

The Reaction Chemistry of Transition-Metal Diphenylphosphorus Complexes with Organoaluminum Compounds. The Synthesis, Characterization, and Crystal and Molecular Structure of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$, an Example of THF Cleavage

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Metathetical and small molecule elimination reactions between appropriate transition-metal carbonyl diphenylphosphorus complexes and organoaluminum compounds have been investigated as synthetic routes to transition-metal derivatives of amphoteric ligands. The synthesis, characterization, and properties of the starting compounds for the metathetical reactions $\text{M}(\text{CO})_5\text{PPh}_2\text{K}\cdot n(\text{dioxane})$ ($\text{M} = \text{Cr}, \text{W}, n = 2$; $\text{M} = \text{Mo}, n = 1$) from $\text{M}(\text{CO})_5\text{PPh}_2\text{H}$ and KH are described. All data confirm that the dioxane molecules in these complexes retain their identity as cyclic ethers. Subsequent reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with AlR_2Br ($\text{R} = \text{Br}, \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) in THF lead to the formation of high yields of fully characterized compounds with the empirical formula $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$. The $(\text{CH}_2)_4\text{O}$ unit arises from the cleavage of the THF molecule. No THF-aluminum adducts are observed. The compound $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$ which incorporates a new amphoteric ligand has also been characterized by an X-ray structural study. The crystal is composed of dimeric units of formula $[\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]]_2$ which are in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 11.939$ (3) Å, $b = 14.940$ (Å), $c = 21.014$ (5) Å, $\beta = 102.88$ (2)°, $V = 3654$ Å³, $Z = 2$ (dimeric units), and mol wt 1301.5. Diffraction data ($2\theta(\text{max}) = 35^\circ$, Mo $K\alpha$ radiation) were collected with a Syntex $P2_1$ automated four-circle diffractometer, the structure was solved by Patterson and difference-Fourier techniques, and the model was refined to $R_F = 9.2\%$ and $R_{wF} = 8.2\%$ for 1515 reflections with $|F_o| > 3\sigma(|F_o|)$. The dimeric molecule lies on an inversion center. Each octahedral $(\text{OC})_5\text{CrPPh}_2$ fragment is linked by an $-(\text{CH}_2)_4\text{O}$ unit (formed by cleavage of THF) to the two $\text{Al}(\text{CH}_2\text{SiMe}_3)_2$ fragments. The central Al-O-Al-O ring is strictly planar, with obtuse Al-O-Al angles of 100.3 (6)° and acute O-Al-O angles of 79.7 (5)°. The second route to chromium derivatives of amphoteric aluminum-phosphorus ligands, small molecule elimination reactions between $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and AlMe_3 or AlMe_2H , does not lead to compounds with Cr-P-Al bonds. Our observations suggest that the major site of reaction for the aluminum compounds is the carbonyl ligand.

Introduction

The new compound $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{NMe}_3]$ can be considered to be a transition-metal derivative of an amphoteric main-group element ligand.¹ This first example of a compound in which the diphenylphosphido group bridges a transition metal and a main-group metal was readily prepared in high yield by an apparent ligand substitution reaction of $\text{Cr}(\text{CO})_5\text{NMe}_3$ by $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ in benzene solution. An alternate synthetic route to these transition-metal derivatives of amphoteric ligands involves starting with a phosphorus derivative of a transition-metal complex and then effecting a chemical reaction which would lead to the formation of the desired phosphorus-main-group element bond. As part of this research effort we have studied the metathetical reactions of transition-metal diphenylphosphide anions with main-group metal halogen compounds as well as attempted small molecule elimination reactions between transition-metal diphenylphosphine derivatives and organoaluminum compounds. Both types of reactions might be expected to give the desired compounds with aluminum-phosphorus bonds,² but novel observations were made instead.

In this paper, the synthesis and characterization of the precursor compounds $\text{M}(\text{CO})_5\text{PPh}_2\text{K}\cdot n(\text{ether})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) from $\text{M}(\text{CO})_5\text{PPh}_2\text{H}$ and KH are described. These reactions are compared to the related deprotonation re-

actions using $n\text{-BuLi}$.³ Then, the reactions of the transition-metal phosphorus compounds with organoaluminum compounds are discussed. In most cases the synthetic reactions did not lead to a final product with a transition metal-phosphorus-aluminum atom sequence. For example, the reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ in THF solution leads to the formation in high yield of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$, an example of THF cleavage. This compound which incorporates a new amphoteric ligand has been fully characterized by analysis, spectroscopic methods, and an X-ray structural study. The reactions of transition-metal phosphorus compounds with other organoaluminum compounds are also considered.

Experimental Section

All compounds were handled in an inert atmosphere employing vacuum line or drybox (99.998% Argon) techniques. Ether solvents were dried, stored, and vacuum distilled from sodium/benzophenone ketyl. Hydrocarbon solvents were treated with sulfuric acid, dried, and stored over sodium and vacuum distilled from P_2O_5 immediately prior to their use. Purification of AlBr_3 and AlMe_3 consisted of sublimation at 60°C or room temperature distillation, respectively, both under high vacuum. The reagent $n\text{-BuLi}$ in hexane was standardized by using solid diphenylacetic acid.⁴ Gaseous HCl and HBr were fractionated through a -78°C into a -196°C trap. Potassium and sodium hydride in paraffin oil (Alfa/Ventron) were washed repeatedly with hexane. The compounds Ph_2PH ,⁵ $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$,⁶ $\text{Mo}(\text{CO})_5\text{PPh}_2\text{H}$,⁶ W -

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(2) Mole, T.; Jeffery, E. A. "Organoaluminum Compounds"; Elsevier: New York, 1972; Chapter 5.

(3) Treichel, P. M.; Douglas, W. M.; Dean, W. K. *Inorg. Chem.* **1972**, *11*, 1615.

(4) Kofron, W. K.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(CO)₅PPh₂H,⁶ KPPH₂·2(dioxane),⁷ AlMe₂H,⁸ and Al(CH₂SiMe₃)₂Br⁹ were prepared and purified by literature procedures. An exchange reaction between 1 mol of AlBr₃ and 2 mol of the trialkylaluminum compound was used to prepare AlMe₂Br and AlEt₂Br. They were judged pure by comparison of their boiling point, vapor pressure, and/or density with literature values.^{10,11} The liquids AlMe₂Br (1.37 g/mL), AlEt₂Br (1.29 g/mL¹¹), and Al(CH₂SiMe₃)₂Br (1.06 g/mL⁹) were measured by volume rather than by weight by using graduated gas-tight syringes in the drybox.

Spectra. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer and were referenced to polystyrene. Spectra of gases were obtained by means of a 10-cm gas cell equipped with KBr plates. Spectra of solids were observed as Nujol mulls using CsI plates. Nujol mulls of the transition-metal phosphido anions retained their bright orange-yellow color and gave reproducible spectra for about 0.5 h. Attempts were made to obtain solution spectra of these complexes. THF solutions were prepared in a drybox and injected into sealed KBr solution cells. Before the spectrum could be scanned completely, decomposition, as evidenced by a greenish color, occurred. In one run of the spectrum of Cr(CO)₅PPh₂K·2(dioxane), the decomposition was successfully monitored over a period of 15 min, allowing us to deduce the spectrum of the complex.

¹H NMR spectra were recorded at 60, 90, and 100 MHz using Varian Model T-60, Varian Model EM-390, and Jeolco Model MH-100 spectrometers, respectively, and are reported in δ units, downfield from tetramethylsilane. The ³¹P NMR spectra were recorded at 40.5 MHz by means of a Varian Model XL-100 spectrometer or at 109.16 MHz by means of a JEOL FX-270 spectrometer and were referenced to 85% H₃PO₄. Proton-decoupled spectra are reported in δ units (+ downfield from H₃PO₄). All NMR tubes were sealed under vacuum.

Molecular Weight Measurements. Cryoscopic molecular weights were determined in benzene solution by using an instrument similar to the one described by Shriver.¹² Molecular weights are reported in terms of calculated molality, observed molecular weight, and association.

Analyses. Analyses of C, H, and P were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Bromine was determined by a standard gravimetric procedure. The following procedure was used for the determination of hydrolyzable alkanes. Accurately weighed samples were hydrolyzed by using water or dilute nitric acid. Methane (-196 °C) and ethane (-78 °C) were measured by using a Toepler pump and gas burette assembly after the hydrolyzed samples were cooled to the required temperature. Tetramethylsilane was separated from the hydrolyzed sample by fractionation through two dry ice/acetone (-78 °C) and a liquid-nitrogen (-196 °C) traps and measured by using a standardized volume of the vacuum line. Gases were identified by vapor pressure measurements of their condensed phases and by infrared spectra.

Synthesis of M(CO)₅PPh₂K·n(Dioxane) (M = Cr, Mo, W). The compounds of general formula M(CO)₅PPh₂K·n(dioxane) were prepared from the reaction of a slight excess of M(CO)₅PPh₂H with KH in dioxane. The experimental procedure for these reactions was identical for all samples of M(CO)₅PPh₂H; therefore, only a typical synthesis of Cr(CO)₅PPh₂K·2(dioxane) will be described in detail. A two-neck flask containing 7.979 g (20.95 mmol) of Cr(CO)₅PPh₂H was equipped with a side arm dumper containing 0.830 g (20.6 mmol) of KH. The reaction vessel was evacuated, and 20 mL of dioxane was vacuum distilled onto the Cr(CO)₅PPh₂H. The KH was slowly added to the stirred pale yellow Cr(CO)₅PPh₂H solution. The KH reacted, as evidenced by vigorous bubbling and the formation of a bright orange-yellow

solution. After 1–2 h, a yellow precipitate formed. The mixture was stirred for about 24 h, until evolution of hydrogen (typically over 95%) had ceased. Hexane (20 mL) was vacuum distilled into the flask to completely precipitate the yellow solid. The dioxane/hexane solution was separated from the solid by filtration. Then the solid was dried at room temperature under high vacuum for 12 h. It is important not to heat the solid during the drying process as irreversible decomposition takes place (see melting points). The complex Cr(CO)₅PPh₂K·2(dioxane) (11.53 g) was isolated in 94% yield. In general, yields ranged 85–95% for M(CO)₅PPh₂K·n(dioxane). These bright orange-yellow compounds are insoluble in aliphatic and aromatic hydrocarbons, are very slightly soluble in diethyl ether and dioxane, and have good solubility in THF and DME but react with halogenated hydrocarbons.

Cr(CO)₅PPh₂K·2(dioxane): mp, irreversible decomposition begins at 45–50 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2074 (m), 1970 (m, sh), 1941 (vs), 1906 (s, sh), (THF) 2035 (m), 1927 (vs). Anal. Calcd: C, 50.67; H, 4.42; P, 5.21. Found: C, 50.06; H, 4.43; P, 5.42.

Mo(CO)₅PPh₂K·dioxane: mp, irreversible decomposition begins at 120 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2058 (vw), 1972 (m, sh), 1952 (s), 1865 (vs), 1823 (vs), 1780 (s). Anal. Calcd: C, 45.99; H, 3.31; P, 5.65. Found: C, 45.91; H, 3.72; P, 5.62.

W(CO)₅PPh₂K·2(dioxane): mp, irreversible decomposition begins at 55–60 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2059 (w), 1972 (m, sh), 1935 (vs), 1896 (m). Anal. Calcd: C, 41.45; H, 3.62; P, 4.78. Found: C, 41.73; H, 3.34; P, 4.74.

Reaction of M(CO)₅PPh₂H with KH in THF. The solvent THF was also a useful solvent for the deprotonation of M(CO)₅PPh₂H by KH. The experimental procedure was identical with that used with dioxane, and the evolution of H₂ was greater than 95%. However, the products usually came out of solution as viscous oils which eventually solidified upon removal of solvent under high vacuum for several hours. Products from these reactions were not characterized by analysis. The number of bound ether molecules were determined from reactions of the products with anhydrous HCl or HBr (vide infra).

Cr(CO)₅PPh₂K·THF: mp, irreversible decomposition begins at 55 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2046 (w), 1988 (m, sh), 1938 (vs), 1920 (vb, s); ³¹P NMR (THF, ppm from 85% H₃PO₄, δ) -21.4 (s).

Mo(CO)₅PPh₂K·2(THF): mp, irreversible decomposition begins at 125 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2038 (m), 1970 (m, sh), 1930 (vs, vb).

Reactions of M(CO)₅PPh₂H (M = Cr, W) with NaH. The reaction of M(CO)₅PPh₂H with NaH was much slower than the analogous KH reaction. At least 1 week was required for complete reaction at room temperature in dioxane. Moderate yields of sodium salts were obtained by refluxing a slight deficiency of NaH with a THF or dioxane solution of M(CO)₅PPh₂H for 6–8 h. Longer reflux times resulted in the formation of undesirable red products. These transition-metal phosphido anions were also characterized by their reaction with HBr (vide infra). However, due to the low solubility of the sodium complexes and NaH in these solvents, it was not possible to quantitatively separate these compounds.

Characterization of Deprotonated Complexes by Reaction with HCl or HBr. A weighed sample of the complex was placed in a reaction bulb with an NMR tube side arm. Deuterated toluene or benzene followed by a slight excess of HX were vacuum distilled into the reaction vessel. The insoluble, brightly colored M(CO)₅PPh₂M₁n(ether) (M₁ = Li, Na, K) completely reacted with HX in less than 8 h, producing a pale yellow or pale orange solution and a white precipitate. The solution was poured into the NMR tube side arm, a Me₄Si marker was added by vacuum distillation, then the tube was sealed, and the ¹H NMR spectrum was recorded by using a Jeolco Model MH 100 spectrometer. In all cases, the only signals observed were those expected for M(CO)₅PPh₂H, the ether, Me₄Si, and the residual protons from the deuterated solvent. Due to the presence of these residual protons from the deuterated solvent, estimates of the number of ether molecules had to be obtained from the integration of the relatively weak P–H signal with respect to the ether signals. The above procedure was used to check the integrity of samples stored in the drybox for prolonged periods. Some samples were observed to be stable to storage for over a year.

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In a similar manner, deprotonated complexes were reacted with HCl or HBr in ether solvents. The infrared spectra of the resulting solutions showed only the simple spectra of $M(\text{CO})_5\text{PPh}_2\text{H}$.

Reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ with *n*-BuLi in Hexane. A solution of 1.019 g (2.694 mmol) of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ in 25 mL of hexane was prepared in a two-neck flask on the vacuum line. Standardized *n*-BuLi solution (1.10 mL, 2.39 M, 2.63 mmol) was slowly added to the stirred $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ by means of an addition tube. The pale yellow solution clarified and a mustard-yellow solid formed initially. Within a few minutes, a small amount of a brown solid also formed as a crust over the yellow solid. The precipitates were washed with hexane several times, and in the drybox the majority of the brown materials were manually removed from the mustard-yellow powder (0.890 g): mp, slow decomposition begins at 40 °C; IR (Nujol mull, cm^{-1}) ν_{CO} 2071 (w), 1978 (m, sh), 1919 (vs), 1873 (s, sh) (occasionally a very weak band at 1658 cm^{-1} was also observed). The mustard-yellow powder, presumably $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$, is extremely unstable, slowly decomposing to a brown solid in drybox atmospheres in which aluminum alkyls are stable. The compound is insoluble in hydrocarbon solvents and soluble in ethers and reacts with halogenated hydrocarbons. The preparative reaction conditions were varied in order to avoid the formation of the brown solids. Slow addition of the *n*-BuLi solution gave the least amounts of brown solids. Lowering the reaction temperature and varying the rate of stirring or the reagent concentrations either had no effect or increased the amount of brown materials. Employing an excess of *n*-BuLi solution gave proportionately larger quantities of the brown solid. Addition of *n*-BuLi by syringe rather than from an addition tube also increased the amount of brown materials.

Reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and $\text{KPPh}_2\cdot 2(\text{dioxane})$ in Diethyl Ether. Diethyl ether (7 mL) was distilled onto 0.195 g (0.515 mmol) of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and 0.202 g (0.504 mmol) of $\text{KPPh}_2\cdot 2(\text{dioxane})$. The pale yellow $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ solution immediately turned to bright yellow as the orange $\text{KPPh}_2\cdot 2(\text{dioxane})$ crystals gradually disappeared. The solution became cloudy, and after being stirred overnight, a fine yellow precipitate and a yellow solution were present. (Both $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}$ and KPPh_2 are essentially insoluble in Et_2O .) Et_2O was removed by vacuum distillation, and the solid was quickly washed with 5 mL of hexane. A ^1H NMR spectrum of the sticky yellow hexane-soluble residue showed that $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and Ph_2PH were present in a ratio of 4/3.

Reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and KPPh_2 in THF. In a separate reaction, 0.328 g (0.867 mmol) of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and 0.914 g (0.866 mmol) of KPPh_2 (prepared in Et_2O) were combined in 10 mL of THF. All components of the reaction mixture were soluble. An aliquot of the reaction mixture was used for the ^{31}P NMR spectrum: two resonances (δ), -21.73 (s) and -40.29 (s). For comparison, THF solutions of the various components had ^{31}P NMR resonances at δ -21.38 ($\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}$), -8.32 (KPPh_2), and 31.21 ($\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$). The literature value¹³ for PPh_2H is -41.1 ppm.

A ^1H NMR spectrum of a THF- d_6 solution of a reaction mixture prepared from 0.170 g (0.449 mmol) of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$, 0.101 g (0.451 mmol) of KPPh_2 , and 5 mL of THF exhibited one pair of lines for the PH protons at δ 5.12 ($J = 218$ Hz). For comparison, THF solutions of PPh_2H and $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ exhibited PH lines at δ 5.14 (d, $J = 218$ Hz) and 6.53 (d, $J = 356$ Hz), respectively.

Synthesis of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$. The complex $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ was prepared by the reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with AlBr_3 in THF. The solvent THF (20 mL) was distilled into a two-neck flask containing 2.54 g (4.27 mmol) of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ and equipped with an addition tube containing 1.14 g (4.27 mmol) of AlBr_3 . The AlBr_3 was added to the stirred suspension, and immediate reaction occurred producing a white precipitate and an orange solution. The reaction mixture was stirred for 18 h, and then THF was removed on the vacuum line, leaving a very fluffy yellow solid. The reaction mixture was extracted several times with toluene (15 mL) to leave an insoluble white precipitate which was identified as KBr by qualitative tests for halogen and potassium. Its

weight (0.506 g) corresponded to a 98.8% yield. The removal of the toluene from the solution produced a very sticky, dark yellow glass. Washing once with 10 mL of hexane followed by fast removal of solvent gave 2.56 g (94%) of the compound identified as $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$, a fluffy, glassy brown-yellow solid; mp, 55–63 °C glass forms, 68–70 °C glass melts with bubbling. Anal. Calcd: C, 39.65; H, 2.85; Br, 25.12. Found: C, 40.52; H, 3.41; Br, 24.69. Analysis for bromine was performed on a sample hydrolyzed by an acetone/THF/water mixture. Normal hydrolysis with dilute nitric acid gave a green solution, presumably containing Cr^{3+} . Addition of 5% AgNO_3 solution gave a clear solution and a black precipitate: ^1H NMR (toluene- d_8 , δ) 7.51 (m, Ph), 7.24 (m, Ph), 3.18 (m, OCH_2), 1.58 (m, b, other CH_2) (the signal due to the residual methyl protons in toluene- d_8 at δ 2.31 was strong, possibly overlapping with the expected PCH_2 signal); ^{31}P NMR (toluene- d_8 , ppm from 85% H_3PO_4 , δ) +72.6 (s); IR (Nujol mull, cm^{-1}) 2071 (m), 1975 (m), 1938 (vs); cryoscopic molecular weight, formula weight $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ 636.1; molality (obsd mol wt, association), 0.0699 (929, 1.46), 0.0566 (992, 1.56), 0.0350 (770, 1.21); solubility, very slightly soluble in hexane, moderately soluble in toluene or diethyl ether, and soluble in THF. This compound exhibited very unusual behavior in hexane. Though it has low solubility in this solvent, $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ swells in hexane. Fast removal of hexane produced a fluffy material that fills a large percent of the flask volume. Slow removal of hexane yielded a tenacious glass which was impossible to quantitatively remove from glassware using spatulas. The fluffy material slowly reverts to the tenacious glass with storage. This process can be slowed considerably by grinding the fluffy material to a fine powder. The fluffy material can be regenerated from the glass by adding hexane and then quickly removing it by vacuum distillation.

Synthesis of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ (R = Me, Et, CH_2SiMe_3). The series of compounds $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ were prepared from the reaction of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ with dialkylaluminum bromides in THF. A specially constructed reaction vessel was used to minimize contact of the reaction mixtures with high vacuum greases. It consisted of a 100-mL round-bottom flask with a built-in addition tube which was separated from the flask by a Teflon valve, a constricted side arm with an inner 14/35 joint, and an arm which allowed attachment to a vacuum system or to other apparatuses through a Teflon valve. The same procedure was followed for the preparations of these three compounds. In the drybox, a hexane or toluene solution of the dialkylaluminum bromide (3–8 mmol in 2–5 mL of solvent) was prepared in the built-in addition tube. A slight excess of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ was added to the flask through the 14/35 joint of the constricted side arm. The flask was evacuated, and 40–50 mL of THF was vacuum distilled into the flask. The constriction was washed of any $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$, and the flask was cooled to -196 °C and sealed at the constriction. The dialkylaluminum bromide solution was added to the stirred $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ suspension at -78 °C. Immediate darkening of the reaction mixture was observed. The reaction mixture was slowly warmed to room temperature by allowing the dry ice in the -78 °C bath (contained in a large beaker) to evaporate (2–3 h). At this point, a brown-yellow solution and a white precipitate were present. Stirring was continued at room temperature for 12–15 h. The THF was removed by vacuum distillation, and the reaction mixture was extracted twice with toluene (50 mL). The insoluble fraction, a light yellow solid, was identified as a mixture of KBr and unreacted phosphide complex by qualitative tests and infrared spectra. (In reactions where 1:1 molar ratios of reagents were used (R = Et, CH_2SiMe_3), a white solid was obtained, corresponding to a 95% yield of KBr.) After removal of toluene, the resultant glass (R = Me) or solid (R = Et or CH_2SiMe_3) was purified as described in the following paragraphs.

The compound $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlMe}_2]$ was obtained as a brown-yellow glassy solid in 83.9% yield from the reaction of 2.15 g (3.62 mmol) of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$ and 0.34 mL (0.47 g, 3.4 mmol) of AlMe_2Br in THF. The product was purified by washing several times with hexane. $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlMe}_2]$ is soluble in ethers and aromatic hydrocarbons and is slightly soluble in hexane. It swells in hexane and undergoes the same reversible glass to fluffy solid behavior as the bromide analogue:

(13) Moedritzer, K.; Maier, L.; Groenweghe, L. C. D. *J. Chem. Eng. Data* 1962, 7, 307.

mp, glass forms at 48–50 °C, 70 °C glass melts with bubbling; ¹H NMR (toluene-*d*₆, δ) 7.74 (m, Ph), 7.44 (m, Ph), 3.84 (m, b, OCH₂), 2.31 (m, PCH₂), 1.51 (m, b, other CH₂), -0.64 (s, AlCH₃), integration OCH₂/AlCH₃ = 1/3; IR (Nujol mull, cm⁻¹) ν_{CO} 2070 (m), 1973 (m), 1929 (vs). Anal. Calcd: C, 54.55; H, 4.77; P, 6.12; MeH, 2.00 mol/mol. Found: C, 56.46; H, 4.46; P, 5.95; MeH, 1.98 mol/mol.

The reaction of 3.78 g (6.36 mmol) of Cr(CO)₅PPh₂K·2(dioxane) and 0.81 mL (1.0 g, 6.3 mmol) of AlEt₂Br in THF produced Cr(CO)₅[PPH₂(CH₂)₄OAlEt₂] as a tan solid in 55.9% yield. The product was purified by washing with hexane at -20 °C. It is slightly soluble in hexane and soluble in aromatic hydrocarbons and ethers: mp 159–160 °C with some decomposition; ¹H NMR (toluene-*d*₆, δ) 7.74 (m, Ph), 7.48 (m, Ph), 3.68 (m, OCH₂), 2.47 (m, PCH₂), 1.62 (m, b, other CH₂), 1.26 (t, *J* = 8 Hz, CH₃), 0.10 (q, *J* = 8 Hz, AlCH₂), integration OCH₂/AlCH₂ = 1/2; ³¹P NMR (toluene-*d*₆, ppm from 85% H₃PO₄, δ) +81.1 (s); IR (Nujol mull, cm⁻¹) ν_{CO} 2067 (m), 1972 (m, sh), 1918 (vs, b); cryoscopic molecular weight, formula weight Cr(CO)₅[PPH₂(CH₂)₄OAlEt₂] 536.4; molality (obsd mol wt, association), 0.0638 (1050, 1.95), 0.0352 (853, 1.59). Anal. Calcd: C, 55.96; H, 5.26; P, 5.77; EtH, 2.00 mol/mol. Found: C, 50.71; H, 4.46; P, 5.97; EtH, 1.97 mol/mol.

The compound Cr(CO)₅[PPH₂(CH₂)₄OAl(CH₂SiMe₃)₂] was obtained in 72.3% yield from the reaction of 3.25 g (5.47 mmol) of Cr(CO)₅PPh₂K·2(dioxane) and 1.34 mL (1.45 g, 5.14 mmol) of Al(CH₂SiMe₃)₂Br in THF. The compound was obtained as a tan solid and was purified by crystallization from hexane or by washing with hexane at -20 °C. It has moderate solubility in hexane and good solubility in aromatic hydrocarbons and ethers: mp 100–101 °C; ¹H NMR (toluene-*d*₆, δ) 7.69 (m, Ph), 7.35 (m, Ph), 3.89 (t, *J* = 7 Hz, OCH₂), 2.54 (m, b, PCH₂), 1.95 (m, CH₂), 1.53 (m, CH₂), 0.41 (s, AlCH₂), 0.29 (s, SiCH₃), 0.12 (s, SiCH₃), -0.69 (s, AlCH₂), integration OCH₂/all aluminum CH₂SiMe₃ = 1/11; IR (Nujol mull, cm⁻¹) ν_{CO} 2070 (m), 1973 (m, sh), 1924 (vs); cryoscopic molecular weight, formula weight Cr(CO)₅[PPH₂(CH₂)₄OAl(CH₂SiMe₃)₂] 650.8; molality (obsd mol wt, association), 0.0682 (794, 1.22), 0.0373 (683, 1.05), 0.0307 (657, 1.01). Anal. Calcd: C, 53.52; H, 6.19; P, 4.76; Me₂Si, 2.00 mol/mol. Found: C, 50.40; H, 5.77; P, 4.78; Me₂Si, 1.98 mol/mol. Crystals suitable for X-ray diffraction were obtained by slow evaporation of solvent from a hexane solution by using a greaseless recrystallization apparatus under the most strict anaerobic conditions: mp 102.5–103 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2070 (m), 1972 (m, sh), 1924 (vs).

Collection of the X-ray Diffraction Data. A number of crystals were sealed into thin-walled capillaries in an argon-filled drybox and were examined by X-ray diffraction procedures. All were thin and of rather poor quality, with a "greasy" appearance, and all gave diffraction patterns with very few discernible data beyond 2θ = 35° (Mo Kα). The best such crystal (dimensions 0.3 × 0.3 × 0.07 mm) was selected for data collection. This was mounted on a Syntex P2₁ automated four-circle diffractometer. The crystal was centered accurately. Unit cell parameters and the orientation matrix were determined; data collection was carried out by using a coupled 2θ(counter)-θ(crystal) scan. The method has been described previously;¹⁴ details appear in Table I. Data were corrected for absorption and for Lorentz and polarization factors and were reduced to |F_o| values. Any reflection with *I*(net) < 0 was assigned a value of |F_o| = 0.

Solution and Refinement of the Structure. All calculations were performed by using our in-house Syntex XTL interactive structure determination system¹⁵ as modified at SUNY—Buffalo. The analytical form of the scattering factors of the appropriate neutral atoms were corrected for both the real (Δ*f*) and the imaginary (iΔ*f*') components of anomalous dispersion.¹⁶ The function minimized during the least-squares refinement process was Σ*w*(|F_o| - |F_c|)², where the weights were obtained from counting statistics modified by an "ignorance factor" (*p*) of 0.02.

The position of the chromium atom was quickly and unequivocally determined from an unsharpened three-dimensional

Table I. Data for the X-ray Diffraction Study of [(OC)₅CrPPh₂(CH₂)₄OAl(CH₂SiMe₃)₂]

(A) Crystal Parameters at 24 °C ^a			
cryst system	monoclinic	<i>V</i> , Å ³	3654
space group	P2 ₁ / <i>n</i>	<i>Z</i>	2
<i>a</i> , Å	11.939 (3)	mol wt	1301.51
<i>b</i> , Å	14.940 (3)	ρ(calcd), g cm ⁻³	1.18
<i>c</i> , Å	21.014 (5)	μ, cm ⁻¹	4.9
β, deg	102.88 (2)		
(B) Measurement of Intensity Data			
diffractometer	Syntex P2 ₁		
radiation	Mo Kα (λ̄ = 0.710 73 Å)		
monochromator	highly oriented graphite (equatorial mode)		
reflectns measd	+ <i>h</i> , + <i>k</i> , ± <i>l</i> for 4.0 < 2θ < 35.0°		
scan type	coupled 2θ (counter)-θ (crystal)		
scan speed	3.0 deg min ⁻¹		
scan width	symmetrical, [2.0 + Δ(α ₁ - α ₂)]°		
bkgd	at beginning and end of scan, each for 0.5 scan time		
reflectns collected	2491 total, yielding 2327 independent data; 1515 with F _o > 3.0σ(F _o)		
stds	3 collected every 97 data; no significant variations		

^a Based on the setting angles of the unresolved Mo Kα components of 24 reflections of the forms {1,1,1̄2}, {1,1,0,1}, {6 2 3̄}, {5 4 2̄}, {4,3,1̄0}, and {4 6 6̄}.

Patterson synthesis. All other non-hydrogen atoms were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. All hydrogen atoms (other than those of the methyl groups, which are indeterminate) were included in calculated positions based upon *d*(C-H) = 0.95 Å,¹⁷ *B* = 6.0 Å², and the appropriate idealized trigonal or tetrahedral geometry. Full-matrix least-squares refinement of positional parameters for all non-hydrogen atoms, anisotropic thermal parameters for the heavier atoms (Cr, P, Si, Al) and isotropic thermal parameters for the lighter atoms (O, C) led to final convergence ((Δ/σ)_{max} < 0.1) with *R_F* = 9.2%, *R_{wF}* = 8.2%, and GOF = 1.82¹⁸ for 186 variables refined against those 1515 reflections with |F_o| > 3σ(|F_o|) [*R_F* = 7.4% and *R_{wF}* = 7.6% for those 1226 reflections with |F_o| > 5σ(|F_o|)].¹⁹

A final difference Fourier map showed no significant features (highest peak 0.54 e Å⁻³); the structure is thus complete. Final positional parameters appear in Table II. Calculated hydrogen atom positions (Table I-S) and anisotropic thermal parameters (Table II-S) have been deposited as supplementary material along with a list of observed and calculated structure factor amplitudes.

Reactions of Mo(CO)₅PPh₂K·Dioxane and W(CO)₅PPh₂K·2(Dioxane) with AlBr₃ or AlEt₂Br in THF. The reactions of the molybdenum and tungsten carbonyl phosphide anions with AlBr₃ or AlEt₂Br were studied by using the same procedure as described for Cr(CO)₅PPh₂K·2(dioxane). These reactions were complicated by several factors. The solubility of both the metal carbonyl phosphide anions and the resultant products is lower than for the chromium derivatives. These properties lead to slower reactions and necessitated more numerous extractions for product isolation. Competing reactions, as evidenced by the presence of brown and black materials, were observed. Characterization data for the products of these reactions are summarized below. Yields are given for reaction on a 2-mmol scale and assuming the product is M(CO)₅[PPH₂(CH₂)₄OAlR₂].

Mo(CO)₅PPh₂K·dioxane + AlBr₃: brick-red solid (50%); mp decomposition begins at 140 °C; IR (Nujol mull, cm⁻¹) ν_{CO} 2080 (vw), 2041 (m), 1992 (m), 1976 (m), 1940 (vs), 1891 (m).

Mo(CO)₅PPh₂K·dioxane + AlEt₂Br: brown oil; IR (Nujol mull, cm⁻¹) ν_{CO} 2046 (m), 1980 (m), 1920 (vs, b); some carbon monoxide was generated by this reaction.

(14) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, 16, 265.

(15) "Syntex XTL Operations Manual", 2nd ed., Syntex Analytical Instruments (now Nicolet XRD): Cupertino, CA, 1976.

(16) "International Tables for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

(17) Churchill, M. R. *Inorg. Chem.* 1973, 12, 1213.

(18) *R_F* = [Σ|F_o| - |F_c|]/Σ|F_o| × 100 (%); *R_{wF}* = [Σ*w*(|F_o| - |F_c|)²]/Σ*w*|F_o|² × 100 (%); GOF = [Σ*w*(|F_o| - |F_c|)²/(*N* - *NV*)]^{1/2}.

(19) The rather high discrepancy indices are a reflection of the poor diffracting power of the best available crystal.

Table II. Positional Parameters for Non-Hydrogen Atoms in $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$

atom	x	y	z	B(ISO)
Cr	0.61884 (25)	0.46049 (21)	0.38569 (15)	
P	0.73965 (42)	0.33172 (32)	0.40235 (24)	
Si(1)	0.22453 (56)	0.14670 (46)	0.55758 (32)	
Si(2)	0.24810 (53)	0.10201 (39)	0.32288 (31)	
Al	0.39439 (46)	0.04483 (40)	0.47512 (27)	
O(1)	0.8238 (12)	0.57939 (87)	0.38537 (60)	5.80 (35)
O(2)	0.6558 (11)	0.47911 (85)	0.53142 (68)	6.10 (35)
O(3)	0.5798 (12)	0.43468 (91)	0.23993 (74)	7.23 (40)
O(4)	0.4007 (12)	0.35636 (91)	0.38522 (63)	6.34 (37)
O(5)	0.4810 (13)	0.6285 (11)	0.36956 (70)	8.06 (43)
O(6)	0.53669 (88)	0.06609 (68)	0.52833 (50)	3.52 (28)
C(1)	0.7445 (17)	0.5316 (14)	0.38437 (88)	5.14 (50)
C(2)	0.6405 (15)	0.4726 (12)	0.4747 (10)	4.40 (48)
C(3)	0.5960 (16)	0.4473 (14)	0.2954 (11)	5.78 (53)
C(4)	0.4850 (17)	0.3956 (13)	0.38837 (91)	4.73 (51)
C(5)	0.5361 (20)	0.5611 (16)	0.3761 (11)	7.37 (65)
C(6)	0.8835 (14)	0.3578 (11)	0.39231 (83)	2.86 (41)
C(7)	0.9637 (16)	0.3911 (12)	0.44282 (87)	4.11 (46)
C(8)	1.0742 (16)	0.4225 (13)	0.4322 (10)	5.68 (55)
C(9)	1.0921 (16)	0.4162 (12)	0.3695 (11)	5.34 (53)
C(10)	1.0123 (18)	0.3823 (13)	0.3194 (10)	5.37 (52)
C(11)	0.9071 (15)	0.3536 (11)	0.33122 (87)	3.99 (45)
C(12)	0.7076 (16)	0.2334 (12)	0.35049 (85)	3.79 (45)
C(13)	0.6035 (18)	0.2238 (13)	0.3067 (10)	5.59 (52)
C(14)	0.5804 (18)	0.1461 (15)	0.2653 (10)	6.38 (57)
C(15)	0.6626 (20)	0.0842 (14)	0.2727 (10)	6.30 (57)
C(16)	0.7631 (20)	0.0872 (14)	0.3179 (11)	6.87 (59)
C(17)	0.7853 (16)	0.1647 (15)	0.35641 (93)	5.51 (53)
C(18)	0.7649 (14)	0.2805 (11)	0.48319 (79)	3.51 (43)
C(19)	0.6579 (15)	0.2342 (12)	0.49667 (84)	4.01 (45)
C(20)	0.6816 (14)	0.1846 (11)	0.56209 (79)	3.40 (43)
C(21)	0.5743 (16)	0.1384 (12)	0.57377 (85)	4.34 (47)
C(22)	0.2736 (15)	0.0438 (13)	0.52391 (85)	4.84 (46)
C(23)	0.3021 (17)	0.1649 (13)	0.6474 (10)	6.20 (56)
C(24)	0.0660 (21)	0.1446 (16)	0.5535 (12)	9.49 (72)
C(25)	0.2546 (17)	0.2505 (14)	0.5102 (10)	7.05 (61)
C(26)	0.3742 (14)	0.1057 (12)	0.39165 (84)	3.98 (44)
C(27)	0.2482 (20)	0.2030 (15)	0.2642 (11)	8.20 (65)
C(28)	0.2464 (19)	-0.0049 (15)	0.2760 (11)	8.26 (68)
C(29)	0.1049 (19)	0.1099 (15)	0.3500 (11)	8.25 (67)

$W(CO)_5PPh_2K \cdot 2(\text{dioxane}) + AlBr_3$: red solid (73%); mp, glass forms at 50 °C, melts to a bubbly liquid at 85 °C; IR (Nujol mull, cm^{-1}) ν_{CO} 2078 (m), 2000 (m), 1968 (m), 1934 (vs).

$W(CO)_5PPh_2K \cdot 2(\text{dioxane}) + AlEt_2Br$: yellow solid (25%, recrystallized from Et_2O); mp 110–115 °C; 1H NMR (toluene- d_6 , δ) 7.52 (q, $J = 8$ Hz, Ph), 7.85 (m, Ph), 7.45 (m, Ph), 3.80 (m, OCH_2), 1.18 (m, other CH_2), 1.14 (t, $J = 7$ Hz, $AlCH_2CH_3$), 0.01 (q with further splitting, $J = 7$ Hz, $AlCH_2$). The compound had a low solubility in toluene. The spectral data were observed for a saturated toluene- d_6 solution, but the strongest absorptions were those of the residual protons in the solvent: IR (Nujol mull, cm^{-1}) ν_{CO} 2060 (m), 2035 (w), 1985 (m), 1910 (vs, vb), 1823 (m, sh).

Reactions of $Cr(CO)_5PPh_2K \cdot 2(\text{Dioxane})$ with Dialkylaluminum Bromides in Diethyl Ether and Dimethoxyethane. All of the following reactions were investigated using the same experimental procedure as previously described for THF.

Diethyl Ether + $[AlEt_2Br]$. The reaction of 0.35 mL (0.45 g, 2.7 mmol) $AlEt_2Br$ with 1.713 g (2.88 mmol) of $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$ in 70 mL of diethyl ether occurred slowly at room temperature. After 24 h a considerable quantity of an insoluble yellow solid, presumably $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$, remained. The ether was removed by vacuum distillation, and then the reaction mixture was extracted twice with 50 mL of toluene. The yellow toluene insoluble solid (1.04 g) inflamed in air. Removal of toluene from the solution and then washing the resultant sticky solid with 10 mL of hexane produced 0.740 g of a tan solid. All data suggest that the tan solid is $Cr(CO)_5[PPh_2AlEt_2 \cdot OEt_2]$: mp 80 °C to a bubbly liquid; 1H NMR (benzene, δ) 3.30 (s, OCH_2), 1.27 (t, $J = 8$ Hz, $AlCH_2CH_3$), 1.19 (m, OCH_2CH_3), 9.82 (q, $J = 8$ Hz, $AlCH_2$), integration $AlCH_2 = 1/1$; IR (Nujol mull, cm^{-1}) 2072 (m), 1964 (m, sh), 1934 (s). Anal. Calcd: EtH, 2.00 mol/mol. Found: EtH, 2.01 mol/mol.

Diethyl Ether + $[Al(CH_2SiMe_3)_2Br]$. The reaction of 1.00 g (1.68 mmol) of $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$ with 0.44 mL (0.41

g, 1.55 mmol) of $Al(CH_2SiMe_3)_2Br$ in 50 mL of diethyl ether appeared slower than the analogous reaction with $AlEt_2Br$. Workup of the reaction mixture was identical with the $AlEt_2Br$ reaction, and 0.45 g of a yellow, toluene insoluble, pyrophoric solid was isolated. The toluene-soluble material, presumably impure $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot OEt_2]$, was a viscous brown oil and was characterized by 1H NMR and IR spectroscopy: 1H NMR (benzene, δ) 3.77 (s, b, OCH_2), 1.43 (d, b, OCH_2CH_3), 0.46 (s, SiMe), 0.32 (s, SiMe), 0.16 (s, SiMe), -0.49 (s, $AlCH_2$), -0.57 (s, $AlCH_2$), -0.67 (s, $AlCH_2$), integration $OCH_2/AlCH_2 = 17/20$ (the lowest field absorptions of both SiMe and $AlCH_2$ protons was much more intense than the higher field absorptions); IR (Nujol mull, cm^{-1}) 2078 (m), 2000 (w), 1974 (m), 1934 (vs).

Dimethoxyethane. The reaction of AlR_2Br ($R = Et$, CH_2SiMe_3) with $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$ in DME was incomplete after 12–15 h, but 1H NMR spectral data for the products were consistent with the occurrence of ether cleavage. The apparent products were sticky brown oils: 1H NMR (benzene, δ) $R = Et$, 3.47 (s, b, OCH_3 and OCH_2), 2.29–0.98 (at least 13 lines, $AlCH_2CH_3$ and other alkyl absorptions), 0.31 (unsymmetrical sextet, $J = 8$ Hz, $AlCH_2$), $R = CH_2SiMe_3$, 3.52 (m, b, OCH_2 and OCH_3), 1.52 (s, b), 1.11 (m, b), 0.48 (m, b, $AlCH_2$), 0.19 (s, SiMe).

Reaction of $Cr(CO)_5PPh_2H$ with $AlMe_3$. A 0.0408-g (0.5570-mmol) sample of $AlMe_3$ was distilled into a trap on the vacuum line. The complex $Cr(CO)_5PPh_2H$ (0.107 g, 0.283 mmol) was placed into a bulb equipped with a NMR tube side arm. Cyclopentane (0.4 mL) followed by the preweighed $AlMe_3$ were vacuum distilled into the bulb. The resulting solution was poured into the NMR tube, and the tube (-196 °C) was sealed. The 1H NMR spectrum was recorded over a period of 20 days, and no change was observed. In a similar fashion, a toluene- d_6 solution of $Cr(CO)_5PPh_2H$ and $AlMe_3$ was prepared. After several days at room temperature no change in the 1H NMR spectrum was observed. This sample was heated at 140 °C for 14 h. The solution

Table III. Intramolecular Distances (Å) for $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$

(A) Distances from the Chromium Atom			
Cr-P	2.383 (6)	Cr-C(3)	1.87 (2)
Cr-C(1)	1.84 (2)	Cr-C(4)	1.88 (2)
Cr-C(2)	1.84 (2)	Cr-C(5)	1.79 (2)
(B) Distances within the Carbonyl Ligands			
C(1)-O(1)	1.18 (3)	C(4)-O(4)	1.15 (3)
C(2)-O(2)	1.17 (3)	C(5)-O(5)	1.19 (3)
C(3)-O(3)	1.15 (3)		
(C) Phosphorus-Carbon Distances			
P-C(6)	1.82 (2)	P-C(18)	1.83 (2)
P-C(12)	1.82 (2)		
(D) Distances within the $(CH_2)_4O$ Fragment			
C(18)-C(19)	1.53 (3)	C(20)-C(21)	1.52 (3)
C(19)-C(20)	1.53 (2)	C(21)-O(6)	1.45 (2)
(E) Aluminum-Carbon and Aluminum-Oxygen Distances			
Al-C(22)	1.95 (2)	Al-O(6)	1.84 (1)
Al-C(26)	1.94 (2)	Al-O(6')	1.86 (1)
(F) Silicon-Carbon Distances			
Si(1)-C(22)	1.84 (2)	Si(2)-C(26)	1.84 (2)
Si(1)-C(23)	1.93 (2)	Si(2)-C(27)	1.95 (2)
Si(1)-C(24)	1.88 (3)	Si(2)-C(28)	1.87 (2)
Si(1)-C(25)	1.92 (2)	Si(2)-C(29)	1.92 (2)
(G) Carbon-Carbon Distances within Phenyl Rings			
C(12)-C(13)	1.38 (3)	C(6)-C(7)	1.36 (3)
C(13)-C(14)	1.44 (3)	C(7)-C(8)	1.46 (3)
C(14)-C(15)	1.33 (3)	C(8)-C(9)	1.38 (4)
C(15)-C(16)	1.36 (3)	C(9)-C(10)	1.35 (3)
C(16)-C(17)	1.40 (3)	C(10)-C(11)	1.40 (3)
C(17)-C(12)	1.37 (3)	C(11)-C(6)	1.38 (3)

changed from pale yellow to dark yellow. Some changes were observed in the 1H NMR spectrum of this solution and are discussed in the Results and Discussion.

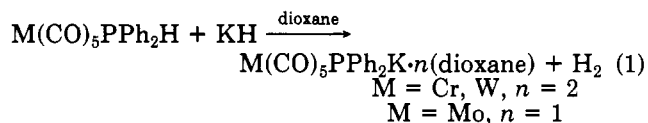
Reaction of $Cr(CO)_5PPh_2H$ with $AlMe_2H$. A 0.0512-g (0.882-mmol) sample of $AlMe_2H$, followed by 2 mL of hexane, was vacuum distilled into a tube equipped with a Teflon stopcock. Hexane (8 mL) was vacuum distilled into a two-neck flask which was fitted with the tube containing the alane solution and 0.3348 g (0.885 mmol) of $Cr(CO)_5PPh_2H$. The two solutions were mixed, and the reaction mixture changed from almost colorless to light yellow (0.5 h), to light brown (3 h), and finally to gray brown over a 24-h period. A small amount (0.14 mmol) of an unidentified noncondensable gas was evolved. The volatile components were removed by vacuum distillation, leaving a sticky light gray solid. Hydrolysis of the volatile components produced 0.426 mmol of a mixture of hydrogen and methane, corresponding to 0.142 mmol (16.1%) of $AlMe_2H$. The infrared spectrum of a Nujol mull of the solid in the 2300–1500 cm^{-1} region had bands at 2259 (w), 2224 (w), 2160 (w), 2078 (m), 1974 (m), 1931 (vs), 1900 (s, sh), 1523 (w) cm^{-1} .

Results and Discussion

The syntheses of transition-metal derivatives of amphoteric aluminum-phosphorus ligands have been investigated by starting with appropriate transition-metal phosphorus complexes and then by attempting to form the desired Al-P bond. Transition-metal phosphide anions would be expected to be ideal starting materials for metathetical reactions with aluminum halogen compounds. The deprotonation reactions of $M(CO)_5PPh_2H$ ($M = Cr, Mo, W$) with $n-BuLi$ in THF solution have been previously reported.³ However, potassium hydride has been described as a superior deprotonating reagent when compared with the more common reagents such as potassium metal,²⁰

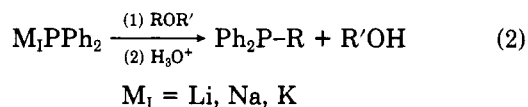
$n-BuLi$,^{20,21} and sodium or lithium hydride.²⁰ Furthermore, KH offers the preparative advantage that the extent of reaction can be easily monitored by measuring the evolved H_2 gas. Another important consideration is that KH does not react with the carbonyl ligands. Potassium hydride has been used to cleave metal-metal bonds in some transition-metal carbonyl dimers to form the related metal anions and to deprotonate metal hydride cluster complexes without altering the carbonyl ligands.²²

The reaction of $M(CO)_5PPh_2H$ ($M = Cr, Mo, W$) with KH in dioxane produces quantitative yields of hydrogen and high isolated yields (>85%) of solid complexes of the general formula $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ —see equation 1. The reaction conditions involve the use of a slight

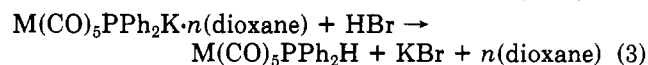


excess of $M(CO)_5PPh_2H$ which is easily removed from the product by extraction with hydrocarbon solvents. The low solubility of the potassium salts in ether solvents required pure KH and precluded the use of excess KH for preparative scale reactions. It is very difficult to separate KH from $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ unless very large quantities of solvent are employed. The compounds $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ are isolated as bright orange-yellow solids which do not melt but decompose on heating.

The presence of dioxane in $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ is easily deduced from the mass of the isolated product and confirmed by elemental analyses. These observations were cause for concern because uncomplexed alkali-metal phosphides cleave ethers²³ as described in eq 2. The



integrity of the bound dioxane molecules in $M(CO)_5PPh_2K \cdot n(\text{dioxane})$ is demonstrated by reacting these complexes with anhydrous HCl or HBr in deuterated benzene or toluene—see eq 3. In all cases a pale yellow



or pale orange solution and a colorless precipitate are formed. The 1H NMR spectra of these solutions indicate that ether cleavage does not occur and integration of the spectra give an estimate of the number of bound dioxane molecules. This experimental method has also been used to show that the phosphido complexes can be stored in a drybox for at least several months with no degradation of the dioxane. Similar experiments have demonstrated that only monosubstituted complexes are formed. Further confirmation of the nature of the complexes was obtained by infrared data. However, solution spectra have not been obtained without observing extensive decomposition. The compounds exhibit an extreme sensitivity to air and water in ether solutions. In contrast, infrared spectra of Nujol mulls can be obtained without decomposition of the sample. In the case of $Mo(CO)_5PPh_2K \cdot \text{dioxane}$ and several other complexes to be discussed later, bands suggestive of

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(22) (a) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* 1978, 154, 337. (b) Inkrott, K.; Shore, S. G. *J. Am. Chem. Soc.* 1978, 100, 3954.

(23) Kosolapoff, G. M.; Maier, L. "Organic Phosphorus Compounds"; Wiley-Interscience: New York, 1972; Vol. 1, Chapter 1.

(20) Brown, C. A. *J. Org. Chem.* 1974, 39, 3913 and references by the author cited therein.

Table IV. Selected Angles (in deg) within the $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$ Molecule

(A) Angles around the Chromium Atom			
C(1)-Cr-C(2)	91 (1)	C(2)-Cr-C(3)	180 (1)
C(1)-Cr-C(3)	89 (1)	C(2)-Cr-C(4)	87 (1)
C(1)-Cr-C(4)	175 (1)	C(2)-Cr-C(5)	89 (1)
C(1)-Cr-C(5)	87 (1)	C(2)-Cr-P	89 (1)
C(1)-Cr-P	90 (1)	C(3)-Cr-C(4)	93 (1)
C(3)-Cr-C(5)	91 (1)	C(3)-Cr-P	91 (1)
C(4)-Cr-C(5)	89 (1)	C(4)-Cr-P	94 (1)
		C(5)-Cr-P	176 (1)
(B) Angles around the Phosphorus Atom			
Cr-P-C(6)	111 (1)	Cr-P-C(18)	116 (1)
Cr-P-C(12)	121 (1)	C(6)-P-C(12)	100 (1)
C(6)-P-C(18)	104 (1)	C(12)-P-C(18)	101 (1)
(C) Angles in the $(CH_2)_4O$ Fragment			
P-C(18)-C(19)	113 (1)	C(19)-C(20)-C(21)	112 (1)
C(18)-C(19)-C(20)	113 (1)	C(20)-C(21)-O(6)	112 (1)
(D) Angles around Aluminum Atom			
O(6)-Al-O(6')	79.7 (5)	O(6)-Al-C(26)	112.3 (7)
O(6)-Al-C(22)	111.9 (7)	O(6')-Al-C(22)	113.6 (7)
O(6')-Al-C(26)	110.4 (7)	C(22)-Al-C(26)	121.5 (8)
(E) Angles around O(6)			
Al-O(6)-Al'	100.3 (6)	Al-O(6)-C(21)	129.7 (10)
Al'-O(6)-C(21)	128.1 (10)		
(F) Aluminum-Carbon-Silicon Angles			
Al-C(22)-Si(1)	122.2 (10)	Al-C(26)-Si(2)	127.6 (10)
(G) Angles around Silicon Atoms			
C(22)-Si(1)-C(23)	111.7 (9)	C(23)-Si(1)-C(25)	106.9 (9)
C(22)-Si(1)-C(24)	111.9 (10)	C(24)-Si(1)-C(25)	107.1 (10)
C(22)-Si(1)-C(25)	111.3 (9)	C(26)-Si(2)-C(27)	111.0 (9)
C(23)-Si(1)-C(24)	107.8 (10)	C(26)-Si(2)-C(28)	111.5 (9)
C(26)-Si(2)-C(29)	113.0 (9)	C(27)-Si(2)-C(28)	109.2 (10)
C(27)-Si(2)-C(29)	105.5 (10)	C(28)-Si(2)-C(29)	107.6 (10)

a disubstituted complex are observed. However, these additional bands appear to be due to solid-state effects because the carbonyl region of the infrared spectrum of the products of $Mo(CO)_5PPh_2$ -dioxane-HBr reaction shows only the bands of $Mo(CO)_5PPh_2H$.

The ease of the deprotonation of $M(CO)_5PPh_2H$ with alkali-metal hydrides depends on the nature of the solvent and metal hydride. KH is reactive in dioxane, THF, and diethyl ether but not in hydrocarbon solvents. The chromium and molybdenum complexes from the reactions in THF are formulated as $Cr(CO)_5PPh_2K \cdot THF$ and $Mo(CO)_5PPh_2K \cdot THF$ on the basis of the products from the HCl reaction. The reactions of $Cr(CO)_5PPh_2H$ and $W(CO)_5PPh_2H$ with NaH have also been studied. These reactions are much slower than those with KH, requiring about 1 week at room temperature before hydrogen evolution ceases. Refluxing these reaction mixtures increases reaction rates but with reflux periods longer than 6-8 h undesirable red products form. Product purification is exceedingly difficult because $M(CO)_5PPh_2Na \cdot n(ether)$, the red product, and NaH exhibit little if any solubility in most solvents, including THF. Reactions of the sodium complexes with HBr show that the bound ether molecules are not cleaved and confirm monosubstitution. The long reaction times and the possibility of impure products severely limit the practical applications of the NaH reactions. The reactions of LiH with $M(CO)_5PPh_2H$ are even slower than those of NaH. In ether solvents, $Cr(CO)_5PPh_2Li$ is best prepared by a previously published route.³ The reaction of $LiBEt_3H$ or lithium metal with $Cr(CO)_5PPh_2H$ was incomplete. The use of $LiAlH_4$ results in destruction of the transition-metal complex.

Attempts to prepare THF-free $Cr(CO)_5PPh_2Li$ have met with limited success. It is not possible to completely remove THF from a solution of $Cr(CO)_5PPh_2Li$ (prepared³ from $n-BuLi$ and $Cr(CO)_5PPh_2H$) by high vacuum distillation, and heating the resultant glassy yellow material to 40-50 °C leads to decomposition. Consequently, the deprotonation of $Cr(CO)_5PPh_2H$ with $n-BuLi$ in hydrocarbon solvents has been investigated. Addition of $n-BuLi$ solution to a hexane or toluene solution of $Cr(CO)_5PPh_2H$

initially leads to the precipitation of a yellow solid, presumably $Cr(CO)_5PPh_2Li$, but within a few minutes a brown precipitate also forms. If the reaction mixture is hydrolyzed, up to one-third of the initial quantity of $Cr(CO)_5PPh_2H$ cannot be isolated. A possible source of these brown compounds is attack by $n-BuLi$ on the carbon monoxide ligands. This may be indicated by the infrared spectrum of impure $Cr(CO)_5PPh_2Li$ which shows a weak band at 1658 cm^{-1} . This type of reaction is known for carbonyl compounds $M(CO)_5L$ ($L = CO, PR_3$) and produces carbene complexes.²⁴ The observation that the brown solids do not form until considerable $Cr(CO)_5PPh_2Li$ has precipitated suggests that the carbonyl groups of this species rather than those of $Cr(CO)_5PPh_2H$ are being attacked. The quantity of the brown precipitate can be minimized by *exceedingly slow* addition of $n-BuLi$ solution to an excess of $Cr(CO)_5PPh_2H$ at room temperature. At the end of the reaction, $Cr(CO)_5PPh_2Li$ is separated from unreacted $Cr(CO)_5PPh_2H$ by filtration. The complex $Cr(CO)_5PPh_2Li$ is extremely sensitive to oxygen and appears to be thermally unstable. This solid is much less stable than its THF solutions.

It is interesting to compare the infrared spectral properties of $M(CO)_5PPh_2K \cdot n(ether)$ with those of related compounds. The idea³ has been advanced that the carbonyl stretching frequencies of $M(CO)_5PPh_2Li$ ($M = Cr, Mo, W$) in THF solution are about 30 cm^{-1} lower than those of $M(CO)_5PPh_2H$ due to the partial delocalization of the charge on the phosphorus back to the metal and, in turn, to the π^* orbitals of the carbonyls. However, a comparison of the structural changes²⁵ within the series $Cr(CO)_5(XPh_3)$ ($X = P, As, Sb$) by X-ray structural studies are not compatible with the expectations for $Cr-X d_{\pi}-d_{\pi}$ bonding. The picture is further confused by the observation that there is no significant difference between the frequencies of $M(CO)_5P(C_6F_5)_2Li$ and $M(CO)_5P(C_6F_5)_2H$

(24) (a) Fischer, E. O. *Adv. Organomet. Chem.* 1976, 14, 1. (b) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* 1972, 72, 545.

(25) Carty, A. J.; Taylor, N. J.; Coleman, A. W.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* 1979, 639.

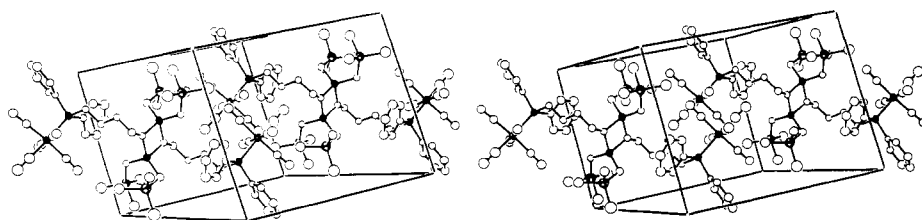


Figure 1. Packing of molecules in crystalline $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$.

(M = Cr, Mo) in chloroform solution.²⁶ The choice of chloroform as solvent for these spectra has been questioned³ because $M(CO)_5PPh_2Li$ reacts with halogenated solvents. The compounds described in the current investigation also react with halogenated solvents. However, our data suggest the decrease in carbonyl stretching frequencies previously observed may be related to the presence of THF as a medium effect rather than a measure of charge delocalization onto the transition metal. The complexes described herein show the large decrease in frequency ($<30\text{ cm}^{-1}$) in the high frequency band, as previously reported,³ but only when THF is tied up in the complex of present as the solvent. No regular pattern of decreased frequencies is observed for the other bands. It should be noted that delocalization of the negative charge on phosphorus need not occur solely to the transition metal. The significantly lower basicity of the uncomplexed diphenylphosphides M_1PPh_2 ($M_1 = Li, Na, K$) with respect to the alkyl- or hydrido-substituted phosphides has been attributed to the ability of the phenyl rings to delocalize the negative charge of the phosphorus.²³ Fluorination of the phenyl rings would be expected to increase their ability to delocalize this charge. It seems possible that the perfluorinated rings could withdraw charge from the phosphorus and reduce its nucleophilicity so that $M(CO)_5P(C_6F_5)_2Li$ may possess stability in halogenated solvents.

A preliminary examination of the basicity of $Cr(CO)_5PPh_2K$ relative to uncomplexed $KPPh_2$ toward the proton has provided both surprising and confusing results. When THF is the reaction solvent, ³¹P and ¹H NMR spectra of the solutions (all components are soluble) prepared by combining equimolar quantities of $Cr(CO)_5PPh_2H$ and $KPPh_2$ suggest that $KPPh_2$ is a significantly stronger base than $Cr(CO)_5PPh_2K$. The data including chemical shifts and coupling constants indicate that $Cr(CO)_5PPh_2H$ might have been deprotonated quantitatively. In contrast when diethyl ether is the reaction medium, the two anionic phosphides ($Cr(CO)_5PPh_2K$ and $KPPh_2$), which are both essentially insoluble in diethyl ether, exhibit similar basicities toward the proton. The soluble components of a reaction mixture produced by combining equimolar quantities of $KPPh_2 \cdot 2(\text{dioxane})$ and $Cr(CO)_5PPh_2H$ contain $Cr(CO)_5PPh_2H$ and PPh_2H in a 4:3 ratio. The reactions of solutions of $Fe(CO)_4PPh_2H$ with $LiPPh_2$ in THF³ and solutions of $Mo(CO)_5PH_3$ with $KPPh_2$ in dimethyl ether²⁷ quantitatively produce the deprotonated transition-metal complex and the free phosphine. It is difficult to ascribe these differences to any one factor as the alkali-metal cation, the transition metal, the substituents on phosphorus, the solvent, and the solubilities of all components could be involved in determining the position of the equilibrium. The solvent THF with its good solvating ability might also render an apparent leveling effect on the equilibrium.

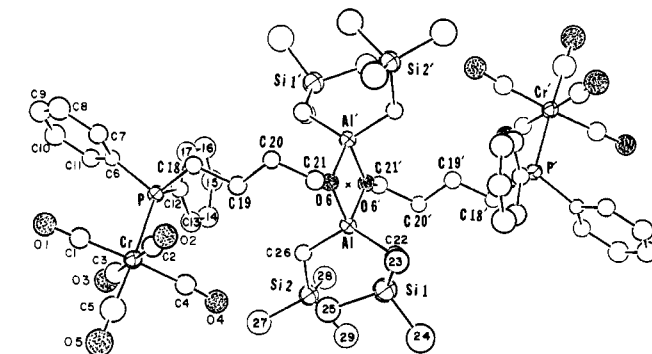
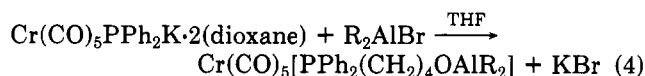


Figure 2. Labeling of atoms in the $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$ molecule. All oxygen atoms are stippled; the molecular and crystallographic center of symmetry is marked with a saltire (x) [ORTEP-II diagram; 30% probability ellipsoids].

The metathetical reactions of $Cr(CO)_5PPh_2K \cdot 2(\text{dioxane})$ with R_2AlBr ($R = Br, Me, Et, CH_2SiMe_3$) in THF at -78°C have yielded compounds of the general formula²⁸ $Cr(CO)_5[PPh_2(CH_2)_4OAlR_2]$ and KBr in 95–99% yields based on eq 4. The reaction chemistry and ¹H NMR spectra of



the aluminum products indicate that the $(CH_2)_4O$ unit is a cleaved THF molecule as opposed to a simple THF adduct. This conclusion has also been substantiated by an X-ray structural study of $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$. For example, attempts to displace the $(CH_2)_4O$ unit by Lewis bases such as NMe_3 and CH_3CN have resulted in the evolution of CO instead of loss of THF. Hydrolysis reactions have failed to produce compounds with P–H bonds as would be expected for compounds with P–Al bonds.⁹ The ¹H NMR spectra of all $Cr(CO)_5[PPh_2(CH_2)_4OAlR_2]$ compounds exhibit a broad absorption as an almost unbroken band in the range 2.5–1.0. The chemical shifts are consistent with the presence of oxygen and phosphorus-bound methylene groups and alkyl residues, but the broadness of the signals makes it difficult to propose a structure solely on the basis of ¹H NMR data. Further details of the ¹H NMR spectra of these compounds are discussed later. It is also significant that the chemical shifts of the lines in the ³¹P NMR spectra of the bromo and ethyl derivatives are similar to those reported for $Cr(CO)_5PPh_2R$ ($R =$ various alkyl groups²⁹).

The X-ray structural study of $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$ reveals that the crystal is composed of dimeric units which result, in part, from the cleavage of C–O bonds in tetrahydrofuran, thereby pro-

(26) Green, M.; Taunton-Rigby, A.; Stone, F. G. A. *J. Chem. Soc. A* 1969, 1875.

(27) Becker, G.; Ebsworth, E. A. V. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 186.

(28) Phosphorus and hydrolyzable alkyl or Br analyses agree well with the proposal formula of the products. Analyses for carbon and hydrogen involved brief exposure of the compound to air and therefore are only approximate.

(29) Grim, S. O.; Wheatland, D. A.; McFarlane, M. *J. Am. Chem. Soc.* 1967, 89, 5573.

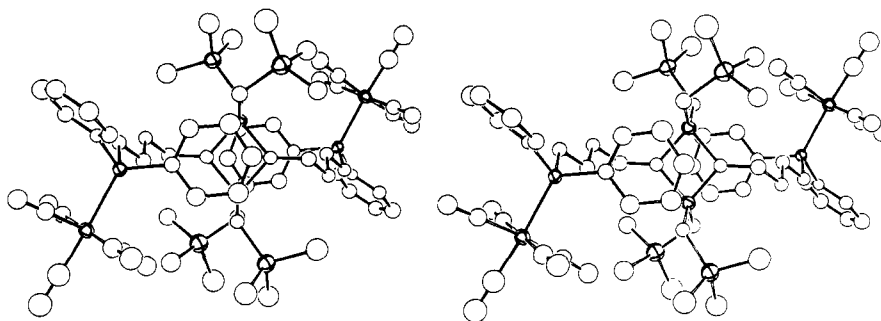


Figure 3. Stereoscopic view of the $[(OC)_5CrPPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]_2$ molecule.

ducing P-[(CH₂)₄-O]-Al bridges.

There are no abnormally short intermolecular contacts. Indeed, as can quickly be seen from Figure 1, the structure is rather open with an appreciable amount of unutilized space. Labeling of atoms in the structure is shown in Figure 2, while Figure 3 provides a stereoscopic view of the molecule. (Note that the dimeric molecule is centered about the inversion center at $1/2, 0, 1/2$. Atoms in the basic asymmetric unit are labeled normally. Those in the other half of the molecule are labeled with a prime, and their coordinates are related to those of the basic unit by the transformation $[x', y', z'] = [1 - x, -y, 1 - z]$.)

The $(OC)_5Cr$ -P portion of the structure has approximate C_{4v} symmetry and lends itself easily to comparison with the corresponding fragments in $(OC)_5Cr(PPh_3)^{30}$ and $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2NMe_3]$.¹ The four equatorial Cr-CO linkages in the present molecule range from 1.84 (2) through 1.88 (2) Å (average = 1.86 [2] Å),³¹ whereas the axial Cr-CO linkage is significantly shorter with Cr-C(5) = 1.79 (2) Å. Analogous values are 1.880 [11] Å vs. 1.845 (4) Å for $(OC)_5Cr(PPh_3)$ and 1.888 [6] Å vs. 1.847 (4) Å for $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2NMe_3]$. In each case this results from the greater competition for d_{π} electron density between the mutually trans pairs of equatorial carbonyl groups and the concomitant lower bond order in the Cr-CO(equatorial) vs. Cr-CO(axial) bonds.

The Cr-P bond length of 2.383 (6) Å in the present molecule is substantially shorter than that of 2.422 (1) Å in $(OC)_5Cr(PPh_3)$ and that of 2.482 (1) Å found in the $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2NMe_3]$ molecule. The P-Cr-CO angles are normal.

The angles about the tetrahedrally coordinated phosphorus atom show a systematic distortion from T_d toward C_{3v} coordination geometry, with expanded Cr-P-C angles (Cr-P-C(6)) = 111 (1)°, Cr-P-C(12) = 121 (1)°, and Cr-P-C(18) = 116 (1)° and contracted C-P-C angles (C(6)-P-C(12) = 100 (1)°, C(6)-P-C(18) = 104 (1)°, and C(12)-P-C(18) = 101 (1)°). The phosphorus-carbon bond lengths appear to be equivalent within the limits of experimental error with the phosphorus-carbon(sp^3) distance being only P-C(18) = 1.83 (2) Å as compared to the phosphorus-carbon(sp^2) linkages P-C(6) = 1.82 (2) Å and P-C(12) = 1.82 (2) Å.

Each all-staggered, zig-zag (CH₂)₄ chain, which connects the $(OC)_5CrPPh_2$ fragment to the central O-Al-O'-Al' ring, has the expected C(sp^3)-C(sp^3) distances, with C(18)-C(19) = 1.53 (3) Å, C(19)-C(20) = 1.53 (2) Å, and C(20)-(21) = 1.52 (3) Å. The C(21)-O(6) distance of 1.45 (2) Å corresponds to a normal single bond, while angles along the P(CH₂)₄O chain are P-C(18)-C(19) = 113 (1)°, C(18)-C-

(19)-C(20) = 113 (1)°, C(19)-C(20)-C(21) = 112 (1)°, and C(20)-C(21)-O(6) = 112 (1)°.

The Al₂O₂ system lies about an inversion center and defines a strictly planar, four-membered ring in which Al-O(6) = Al'-O(6') = 1.84 (1) Å and Al'-O(6) = Al-O(6') = 1.86 (1) Å. The O-Al-O angles are acute [O(6)-Al-O(6') = O(6')-Al'-O(6) = 79.7 (5)°] while Al-O-Al angles are obtuse [Al-O(6)-Al' = Al'-O(6')-Al = 100.3 (6)°]—consistent with an electron-precise species with no direct Al...Al' bonding. The geometry of this central Al₂O₂ system is rather similar to that found in the centrosymmetric dimeric species $[Me_3SiOAlBr_2]_2$ ³² in which Al-O = 1.79 (1)-1.80 (1) Å, O-Al-O' = 84.4 (4)°, and Al-O-Al' = 95.6 (4)°.

The coordination environment about the ring oxygen atoms (O(6) and O(6')) is trigonal and close to planar, with Al-O(6)-Al' = 100.3 (6)°, Al-O(6)-C(21) = 129.7 (10)°, and Al'-O(6)-C(21) = 128.1 (10)°.

The aluminum atoms are each bonded to two oxygen atoms (vide supra) and to two (trimethylsilyl)methyl ligands with Al-C(22) = 1.95 (2) Å and Al-C(26) = 1.94 (2) Å. The tetrahedral coordination environment of each aluminum atom is extremely irregular with O(6)-Al-O(6') = 79.7 (5)°, O-Al-C angles in the range 110.4 (7)-113.6 (7)°, and C(22)-Al-C(26) = 121.5 (8)°.

All other geometric features of the molecule are normal.

The nature of $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$ in benzene solution has also been investigated. All data are consistent with the existence of a monomer-dimer equilibrium which is slow on the NMR time scale. Cryoscopic molecular weight data indicate that association varies from 1.01 to 1.22 in the concentration range 0.0307-0.0682 m. This low association also suggests that species more associated than dimers are probably not present in significant concentrations. The ¹H NMR spectrum of the compound in benzene solution exhibits two sets of two lines for the (trimethylsilyl)methyl protons which are concentration dependent and consistent with a slow monomer-dimer equilibrium. At the lowest concentration of 0.101 m, the monomeric species with chemical shifts of δ 0.42 (AlCH₂) and 0.12 (SiMe₃) and the dimeric species with chemical shifts of δ 0.29 (SiMe₃) and -0.69 (AlCH₂) are present in approximately equal concentrations. At a higher concentration of 0.305 m, the monomeric species has virtually disappeared. The large differences in chemical shifts for the aluminum methylene protons of δ 0.42 and -0.69 further support the identification of monomers and dimers. If more associated species such as dimers and trimers were present in solution instead of monomers and dimers, the chemical shifts of the lines would be expected to be similar. Furthermore, calculations of net association from ¹H NMR integrations and cryoscopic molecular weight data show a fairly regular transition from monomeric to dimeric as-

(30) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

(31) Esd's of average values, shown in square brackets, are calculated by the "scatter equation" below: $[\sigma] = [\sum_{i=1}^N (d_i - \bar{d})^2 / (N - 1)]^{1/2}$. Here d_i is the i th and \bar{d} is the mean of N "equivalent" bond lengths or angles.

(32) Bonamico, M.; Dessy, G. *J. Chem. Soc. A* **1967**, 1786.

sociation with increasing concentration. The possibility that the monomer exists as a chelated species with the aluminum bound to a carbonyl oxygen has not been investigated.

The ethyl derivative $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$ is probably very similar in nature to the (trimethylsilyl)methyl compound in the solid phase and in solution. Both compounds can be crystallized and exhibit true melting point behavior. Cryoscopic molecular weight measurements in benzene solution also indicate that a monomer-dimer equilibrium exists but a larger percentage of the ethyl derivative exists as a dimer at similar concentrations. However, the ^1H NMR spectra of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$ do not exhibit an apparent large concentration dependence at the concentrations studied, but small effects can be observed. The individual lines due to the protons on the α -carbon of the ethyl group bound to aluminum are broader than those of the triplet for the protons on the β -carbon. This may indicate that the reactions of the equilibrium are faster than those for the more bulky (trimethylsilyl)methyl substituted derivative.

The reactions of AlMe_2Br and AlBr_3 with chromium diphenylphosphide anions in THF also yield products indicative of THF cleavage. Even though analytical²⁸ and ^1H NMR data indicate the general formula $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ ($\text{R} = \text{Me}, \text{Br}$), these compounds exhibit some unusual properties which suggest that their associations in the condensed phase are different from the CH_2SiMe_3 and C_2H_5 derivatives. The complexes $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlMe}_2]$ and $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ are glasses at room temperature. They do not melt but undergo several phase transitions when heated. All attempts to crystallize these compounds have been unsuccessful. Fast removal of ether or hydrocarbon solvents under high vacuum from these complexes leaves a fluffy, airy, golden brown material. If the solvent is removed slowly a viscous glass remains. This phenomenon is independent of the solubility of the complex in the solvent. In a solvent such as hexane, in which these complexes have only very slight solubility, the fluffy glass form of these compounds immediately changes to the viscous glass on contact. The glass appears to swell with hexane. The glass can also be obtained by storing the fluffy solid for several days, and this process can be reversed by adding a solvent and quickly removing it under vacuum. These types of behavior are indicative of changing association and are observed with noncrystalline polymers.³³ Cryoscopic molecular weight data of $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$ in benzene solution suggest that a monomer-dimer equilibrium is present. However, the association did not vary in a regular fashion with concentration, possibly indicating that equilibrium is only slowly attained.

A fundamental question concerning the reaction of chromium diphenylphosphide anions with aluminum halides to yield final products indicative of THF cleavage is whether a species with a Cr-P-Al atom sequence is initially formed. Subsequent reaction of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlR}_2\cdot\text{THF}]$ by dissociation at the Al-P bond with formation of ion pairs followed by nucleophilic attack of a $\text{Cr}(\text{CO})_5\text{PPh}_2^-$ anion on a $\text{R}_2\text{Al}\cdot\text{THF}^+$ cation provides a reasonable pathway in the polar solvent THF (pathway 1). This pathway is consistent with our experimental observations. A "concerted" reaction of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlR}_2\cdot\text{THF}]$ is also a possible route for THF cleavage (pathway 2). If the Cr-P-Al atom sequence is not formed, then a $\text{R}_2\text{AlBr}\cdot\text{THF}$ adduct would have to undergo a nu-

cleophilic attack by $\text{Cr}(\text{CO})_5\text{PPh}_2^-$ (pathway 3). On the basis of current data, pathway 1 is favored but a "concerted" process (pathway 2) cannot be ruled out. The compound¹ $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]$ reacts with THF at room temperature over 24 h to form $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$. The observed long P-Al bond¹ in $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]$ and its reaction chemistry with HBr suggest that dissociation at the Al-P bond to form ion pairs should be a facile process especially in THF solution. Another significant observation is that organoaluminum phosphides, R_2AlPPh_2 ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$), cleave THF under mild conditions,⁹ suggesting that THF cleavage is a facile process even in the absence of a transition metal. Our data suggest that dimethoxyethane can also be cleaved during reactions of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}$ with AlR_2Br ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$). The spectral data for products from these reactions in DME are consistent with ether cleavage, but pure products could not be isolated. In contrast to these observations, diethyl ether is not cleaved. The phosphide $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2$ -dioxane reacts with $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ or AlEt_2Br in diethyl ether to give high yields of products whose spectral properties are consistent with the formation of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlR}_2\cdot\text{OEt}_2]$ ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$). Pathway 3, nucleophilic attack of aluminum ether adduct by $\text{Cr}(\text{CO})_5\text{PPh}_2^-$, is considered the least likely. A preliminary study of a reaction mixture of 1 mol of $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2$ -dioxane and 1 mol of AlMe_3 in THF indicates that only slight ether cleavage occurs after 3 days at room temperature.

The reactions of $\text{Mo}(\text{CO})_5\text{PPh}_2\text{K}\cdot\text{dioxane}$ and $\text{W}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2$ (dioxane) with AlEt_2Br or AlBr_3 in THF have also been examined. Reactions of these molybdenum and tungsten complexes are much slower, the number of byproducts is greater, and the isolation of major products is more difficult than for the chromium complex. All of the factors are probably related to the lower solubility of the molybdenum and tungsten reactants and products. Available data suggest that with tungsten, complexes of simplest formula $\text{W}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlR}_2]$ are isolated. The main products of the molybdenum reactions and the secondary products of the tungsten reactions appear to be disubstituted complexes.

A second possible route to transition-metal derivatives of amphoteric aluminum phosphorus ligands involves small molecule elimination reactions between $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ and AlMe_3 or AlMe_2H , a common class of reaction in main-group chemistry.^{2,9,34} Methane or H_2 would be the expected small molecule products. Even though the chemistry of transition-metal complexes of phosphines containing reactive substituents has been found to resemble that of the free phosphine,³⁵ the predicted elimination reaction with formation of the desired Al-P bond does not occur. The majority of the aluminum compound is consumed but most $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ does not react. These observations suggest that the major site of reaction for the aluminum compound is the carbonyl ligand. Kinetic studies of related elimination reactions³⁶ suggest that the geometry of the transition state is very important in these types of reactions. The aluminum-phosphorus bond would be formed as the small molecule is being eliminated. Consequently, the existence of the Cr-P bond by use of the phosphorus lone pair in $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$ precludes the necessary transition state for elimination.

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It is interesting to compare and contrast our attempts to synthesize compounds of the type $M(\text{CO})_5[\text{PPh}_2\text{AlR}_2]$ with a study in which compounds of the type $M(\text{CO})_5[\text{PPh}_2\text{B}(\text{NR}_2)_2]$ were reported.³⁷ The boron-phosphorus compounds were obtained by the reaction of $M(\text{CO})_5\text{PPh}_2^-$ and $\text{B}(\text{NR}_2)_2\text{Br}$ in THF and the ligand displacement reactions of $M(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}, \text{THF}, \text{CH}_3\text{CN}$) by $\text{B}(\text{NR}_2)_2\text{PR}_2$. The analogous reactions to produce the aluminum compounds have yielded compounds in which the Al-P bond is cleaved and the Al and P atoms are bound to first-row elements instead. The only successful route to compounds of the type $M(\text{CO})_5[\text{PPh}_2\text{AlR}_2]$ has involved displacement of the relatively unreactive ligand NMe_3 of $\text{Cr}(\text{CO})_5\text{NMe}_3$ by $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$.

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$(\text{CO})_5\text{PPh}_2\text{H}-\text{KPPH}_2-\text{THF}$ reaction mixtures for NMR spectral studies.

Registry No. $\text{Cr}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$, 85883-53-0; $\text{Mo}(\text{CO})_5\text{PPh}_2\text{K}\cdot \text{dioxane}$, 85883-56-3; $\text{W}(\text{CO})_5\text{PPh}_2\text{K}\cdot 2(\text{dioxane})$, 85883-58-5; $\text{Cr}(\text{CO})_5\text{PPh}_2\text{H}$, 18399-60-5; $\text{W}(\text{CO})_5\text{PPh}_2\text{H}$, 18399-62-7; $\text{Mo}(\text{CO})_5\text{PPh}_2\text{H}$, 18399-61-6; KH, 7693-26-7; NaH, 7646-69-7; $\text{Cr}(\text{CO})_5\text{PPh}_2\text{Li}$, 85883-59-6; KPPH_2 , 15475-27-1; THF, 109-99-9; $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$, 85883-60-9; AlBr_3 , 7727-15-3; $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlMe}_2]$, 85883-61-0; $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$, 85883-62-1; $[\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]]_2$, 85883-63-2; BrAlMe_2 , 3017-85-4; BrAlEt_2 , 760-19-0; $\text{BrAl}(\text{CH}_2\text{SiMe}_3)_2$, 85004-93-9; $\text{Mo}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$, 85883-64-3; $\text{Mo}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$, 85883-65-4; $\text{W}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlBr}_2]$, 85883-66-5; $\text{W}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAlEt}_2]$, 85883-67-6; $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{AlEt}_2\cdot\text{OEt}_2]$, 85883-68-7; $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{OEt}_2]$, 85883-69-8; AlMe_3 , 75-24-1; AlMe_2H , 865-37-2; dimethoxyethane, 110-71-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, calculated hydrogen atom parameters (Table I-S), and anisotropic thermal parameters (Table II-S) (15 pages). Ordering information is given on any current masthead page.

Rhodium Complexes of the Water-Soluble Phosphine $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3^+$. Their Complexes with Hydride, Olefin, and Carbon Monoxide Ligands. Their Use as Olefin Hydrogenation and Hydroformylation Catalysts in Aqueous Solution and in Aqueous/Organic Solvent Two-Phase Systems and Adsorbed on a Cation-Exchange Resin

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Treatment of $[(\text{norbornadiene})\text{RhCl}]_2$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3^+\text{NO}_3^-$ (amphos nitrate) results in chloride bridge splitting to give $[\text{NBDRhCl}(\text{amphos})]^+\text{NO}_3^-$ (I). I reacts further with amphos to give $[\text{NBDRh}(\text{amphos})_2]^{3+}$ (II), which in turn reacts with hydrogen or water to give $[\text{RhH}_2(\text{amphos})_2(\text{solvent})_2]^{3+}$ or, if excess amphos is available, $[\text{RhH}_2(\text{amphos})_3(\text{solvent})]^{4+}$. While the latter complex is stable with respect to reductive elimination of hydrogen, the former readily loses hydrogen to give $[\text{Rh}(\text{amphos})_2(\text{solvent})_2]^{3+}$. Carbonylation of I and II appears to give $[\text{cis-RhCl}(\text{CO})_2(\text{amphos})]^+$ and $[\text{cis-Rh}(\text{CO})_2(\text{amphos})_2]^{3+}$, respectively. Aqueous solutions of II catalyze the hydrogenation of water-soluble olefins in single-phase systems, and the hydrogenation and hydroformylation of water-immiscible olefins dissolved in *n*-pentane, methylene chloride, and ethyl ether. Adsorption of II onto the sodium form of a strong acid, ion-exchange resin results in a novel supported catalyst system for the hydrogenation and hydroformylation of olefins in acetone solution. Virtually no leaching of rhodium into the olefin-containing phases occurs in the two-phase systems, although the rhodium can be readily recovered from the resin by elution with acid.

Introduction

The potential advantages of homogeneous over heterogeneous catalysis (relatively high selectivity, activity) are well recognized, but a major impediment to more general utilization of homogeneous systems revolves around the problem of separation of products from catalysts.¹ A common solution to this problem involves the attachment

of a normally soluble catalyst to an insoluble support, in an attempt to combine the virtues of both homogeneous and heterogeneous catalysts.²⁻⁴ Unfortunately, the anchoring of soluble metal catalyst precursors to, for instance, a variety of tertiary phosphine-functionalized supports has not in general led to useful catalysts; problems encountered

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