR studies on 1 and 2 in acetone or methylene chloride showed only slight broadening of the ^{31}P resonances at −95 °C. Low-temperature spectra of 3 were recorded in CD$_2$Cl$_2$/CCl$_2$FH (1/1 v/v) down to −140 °C. The ^{31}P resonance was observed to broaden and coalesce between −130 and −140 °C, but well-resolved spectra could not be obtained below that temperature. These data rule out the locked structure, but they also give no indication of the structure of these complexes in solution.

X-ray Crystal Structure of [Pt(depe)$_2$H]PF$_6$ (3). To obtain information on the structure of the five-coordinate hydrides in the solid state, the structure of 3 was determined using X-ray diffraction. The crystal structure consists of discrete platinum hydride cations and PF$_6^-$ anions at general positions in the unit cell. The PF$_6^-$ anions are rotationally disordered; this was treated by refining the occupancies of four of the fluorine atoms in two possible configurations. As Figure 1 shows, the two diphosphine ligands are arranged around the platinum atom in a distorted tetrahedral geometry. The Pt–P bond lengths fall between 2.27 and 2.41 Å, with two being equal at 2.32 Å, one 0.05 Å shorter than these, and the Pt–P(4) bond being longer than these by more than 0.08 Å. These distances are comparable to those found for the two other five-coordinate platinum hydrides that have been structurally characterized.[13,16] The hydride hydrogen was not located, but its position trans to P(4) is suggested by the long Pt–P(4) bond length and the high value of the Pt–H stretching frequency. This is due to the strong trans directing influence of the hydride ligand, which causes the bond trans to it to be weaker and therefore longer than the other Pt–P bonds.[15] The P–Pt–P angles that are spanned by the chelate rings are both 86°, which is consistent with values found in structures of other Pt-bidentate phosphine complexes with five-membered chelate rings.[15,21] The P(2)–Pt–P(3) and P(2)–Pt–P(4) angles are 105.9 (1) and 109.2 (1)°, respectively, values very near the optimal tetrahedral angle. The P(1)–Pt–P(3) and P(1)–Pt–P(4) angles are much larger, with values of 147.6 (1) and 118.6 (1)°, respectively, reflecting the distortion.

Reactions of Hydride Complexes with Cationic Metal Carbonyl Complexes. All three metal hydride complexes react with [CpRe(CO)$_2$(NO)]$^+$ to form the well-characterized formyl complex CpRe(CO)(NO)(CHO),[4a,b,j]

---

[15] Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1983**, *22*, 2324.

[16] Gieren, V. A.; Bruggeller, P.; Hofer, K.; Hubner, T.; Ruiz-Perez, C. *Acta Crystallogr., Sect. C* **1989**, *45*, 196.

[17] Stewart, R. P.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32.

[18] ^{1}H NMR (CD$_3$CN, δ): 16.33 (s, 1H, CHO), 5.50 (s, 5H, Cp). The resonance due to the CH$_3$CN ligand was observed at the shift of free acetonitrile (1.95 ppm), indicating that exchange with the solvent had occurred. The formyl complex rapidly decomposes to the hydride, CpRe(CO)(NO)H, with loss of the acetonitrile ligand.

[19] ^{1}H NMR (CD$_3$CN, δ): 16.70 (d, 1H, $^3J_{P-H}$ = 0.7 Hz, CHO), 5.52 (s, 5H, Cp), 1.85 (m, 6H, PCH_2CH$_3$), 1.00 (d of t, 9H, $^3J_{P-H}$ = 16.7 Hz, $^3J_{H-H}$ = 7.7 Hz, PCH$_2$CH_3).

[20] Hommeltoft, S. I.; Bair, M. C. *Organometallics* **1986**, *5*, 190.

[21] Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554.

an example of which is shown in reaction 1. The ^{1}H NMR

$$\mathrm{CpRe(CO)_2(NO)^+ + Ni(dmpe)_2H^+ \rightarrow CpRe(CO)(NO)(CHO) + Ni(dmpe)_2{}^{2+}} \quad (1)$$

spectrum obtained on reaction solutions in CD_3CN exhibits a formyl proton resonance at 16.13 ppm and a cyclopentadienyl proton resonance at 5.83 ppm, in agreement with published data. During the course of the reaction the ^{31}P resonances of the $[M(diphos)_2H]^+$ complexes disappear and the resonances of the $[M(diphos)_2]^{2+}$ cations grow in. The reactions of the rhenium carbonyls are reasonably fast, requiring $^1/_2$–1 h to go to completion in the NMR-scale reactions carried out at room temperature. The ruthenium carbonyl reacts more slowly, requiring several hours to go to completion. Using $[Pt(dmpe)_2D]^+$ (prepared using $NaBD_4$) in reaction 1 results in the formation of CpRe(CO)(NO)(CDO), which was characterized by ^{2}H NMR spectroscopy (δ(CDO) = 16.18 ppm).

Reaction 1 appears to be fairly general. Other metal carbonyls known to form stable formyl complexes when reduced with borohydride reagents can also be reduced to formyl complexes using **1**–**3** (Table I). The formyls produced were identified by comparison of their ^{1}H NMR spectra with the published spectra of the known formyl complexes. In several cases, chemical shifts obtained in CD_3CN differed significantly from those reported in the literature in different (often nonpolar) solvents. In these cases, authentic samples of the formyl complexes were synthesized and examined in CD_3CN for comparison. The chemical shifts in CD_3CN were within 0.2 ppm of the values cited in the literature in other solvents for all of the formyls except *cis*-$Mn(CO)_4(PPh_3)(CHO)$ and Cp*Re(CO)(NO)(CHO). The manganese formyl proton resonance is observed as a single, broad peak at 14.26 ppm in C_6D_6[4g] but appears as a doublet at 13.59 ppm ($^3J_{P-H}$ = 1.8 Hz) in CD_3CN. Similarly, Cp*Re(CO)(NO)(CHO) was observed at 16.59 ppm in methylcyclohexane-d_{14}[4b] and shifts to 15.91 ppm in CD_3CN. A strong dependence of chemical shift on solvent was also observed for CpRe(CO)(NO)(CHO) by Casey and co-workers.[4a]

A new formyl complex, tentatively identified as $CpRe(NO)(CH_3CN)(CHO)$, was observed by ^{1}H NMR[18] in the reaction of **2** with $[CpRe(CO)(NO)(CH_3CN)]^+$. This complex is only transiently stable, however, as expected for a formyl complex containing a labile ligand. It converts rapidly to CpRe(CO)(NO)H with loss of the acetonitrile ligand and migration of the formyl hydrogen to the metal. For this reason, it was not further characterized.

Hydride **2** reacts faster and with a wider range of carbonyl complexes than either **1** or **3**, but it cannot be generated electrochemically. Reduction of $Pt(dmpe)_2{}^{2+}$ in the presence of weak acids generates H_2 and regenerates the Pt(II) complex. We are also interested in the basicity of M(0) complexes and the factors that determine which complexes are protonated to kinetically-stable hydrides and which go on to evolve hydrogen in acid media. Quantitative determination of hydride acidities (or M(0) basicities) has been hampered by low solubility of either the metal hydride cations or the zerovalent complexes in most solvents. Complex **3** was studied qualitatively in THF, where it is sparingly soluble and $Pt(depe)_2$ is very soluble. Complex **3** was completely deprotonated by 1.1 equiv of potassium *tert*-butoxide to give the Pt(0) complex [^{31}P{^{1}H} NMR: δ 26.5 (s, $^1J_{Pt-P}$ = 3617 Hz)], and this was reprotonated with excess methanol (~5 fold) to yield **3**. This indicates that the acidity of **3** lies between that of methanol and that of *tert*-butyl alcohol in THF.

Reaction 1 illustrates that an electrochemically generated hydride reagent can be used to reduce coordinated carbon monoxide. Unfortunately, the potential required to generate the nickel hydride (–1.36 V vs ferrocene) is more negative than the reduction potentials of the rhenium carbonyls with which it reacts ($CpRe(CO)_2(NO)^+$, –0.89 V; $Cp^*Re(CO)_2(NO)^+$, –0.97 V vs ferrocene), so formyl generation is not yet possible in an electrochemical process. Studies are underway to extend the generality of reaction 1 to include other classes of electrochemically generated hydrides and electrophilic carbonyl complexes and to develop structure–reactivity relationships with the goal of developing a catalytic system for electrochemical CO reduction.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division.

Supplementary Material Available: Tables of crystal data, solution and refinement details, bond lengths and angles, anisotropic displacement parameters, and H atom coordinates for **3** (12 pages). Ordering information is given on any current masthead page.

OM9203892