experimental details of the kinetic runs are given in Table I.

Results

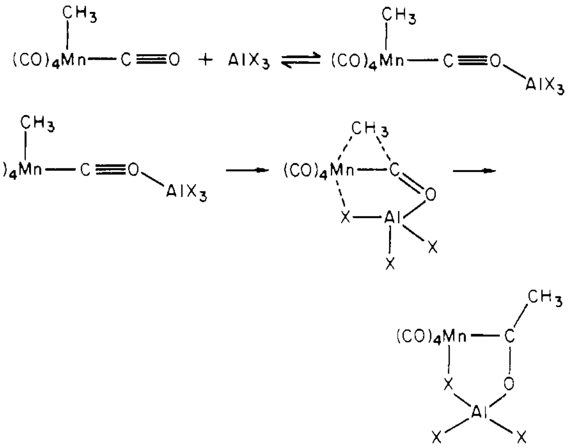
For both $AlBr_3$ and $AlCl_3$, the reaction was complete in the time of mixing, ca. 5 ms. Calculated and observed absorbance changes agreed to within 5%. Because of the sensitivity of $AlCl_3$ and $AlBr_3$ to water, it was not possible to use lower acid concentrations than those listed in Table I. Although the rate of reaction was measurable for $AlCl_2Et$ ($k_{obsd} = 10 \pm 1\ s^{-1}$) and $AlClEt_2$ ($k_{obsd} = 0.37 \pm 0.02\ s^{-1}$), infrared, NMR, and UV-vis spectroscopy showed that Ia was formed, presumably following redistribution of the alkylaluminum chloride.[5] For example, NMR data indicate that only one-third of $CH_3Mn(CO)_5$ reacts to form an acetyl product in a benzene solution containing equimolar amounts of $AlClEt_2$ and $CH_3Mn(CO)_5$. Similarly, the IR spectrum of the reaction product obtained following addition of excess $AlClEt_2$ to $CH_3Mn(CO)_5$ is identical with that of Ia prepared from $AlCl_3$.[3] This implies that the rate-determining redistribution (eq 4) of $AlClEt_2$

$$3AlClEt_2 \rightleftharpoons AlCl_3 + 2AlEt_3 \qquad (4)$$

occurs before the alkyl migration reaction of interest. Nevertheless, the overall reaction to form Ia is significantly faster than that observed in the absence of a Lewis acid. Attempts to promote reaction 1 with other Lewis acids resulted in alkyl cleavage for BCl_3,[3] BBr_3,[3] Ph_2BBr, and $GaCl_3$,[6] while no reaction was observed for $(i\text{-}PrO)_3Al$, Et_2AlOEt, $InCl_3$, or $LaCl_3$.

Discussion

A lower limit can now be placed on the rate of reaction 1. Since the reaction was complete within the time required for mixing in the stopped-flow spectrophotometry, a reasonable estimate of the half-life would be less than 4 ms, corresponding to a $k_{obsd} > 170\ s^{-1}$. This can be compared to the k_1 value of $2 \times 10^{-6}\ s^{-1}$ observed for eq 3a with L = cyclohexylamine in mesitylene solution at 25.5 °C.[7] (Under similar conditions, k_1 in hexane is too small to measure.) This large rate enhancement (ca. 10^8) indicates that the Lewis acid is involved in the primary alkyl migration step (eq 3a) and does not merely intercept the coordinatively unsaturated intermediate (eq 3b) in the mechanism outlined above. One possible mechanism for this rate enhancement is coordination of the Lewis acid to the oxygen atom of a terminal carbonyl in $CH_3Mn(CO)_5$, thereby affording the reaction scheme (5a) and (5b). Although there is no direct experimental evidence for the preequilibrium (5a), Lewis acid adducts are well-known for cyclopentadienyl, anionic, and donor-substituted metal carbonyls.[8] In these systems, the bifunctionally coordinated CO exhibits a greatly reduced CO stretching frequency and bond order. In addition, extended Hückel molecular orbital calculations on the alkyl migration reaction carried out by Berke and Hoffmann[9] indicate that coordination of an electrophile such as H^+ or Li^+ to a terminal carbonyl stabilizes the transition state (eq 3a) by ca. 3 kcal/mol. We[10] have previously observed a small rate enhancement of methyl migration in the presence of carboxylic acids, and Collman et al.[11] reported a 2400-fold increase in the alkyl migration rate in $RFe(CO)_4^-M^+$ when M^+ is changed from $((C_6H_5)_3P)_2N^+$ to Li^+. Although the observed rate enhancement for $AlBr_3$ requires a significantly larger reduction in the activation energy than that calculated by Berke and Hoffmann, their arguments are in qualitative agreement with the present result.



(5a)

(5b)

Acknowledgment. This work was supported by a grant from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank the National Science Foundation for a Graduate Fellowship award to T.G.R. We appreciate helpful discussions with R. E. Stimson.

Registry No. Ia, 74417-97-3; Ib, 72319-91-6; $CH_3Mn(CO)_5$, 13601-24-6; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; $AlCl_2Et$, 563-43-9; $AlClEt_2$, 96-10-6.

---

(5) Jeffrey, E. A.; Mole, T. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972; pp 9-43.

(6) For $GaCl_3$, the insertion reaction is competitive with alkyl cleavage and approximately 50% inserted product is observed by NMR and IR spectroscopy.

(7) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994-3999.

(8) Shriver, D. F. *J. Organomet. Chem.* **1975**, *94*, 259-271 and references therein.

(9) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224-7236.

(10) Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278-280.

(11) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766-4772.

(12) Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* **1956**, 1164-1167.

Contribution from the Sterling Chemistry Laboratory,
Yale University, New Haven, Connecticut 06511

Improved Synthesis of Some Molybdenum and Tungsten Tetrahydrides

Robert H. Crabtree* and Gregory G. Hlatky

Received July 27, 1981

Polyhydride complexes of the type MH_xL_y ($x \gtrsim 3$) have been increasingly studied recently.[1] We have considered the tertiary phosphine tetrahydrides of molybdenum and tungsten as possible sources of highly reactive, highly ligand-deficient species, but a detailed study of their chemistry has required that we develop better synthetic routes to these compounds.

The most common method to date of preparing molybdenum and tungsten tetrahydrides is $NaBH_4$ reduction of MCl_4L_2 (M = Mo or W; L = tertiary phosphine) in ethanol in the presence of excess phosphine (eq 1, 2).[2-5] The yields of the last step

$$MoCl_5 \xrightarrow{CH_3CN} \underset{80\%}{MoCl_4(CH_3CN)_2} \xrightarrow[CH_2Cl_2]{2L} \underset{50\%}{MoCl_4L_2} \xrightarrow[\substack{2L\\ EtOH}]{NaBH_4} \underset{15\%}{MoH_4L_4} \qquad (1)$$

$$WCl_6 \xrightarrow[\substack{Zn\\ CH_2Cl_2}]{PPh_3} \underset{35\%}{WCl_4(PPh_3)_2} \xrightarrow[CH_2Cl_2]{2L} \underset{90\%}{WCl_4L_2} \xrightarrow[\substack{2L\\ EtOH}]{NaBH_4} \underset{15\%}{WH_4L_4} \qquad (2)$$

---

(1) A. P. Borisov, V. D. Makhaev, and K. N. Semenenko, *Koord. Khim.*, **6**, 1139 (1980).

are usually low, and the purifications are often made difficult by the presence of considerable amounts of byproducts. Although the required $MoCl_4L_2$ intermediates can be prepared in fairly good yield from $MoCl_5$, the tungsten analogues can only be prepared in about 30% yield from WCl_6.[6,7] One-step preparations of the tetrahydrides directly from the metal chlorides using metal tetrahydridoborates are also inefficient.[8,9] We report here a greatly improved method for preparing molybdenum and tungsten tetrahydrides using $LiEt_3BH$.

Experimental Section

All reactions were carried out in a prepurified argon atmosphere.[10] Glassware was oven-dried before use. Tetrahydrofuran, petroleum ether (35–60 °C), and benzene were distilled from sodium benzophenone ketyl. Acetonitrile was distilled from CaH_2. These solvents were stored over molecular sieves in an argon atmosphere. Absolute methanol, ethanol, and 2-propanol were dried with molecular sieves and deaerated by argon purge. ^1H NMR spectra were recorded on JEOL FX-90 and Bruker HX-270 spectrometers (other physical data can be found in ref 4). $MoCl_4(CH_3CN)_2$ and $MoCl_4(THF)_2$ were prepared by literature methods.[6] WCl_6, dppe (Alfa-Ventron), $PMePh_2$, $PEtPh_2$ (Strem Chemicals), and $LiEt_3BH$ (1 M solution in THF from Aldrich Chemicals) were used as received.

Tetrahydridotetrakis(methyldiphenylphosphine)molybdenum(IV). Freshly-prepared $MoCl_4(THF)_2$ (1.91 g, 5.0 mmol) was added to $PMePh_2$ (5.0 mL 25 mmol) in THF (50 mL) and refluxed for 30 min, depositing an orange-red solid. On cooling to 20 °C, $LiEt_3BH$ solution (65 mL 65 mmol) was added slowly by syringe over 10 min. The deep-red solution was stirred at 20 °C for 12 h. Ethanol (10 mL) was added *carefully* (there is a vigorous effervescence) to destroy the residual borohydride. The solvent was evaporated in vacuo to give a deep-red oil. Addition of methanol (100 mL) precipitated an orange-yellow solid, which was filtered off and washed with methanol (3 × 10 mL). Recrystallization from benzene/methanol affords 3.00 g (67%) of yellow powder. Anal. Calcd for $C_{52}H_{56}P_4Mo$: C, 69.33; H, 6.27. Found: C, 69.49; H, 6.30. NMR (C_6D_6): δ −2.05 (quintet, J_{PH} = 33 Hz).

Tetrahydridotetrakis(methyldiphenylphosphine)tungsten(IV). WCl_6 (1.60 g, 4.0 mmol) was dissolved in THF (40 mL), and $PMePh_2$ was (4.0 mL, 20 mmol) added. The mixture was refluxed for 1 h, depositing an off-white solid. On cooling to 20 °C, $LiEt_3BH$ solution (50 mL, 50 mmol) was added by syringe to give a deep-red solution. After 12 h of stirring at 20 °C, ethanol was added as above, the solution evaporated in vacuo, and the crude product precipitated by slow addition of ethanol (100 mL). Recrystallization from benzene/ethanol gave 2.78 g (70%) of yellow microcrystalline product. Anal. Calcd for $C_{52}H_{56}P_4W$: C, 63.16; H, 5.70. Found: C, 63.01; H, 5.81. NMR (toluene-d_8, 60 °C): δ −1.72 (quintet, J_{PH} = 31 Hz).

Tetrahydridobis(1,2-bis(diphenylphosphino)ethane)molybdenum(IV). $MoCl_4(THF)_2$ (0.77 g, 2.0 mmol) was added to dppe (dppe = 1,2-bis(diphenylphosphino)ethane; 1.65 g, 4.1 mmol) in THF (30 mL) and refluxed for 30 min. The mixture was cooled to 20 °C, and $LiEt_3BH$ solution (32 mL, 32 mmol) was added slowly by syringe. The deep-red solution was stirred at 20 °C for 12 h. After ethanol (5 mL) was added, the solution was evaporated in vacuo and the crude product precipitated with ethanol (80 mL). Recrystallization from warm benzene/ethanol gave 0.89 g (50%) of yellow product. Anal. Calcd for $C_{52}H_{52}P_4Mo$: C, 69.64; H, 5.84. Found: C, 69.15; H, 5.99. NMR (CD_2Cl_2): δ −4.06 (quintet, J_{PH} = 30 Hz).

Table I. Comparison of Yields (%) from $NaBH_4$ and $LiEt_3BH$

compd	$NaBH_4$	$LiEt_3BH$
$MoH_4(PMePh_2)_4$	$45^{a,c}$	67^b
$MoH_4(dppe)_2$	$15^{a,d}$	50^b
$WH_4(PMePh_2)_4$	4^{d-f}	70^e
$WH_4(PEtPh_2)_4$	$2.5^{d,e,g}$	49^e

[a] Yield from $NaBH_4$ reduction of $MoCl_4L_2$. [b] Yield from $LiEt_3BH$ reduction of $MoCl_4(THF)_2$. [c] Reference 5. [d] Reference 4. [e] Overall yield from WCl_6. [f] 16% yield from WCl_4L_2. [g] 8% yield from WCl_4L_2.

Tetrahydridotetrakis(ethyldiphenylphosphine)tungsten(IV). WCl_6 (1.20 g, 3.0 mmol) and $PEtPh_2$ (3.24 mL, 15 mmol) were refluxed in THF (30 mL) for 1 h, depositing an off-white solid. After cooling to 20 °C, $LiEt_3BH$ solution (50 mL, 50 mmol) was added by syringe. The solution was stirred at 20 °C for 6 h. Methanol (5 mL) was added slowly, and, after effervescence ceased, the solvent was evaporated in vacuo. 2-Propanol (20 mL) and petroleum ether (40 mL) were added slowly, and the mixture was cooled at −20 °C for 1 day. The orange-yellow solid was filtered off and recrystallized from benzene/petroleum ether to afford 1.54 g (49%) of orange-yellow microcrystals. Anal. Calcd for $C_{56}H_{64}P_4W$: C, 64.73; H, 6.17. Found: C, 64.44; H, 6.25. NMR (toluene-d_8, 60 °C): δ −1.91 (quintet, J_{PH} = 32 Hz).

Results and Discussion

Lithium triethylborohydride has high nucleophilicity[11] and, with only one available hydride, little or no tendency to form chelated or borohydride-bridged metal complexes. The borane-derived hydrolysis byproducts are alcohol soluble, making isolation and purification of the desired compound much more convenient.

In Table I, yields of tetrahydrides prepared from $LiEt_3BH$ are compared with yields from $NaBH_4$. The improvement is particularly striking for the tungsten compounds. Indeed, an advantage of this method is that the tungsten tetrahydrides can be prepared directly from WCl_6 (eq 3), avoiding the need

$$\mathrm{WCl_6} \underset{\text{THF}}{\xrightarrow[4\text{L}]{\text{LiEt}_3\text{BH}}} \mathrm{WH_4L_4} \tag{3}$$

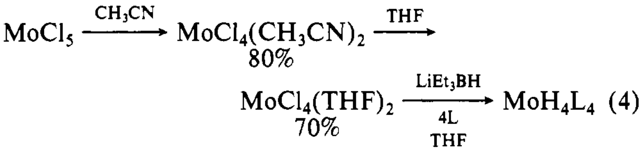
to isolate the corresponding WCl_4L_2 complexes. $WH_4(dppe)_2$ is formed by this reaction in yields of about 35% (vs. 4% overall in three steps from WCl_3 with $NaBH_4$[4]), but isolation of this compound is difficult and analyses were variable and poor. The same was true, in our hands, of the complex prepared by standard methods.[4] Reaction of $LiEt_3BH$ with WCl_6 and PMe_2Ph in THF gives only $WH_6(PMe_2Ph)_3$[12] (NMR (C_6D_6): δ −1.20, quartet, J_{PH} = 36 Hz) in 17% yield; no $WH_4(PMe_2Ph)_4$ is formed.

Yields are not greatly affected for reaction times of 3–18 h but 6–12 h appear to be optimum. Isolation of the tungsten complexes is more difficult, and yields are lower if the phosphine and WCl_6 are not refluxed before adding $LiEt_3BH$. We find the overall yields for the reduction step of the molybdenum compounds are lower when $MoCl_4L_2$ is used instead of $MoCl_4(THF)_2$. The preparation of $MoCl_4(THF)_2$ gives a yield at least comparable to those of the $MoCl_4L_2$ complexes (eq 4);[13] eq 1 and 4 are thus similar until the hydride reduction step.

All the tetrahydrides are stable to air in the solid state for prolonged periods, but $MoH_4(PMePh_2)_4$ shows some degra-

---

(2) F. Pennella, *J. Chem. Soc., Chem. Commun.*, 158 (1971).
(3) B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J. Chem. Soc., Chem. Commun.*, 34 (1972).
(4) P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 1467 (1973).
(5) F. Pennella, *Inorg. Synth.*, **15**, 42 (1974).
(6) J. R. Dilworth and R. L. Richards, *Inorg. Synth.*, **20**, 119 (1980).
(7) A. V. Butcher, J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1064 (1972).
(8) K. N. Semenenko, V. D. Makhaev, and A. P. Borisov, *Koord. Khim.*, **4**, 146 (1978).
(9) K. N. Semenenko, V. D. Makhaev, A. P. Borisov, and G. N. Boiko, *Koord. Khim.*, **4**, 1550 (1978); A. P. Borisov, *Chem. Abstr.*, **91**, 185824s (1979).
(10) Yields for these reactions are, in general, lower when run in a dinitrogen atmosphere. We are currently investigating whether dinitrogen reduction is occurring in these reactions (we thank Dr. Jonathan Dilworth for this suggestion). Argon is recommended for the preparation of molybdenum and tungsten hydrides. A dihydrogen atmosphere does not increase the yields.
(11) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973).
(12) J. R. Moss and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1910 (1972).
(13) A. V. Butcher and J. Chatt. *J. Chem. Soc. A*, 2652 (1970).



$$\mathrm{MoCl_5} \xrightarrow{\mathrm{CH_3CN}} \underset{80\%}{\mathrm{MoCl_4(CH_3CN)_2}} \xrightarrow{\mathrm{THF}} \underset{70\%}{\mathrm{MoCl_4(THF)_2}} \xrightarrow[\substack{4\mathrm{L}\\ \mathrm{THF}}]{\mathrm{LiEt_3BH}} \mathrm{MoH_4L_4} \quad (4)$$

dation after a month; this compound is best stored in an inert atmosphere.

Acknowledgment. We thank the U.S. Department of the Army for support of this work and the Alfred P. Sloan Foundation for a fellowship (to R.H.C.).

Registry No. $MoH_4(PMePh_2)_4$, 32109-07-2; $WH_4(PMePh_2)_4$, 36351-36-7; $MoH_4(dppe)_2$, 32109-09-4; $WH_4(PEtPh_2)_4$, 41627-13-8; $LiEt_3BH$, 22560-16-3; $MoCl_4(THF)_2$, 16998-75-7; WCl_6, 13283-01-7.

Contribution from the Department of Chemistry,
Wesleyan University, Middletown, Connecticut 06457

Homogeneous Reduction of Ligated Carbon Dioxide and Carbon Monoxide to Alkoxymethyl Ligands

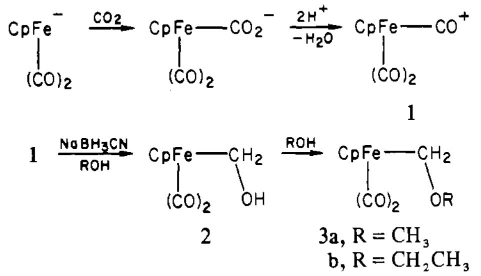
Thomas Bodnar, Eugene Coman, Kevin Menard,
and Alan Cutler*

Received July 23, 1981

Studies on the stoichiometric reduction of ligated carbon monoxide to C_1 formyl, hydroxy- or alkoxymethyl, and methyl ligands are pertinent to the rational design of homogeneous catalysts that convert synthesis gas—CO/H_2 mixtures—to organic products.[1] Borohydride reagents (BH_4^-, HBR_3^-, $HB(OR)_3^-$) reduce, for example, neutral metal carbonyl systems to anionic formyl complexes,[2a–d] cationic metal carbonyls to neutral formyls,[2c,d] $CpRe(CO)_2NO^+$ to hydroxymethyl (also with $Et_2AlH_2^-$) and methyl compounds,[2d,e] $CpM(CO)_3PPh_3^+$ (M = Mo, W) into $CpM(CO)_2PPh_3(CH_3)$,[2f] and CO ligated to BH_3 or BEt_3.[2g] Transition-metal hydride complexes also have been used in fixing CO ligands.[3]

Our interest lies in probing reaction pathways for converting ligated CO to hydroxymethyl functionalities and then to C_2 or higher coordinated ligands. Alkoxymethyl complexes represent convenient products of CO fixation during stoichiometric studies since the anticipated instability of the analogous hydroxymethyl compounds is eliminated.[2d,e,4] Others have contemplated the intermediacy of hydroxymethyl complexes in homogeneous catalysis and have modeled facets of this chemistry with alkoxymethyl or acyloxymethyl derivatives.[5] We recently reported the selective conversion of $CpFe(CO)_2CH_2OCH_3$ to the phosphine-substituted complexes and their respective C_2 organic molecules: $CpFe(CO)L(CH_2CH_3)/CH_2{=}CH_2$, $CpFe(CO)L(CH_2CO_2CH_3)/CH_3CO_2CH_3$, and $CpFe(CO)L(CH_2CHO)/CH_3CHO$.[6]

This paper reports two observations on the fixation of CO and CO_2 ligands appended to $CpFe(CO)_2$. First, sodium cyanoborohydride in methanol or ethanol efficiently reduces a carbonyl on $CpFe(CO)_3^+$ (**1**), via a hydroxymethyl intermediate, to an alkoxymethyl ligand. Second, CO_2 is incorporated into this sequence by generating **1** from the reaction of $CpFe(CO)_2^-Na^+$ and CO_2 and then adding acid. Together both sequences constitute novel conversion of ligated CO_2 to an alkoxymethyl ligand.



Experimental Section

General Manipulations and Physical Measurements. All synthetic manipulations were performed under a nitrogen atmosphere with standard Schlenk techniques and glassware suitably modified for inert-atmosphere work.[7] A nitrogen atmosphere was routinely provided for the following four operations: (a) carrying out reactions, (b) handling all solutions of metal complexes, (c) column chromatography, and (d) breaking the vacuum to evacuated vessels, including the Buchi rotovaporator. Solvents for synthetic work and recording of spectral data were deoxygenated by bubbling dinitrogen through for 20 min. Camag alumina (neutral, activity 3) was used in column chromatography.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 M) with NaCl amalgam-spaced (1.0-mm) solution cells and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601-cm^{-1} absorption. ^1H NMR spectra were taken of concentrated $CDCl_3$ solutions, after centrifugation off of insoluble residues. Varian models EM-360 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as δ values downfield from internal Me_4Si. Combustion microanalyses were performed by Baron Consulting Co., Orange, CT.

---

(1) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 749. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(2) (a) Casey, C. P.; Neuman, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395; **1978**, *100*, 2544. Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, c1. Winter, S. R.; Cornett, G. W.; Thompson, E. A. *Ibid.* **1977**, *133*, 339. Gladysz, J. A.; Selover, J. C. *Tetrahedron Lett.* **1978**, 319. Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. Gladysz, J. A.; Tam, W. *Ibid.* **1978**, *100*, 2545. Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65. Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *Ibid.* **1981**, *206*, 317. (b) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *Ibid.* **1979**, *182*, c57. Johnson, B. F. G.; Kelly, R. L.; Lewis, J.; Thornback, J. R. *Ibid.* **1980**, *190*, c91. Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *Ibid.* **1981**, *206*, c43. Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (c) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. Tam, W.; Wong, W.-K.; Gladysz, J. A. *Ibid.* **1979**, *101*, 1589. (d) Casey, C. P.; Andrews, M. A.; McAbster, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927. (e) Stewart, R. P.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, c32. Sweet, J. R.; Graham, W. A. G. *Ibid.* **1979**, *173*, c9. (f) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328. (g) Brown, H. C.; Hubbard, J. L. *J. Org. Chem.* **1979**, *44*, 467. Rathke, M. W.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 2606.

(3) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Labinger, J. A.; Wong, K. S.; Scheidt, W. R. *Ibid.* **1978**, *100*, 3254. Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *162*, c11. Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Ibid.* **1980**, *102*, 2858. Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1981**, *103*, 2650.

(4) (a) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371. (b) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, c7. (c) Elroi, H.; Myerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540. Espenson, J. H.; Bakoč, A. *Ibid.* **1980**, *102*, 2488; **1981**, *103*, 2721, 2728. (d) Lead reference α-hydroxyalkyl complexes: Vaugh, G. D.; Gladysz, J. A. *Ibid.* **1981**, *103*, 5608.

(5) Pruett, R. L. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 239. Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466. Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *Ibid.* **1978**, *100*, 6766.

(6) Bodnar, T.; Coman, E.; LaCroce, S.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2471.

(7) Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975. Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969. King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1.