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Transition-Metal Complexes of Organoaluminum Phosphides. Synthesis, Characterization, and Crystal and Molecular Structure of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$

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The reactions of organoaluminum phosphides with a variety of transition-metal carbonyl complexes containing labile ligands have been investigated. The reaction of $Cr(CO)_5NMe_3$ with $(Me_3SiCH_2)_2AlPPh_2$ in benzene solution leads to the formation of $Cr(CO)_5[PPh_2Al(CH_2SiMe_2)_2{\cdot}NMe_3]$, a fully characterized new compound. An X-ray structural study has identified discrete isolated molecules of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$, separated by normal van der Waals distances, in the monoclinic crystal space group $P2_1/n$ with $a = 11.839$ (4) Å, $b = 18.517$ (5) Å, $c = 16.158$ (4) Å, $\beta = 90.32$ (2)°, and ρ(calcd) = 1.20 g/cm^3 for $Z = 4$ with molecular weight 637.82. Diffraction data were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to $R_F = 6.4\%$ for all 4948 reflections. There are no abnormally short intermolecular contacts. The unusual features identified in the investigation are the long bond distances for Al–P of 2.485 (1) Å and Cr–P of 2.482 (1) Å. The Al–N bond seems to be normal. The geometry about the tetrahedrally coordinated phosphorus atom is decidedly irregular. Similarly, the aluminum atom has a rather distorted tetrahedral environment. The reaction of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_2]$ with anhydrous HBr leads to the formation of $Cr(CO)_5PPh_2H$, Br_3AlNMe_3, and $SiMe_4$. A likely path for this reaction involves the initial cleavage of the long P–Al bond. In attempts to find other preparative reactions to compounds with a Cr–P–Al bond sequence, the related reactions of $Cr(CO)_5L$ (L = CO, CH_3CN, THF) with R_2AlPPh_2 (R = Me, Et) were studied but the desired compounds were not formed. Available data suggest that the labile ligand on chromium was attacked by the aluminum–phosphorus reagent.

Introduction

The diphenylphosphido group has been recognized as an excellent bridging ligand in many transition-metal and main-group-metal complexes. It has served as a building block for transition-metal clusters and main-group-element polymers. However, there is only one previous example as a well-defined compound in which the phosphido group bridges a transition metal and main-group-element moiety. The novel compound[1] $Cr(CO)_5PPh_2B(NMe_2)_2$ was prepared from $Cr(CO)_5$(THF) and $PPh_2B(NMe_2)_2$. Since there are no examples of fully characterized compounds in which the phosphido group bridged a transition-metal and a main-group organometallic moiety, the goal of our research was the synthesis of a complex with the formula $Cr(CO)_5(PR_2AlR_2)$. A logical route to a compound of this type involves the reaction of a transition-metal complex containing a labile ligand with a reactive and basic main-group organometallic phosphide. However, all known compounds of the type R_2AlPR_2 exist as dimers or trimers[2,3] with coordinatively saturated aluminum and phosphorus atoms. Consequently, a method had to be found to provide an aluminum–phosphorus species that could react as a Lewis base with $Cr(CO)_5$. For comparison, the boron compound,[1] $PPh_2B(NMe_2)_2$, used to prepare the complex with the Cr–P–B bond sequence, is a monomer and has a basic phosphorus atom. There are two experimentally attractive ideas for generating a monomeric aluminum–phosphorus species with a three-coordinate phosphorus atom. Bulky substituents on aluminum might decrease the stability of an associated species and enable a monomeric R_2AlPR_2 species to be available for reaction. However, the substituents on aluminum must not reduce the basicity of the phosphorus atom. Another way to obtain a potentially reactive aluminum–phosphorus compound is to disrupt an associated species with a Lewis base. Some ^{1}H NMR spectral data and some reaction chemistry[2,3] suggest that dimers can be cleaved, often reversibly, with a Lewis base to form $:Pr'_2{-}AlR_2{\cdot}$base. The known lability of an amine or other nitrogen and oxygen bases for a $Cr(CO)_5L$ complex would provide the necessary Lewis base to distrupt the aluminum–phosphorus dimer as well as produce the reactive $Cr(CO)_5$ moiety.

In this paper was focus on the reactions of $Cr(CO)_5NMe_3$ with organoaluminum diphenylphosphides in hydrocarbon solvents. The first example of the desired class of compounds, $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$, has been prepared and characterized by analysis, spectroscopic methods, and an X-ray structural study. The choices of the specific organoaluminum phosphide and the transition-metal derivative are crucial for the successful synthesis of the desired type of compound. The reactivity of $(Me_3SiCH_2)_2AlPPh_2$, which exists as a mixture of monomer and dimer species in benzene solution,[4] is compared with that of Me_2AlPPh_2[5] and Et_2AlPPh_2,[6] which are dimers. The reactions of $Cr(CO)_5$(THF), $Cr(CO)_5(CH_3CN)$, and $Cr(CO)_6$ with $[R_2AlPPh_2]_2$ (R = Me, Et) are also described, but they do not provide good routes to the desired class of compounds because the labile chromium ligand reacts with the aluminum phosphide under reaction conditions.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum line or a purified argon atomosphere. Reagent grade solvents were employed. Aliphatic hydrocarbon solvents were treated with concentrated sulfuric acid to remove unsaturated compounds. All hydrocarbon solvents were refluxed with and stored over sodium and then vacuum distilled from phosphorus pentoxide immediately prior to use. Ethers were refluxed with and vacuum distilled from sodium–benzophenone ketyl. The preparations of Me_2AlPPh_2,[5] Et_2AlPPh_2,[6] $(Me_3SiCH_2)_2AlPPh_2$,[4] $Cr(CO)_5NMe_3$,[7] and $Cr(CO)_5(CH_3CN)$[8] have been described elsewhere. As a final purification, $Cr(CO)_5NMe_3$ and $Cr(CO)_5(CH_3CN)$ were sublimed at room temperature under vacuum. Even though these chromium compounds possess considerable air stability as solids, they were handled as air- and water-sensitive materials. The waters of hydration

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in Me_3NO and NEt_4Cl, starting materials for the preparation of $Cr(CO)_5NMe_3$ and $Cr(CO)_5(CH_3CN)$, were removed by heating at 110 °C under vacuum. Due to the extreme sensitivity to oxygen and water of the aluminum-containing reaction mixtures, most reactions were carried out in break-seal tubes, a 25 × 3 cm tube equipped with a constricted side arm and a side-arm break-seal. The reagents and solvents were loaded through the constricted side arm, and then it was sealed under vacuum.

Analyses. Microanalytical analyses were peformed by Pascher Microanalytisches Laboratorium, Bonn, Germany. The (trimethylsilyl)methyl deriatives were analyzed for hydrolyzable CH_2SiMe_3 groups by measuring the $SiMe_4$ evolved upon hydrolysis with dilute HNO_3. $SiMe_4$ was separated from all other volatile componentns by passage through two −78 °C traps and into a −196 °C trap and measured by using a known volume in the vacuum line. The purity and identity of the $SiMe_4$ were verified by vapor pressure measurements and its infrared spectrum.

Infrared Spectra. Infrared spectra of Nujol mulls were recorded by means of a Perkin-Elmer Model 457 spectrometer using CsI plates and referenced to polystyrene. Absorption intensities are reported with the abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder).

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 90 MHz with a Varian Model EM-390 spectrometer. Chemical shifts were measured from solvent signals or residual proton signals of deuterated solvents and referenced to tetramethylsilane as $\tau = 10.00$. The multiplicity of an NMR signal is reported with the abbreviations s (singlet), d (doublet), m (multiplet), and b (broad). All NMR tubes were sealed under vacuum.

Synthesis of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$. The complex $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ was prepared by the reaction of $(Me_3SiCH_2)_2AlPPh_2$ and $Cr(CO)_5NMe_2$ in benzene. a break-seal tube containing 0.58 g (1.5 mmol of $(Me_3SiCH_2)_2AlPPh_2$, 0.58 g (2.3 mmol) of $Cr(CO)_5NMe_3$, and 10 mL of benzene was prepared. The reaction mixture was stirred for 48 h. After 12 h, a distinct color change had occurred; the solution had changed from bright orange to yellow. The tube was opened under vacuum, and the solution was filtered into a flask. Pentane (5 mL) was vacuum distilled into the flask; the resulting solution was kept at 0 °C for 12 h, and 0.40 g (42%) of yellow crystals of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ (mp 109–111 °C) was isolated by filtration. A second crop of crystals (0.15 g, 16%) was obtained by removing the solvent by vacuum distillation, dissolving the residue in a minimum amount of pentane, and cooling the solution to −20 °C. The combined crystals were subjected to high vacuum for 12 h (until no more yellow $Cr(CO)_5NMe_3$ condensed in the trap) and then recrystallized from pentane. Mp: 110–111 °C. Anal. Calcd: C, 52.73; H, 6.48; N, 2.20; P, 4.86 (Me_4Si, 2.00 mol/mol). Found: C, 52.27; H, 6.30; N, 2.02; P, 4.99 (Me_4Si, 1.97 mol/mol). ^1H NMR, (benzene-d_6): τ 2.23 (t, J = 9 Hz, Ph), 3.03 (m, Ph), 8.52 (s, NCH_3), 9.99 (s, $SiCH_3$), 10.02 (s, $SiCH_3$), 10.05 (s, $SiCH_3$), 10.19 (s, $AlCH_2$), 10.63 (s, $AlCH_2$), 10.73 (d, $AlCH_2$). IR (cm^{-1}): ν_{CO} 2069 (m), 1970 (m, sh), 1922 (vs, b).

The reaction of equimolar quantities of $(Me_3SiCH_2)_2AlPPh_2$ and $Cr(CO)_5NMe_3$ was followed by ^1H NMR technqiues. About 0.4 mL of benzene-d_6 was vacuum distilled at −196 °C onto 0.035 g (0.91 mmol) of $(Me_3SiCH_2)_2AlPPh_2$ and 0.023 g (0.91 mmol) of $Cr(CO)_5NMe_3$ contained in an NMR tube. The tube was sealed at −196 °C under vacuum and kept frozen until just prior to recording the first ^1H NMR spectrum. The spectrum was again recorded at intervals of 2, 9.5, 21.0, 25.5, 35.0, 46.5, and 72 h. After 9.5 h the bright orange solution had lightened considerably, and by the end of the experiment a nearly colorless solution was present. These spectra are discussed in the Results and Discussion.

Reaction of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ with Anhydrous HBr. The nature of the reaction of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ with HBr was studied by using ^1H NMR techniques. A quantity of HBr was measured on the vacuum line and distilled onto a benzene-d_6 solution of a known mass of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ contained in a bulb with a side-arm NMR tube. Reaction was allowed to take place for 8 h. The resultant solution was poured into the NMR tube, the tube was frozen to −196 °C to ensure that no volatile components were lost, the tube was sealed, and the ^1H NMR spectrum was recorded.

The reaction of a benzene-d_6 solution of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ with HBr in a 1:3.2 mole ratio caused the light yellow solution to become virtually colorless. The ^1H NMR spectrum showed absorbances for $Cr(CO)_5PPh_2H$, $SiMe_4$, and $Br_3Al{\cdot}NMe_3$ (τ = 8.44). A reaction mixture with a mole ratio of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$:HBr of 1:4.8 produced a nearly colorless solution, a white solid, a green solid, and some CO. The ^1H NMR spectrum of the resulting solution showed lines consistent with the presence of $Cr(CO)_5PPh_2H$ and $SiMe_4$.

Table I. Data for the X-ray Diffraction Study of $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$

(A) Crystal Parameters

cryst syst	monoclinic	V, Å^3	3542 (2)
space group	$P2_1/n$	Z	4
a, Å	11.839 (4)	mol wt	637.82
b, Å	18.517 (5)	ρ(calcd), g cm^{-3}	1.20
c, Å	16.158 (4)	μ, cm^{-1}	5.1
β, deg	90.32 (2)	T, °C	24

(B) Measurement of Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: pyrolytic graphite (equatorial)
reflcns measd: $+h, +k, \pm l$ for $3.0° < 2\theta < 46.0°$
scan type: θ–2θ
scan speed, deg/min: 4.5
scan range, deg: symmetrical, $[2.0 + \Delta(\alpha_1 - \alpha_2)]$
bkgd: at beginning and end of scan; each for $^1/_2$ scan time
total measurement: 5590 reflections; yielding 4948 unique data

Crystallographic Studies. The crystal used for X-ray study was obtained by dissolving $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ in a minimum of pentane and then cooling to 0 °C for 5 h. After the crystals were separated by filtration, a crystal (maximum orthogonal dimensions 0.47 × 0.25 × 0.20 mm) was selected in an argon-filled drybox and then sealed in a thin-walled glass capillary.

The crystal was mounted on a Syntex $P2_1$ automated four-circle diffractometer. The unit cell parameters and the orientation matrix were determined as described previously;[9] data collection was peformed by using the θ–2θ scan method (details see Table I). Data were corrected for Lorentz and polarization factors and for absorption and were reduced to $|F_o|$ values; any reflection with $I_{net} < 0$ had its $|F_o|$ value reset to zero.

Solution and Refinement of the Structure. All calculations were performed by using our in-house Syntex XTL structure determination system.[10] The analytical scattering factors of neutral atoms were corrected for the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[11] The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$, where the weights (w) are obtained from counting statistics modified by an ingnorance factor (p) of 0.02.

The structure was solved by direct methods using MULTAN[12] and was refined by difference-Fourier and full-matrix least-squares refinement techniques to R_F = 6.4%, R_{wF} = 5.7%, and GOF = 1.63[13] for all 4948 independent reflections (none rejected) or R_F = 5.0%, R_{wF} = 5.4%, and GOF = 1.71 for those 4134 reflections with $|F_o| > 3\sigma(|F_o|)$. The NO:NV ratio was 4948:352 or approximately 14.1:1.

All hydrogen atoms were included in calculated positions with d(C–H) = 0.95 Å;[14] these positions were updated but not refined.

Final positional parameters appear in Table II. Anisotropic thermal parameters are collected in Table III-S (supplementary data).

Reaction of $Cr(CO)_5NMe_3$ with Et_2AlPPh_2 in Toluene. $Cr(CO)_5NMe_3$ (0.530 g, 2.11 mmol) and Et_2AlPPh_2 (0.550 g, 2.03 mmol) were stirred in 10 mL of toluene at room temperature for 12 h in a break-seal tube. No change in the reaction color was observed. The tube was then heated at 70 °C for 3 h. Decomposition of $Cr(CO)_5NMe_3$ occurred, producing $Cr(CO)_6$ and a small amount of

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Table II. Fractional Coordinates for Atoms in the $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$ Molecule

atom	x	y	z
Cr	0.002 86 (4)	0.343 03 (3)	0.019 61 (3)
Al	0.293 29 (8)	0.263 05 (5)	−0.122 06 (6)
P	0.106 01 (7)	0.246 99 (4)	−0.055 87 (5)
Si(1)	0.423 39 (10)	0.098 42 (6)	−0.112 08 (8)
Si(2)	0.533 54 (8)	0.356 32 (6)	−0.061 72 (6)
N	0.253 62 (22)	0.325 92 (15)	−0.222 43 (16)
C(11)	0.129 31 (28)	0.173 63 (17)	0.019 50 (20)
C(12)	0.220 86 (31)	0.177 08 (20)	0.073 86 (22)
C(13)	0.237 30 (39)	0.124 21 (27)	0.134 35 (26)
C(14)	0.161 79 (51)	0.068 80 (27)	0.141 72 (30)
C(15)	0.070 36 (44)	0.064 61 (23)	0.089 42 (32)
C(16)	0.052 92 (33)	0.116 79 (20)	0.029 29 (24)
C(21)	0.022 42 (26)	0.199 37 (18)	−0.135 88 (19)
C(22)	−0.078 89 (29)	0.225 73 (21)	−0.166 77 (22)
C(23)	−0.136 12 (35)	0.190 29 (27)	−0.229 72 (27)
C(24)	−0.092 77 (41)	0.128 35 (27)	−0.262 66 (27)
C(25)	0.006 67 (40)	0.100 52 (22)	−0.232 77 (26)
C(26)	0.064 03 (32)	0.135 87 (19)	−0.170 40 (23)
C(27)	0.496 30 (41)	0.126 74 (29)	−0.015 09 (31)
C(28)	0.313 02 (42)	0.031 39 (24)	−0.086 16 (34)
C(29)	0.530 20 (43)	0.051 63 (29)	−0.177 10 (34)
C(30)	0.604 27 (34)	0.360 94 (25)	0.041 05 (25)
C(31)	0.532 95 (41)	0.449 58 (25)	−0.105 76 (30)
C(32)	0.622 68 (30)	0.300 57 (26)	−0.131 06 (25)
C(1A)	0.362 41 (29)	0.176 42 (19)	−0.170 11 (22)
C(1B)	0.388 79 (28)	0.320 84 (21)	−0.047 36 (21)
C(2A)	0.358 07 (32)	0.342 65 (23)	−0.268 17 (24)
C(2B)	0.176 00 (38)	0.290 38 (29)	−0.281 27 (26)
C(2C)	0.205 50 (46)	0.395 22 (26)	−0.195 15 (29)
C(1)	−0.057 13 (30)	0.387 75 (20)	−0.076 49 (24)
C(2)	0.125 02 (32)	0.408 77 (20)	0.020 17 (24)
C(3)	−0.080 55 (31)	0.407 13 (21)	0.081 96 (24)
C(4)	−0.113 42 (29)	0.273 42 (21)	0.024 83 (20)
C(5)	0.061 83 (28)	0.308 45 (21)	0.120 32 (24)
O(1)	−0.094 37 (26)	0.418 47 (17)	−0.131 91 (19)
O(2)	0.196 31 (25)	0.450 13 (16)	0.025 35 (22)
O(3)	−0.132 24 (24)	0.445 67 (17)	0.122 45 (20)
O(4)	−0.181 80 (22)	0.230 02 (16)	0.030 93 (17)
O(5)	0.094 16 (24)	0.291 35 (19)	0.184 22 (17)

green material. Et_2AlPPh_2 was isolated unchanged from the toluene solution.

Reactions of $Cr(CO)_5(CH_3CN)$ with Organoaluminum Phosphides. (a) With Me_2AlPPh_2. A mixture of 0.235 g (1.01 mmol) of $Cr(CO)_5(CH_3CN)$ and 0.244 g (1.01 mmol) of Me_2AlPPh_2 (in 5 mL of diethyl ether) was stirred at room temperature for 20 days. The initial bright yellow solution and the white solid were slowly replaced by a pale orange solution and a pale yellow solid. The ether and a trace of unreacted $Cr(CO)_5(CH_3CN)$ were removed by vacuum distillation, yielding 0.40 g of a pale yellow powder. Mp data: 175 °C, darkens; 187 °C, melts to a red liquid. IR (cm^{-1}): ν_{CO} 2075 (m), 1975 (m), 1938 (sh), 1915 (vs); $\nu_{C=N}$ 1601 (m). This compound had very low solubility in both hydrocarbon and ether solvents.

(b) With Et_2AlPPh_2. A mixture of 0.636 g (2.73 mmol) of $Cr(CO)_5(CH_3CN)$ and 0.737 g (2.73 mmol) of Et_2AlPPh_2 (in 5 mL of diethyl ether) was stirred for 2 h. A tan solid (0.659 g) precipitated and was isolated by filtration. Mp data: 148 °C, darkens; 160–162 °C, melts to a red liquid. IR (cm^{-1}): $\nu_{C\equiv N}$ 2156 (w); ν_{CO} 2070 (m), 1980 (m, sh), 1939 (s, sh), 1909 (vs); $\nu_{C=N}$ 1601 (m). This compound had low solubility in both hydrocarbon and ether solvents.

Reaction of $Cr(CO)_6$ with Me_2AlPPh_2. A break-seal tube containing 0.529 g (2.18 mmol) of Me_2AlPPh_2, 0.602 (2.74 mmol) of $Cr(CO)_6$, and 10 mL of toluene was heated at 140 °C for 22 h. The reaction mixture consisted of a brown solid and a brown solution after cooling to room temperature. The tube was opened under vacuum, the evolved carbon monoxide (0.501 mmol, 23%) was measured, and the reaction mixture was extracted several times with the toluene. After the volatile components were removed on the vacuum line, a brown residue remained. Virtually all the expected excess $Cr(CO_6$ (0.1342 g, 0.53 mmol) was separated from the volatile components. The brown residue was extracted several times with 10 mL of hexane. After removal of solvent by vacuum distillation a small amount of a sticky yellow material was obtained. Attempts to crystallize this material from hexane were unsuccessful. ^1H NMR (toluene-d_8): τ 2.75 (m, Ph), 3.00 (m, Ph), 9.74 (s, $AlCH_3$). IR (cm^{-1}): ν_{CO} 2075 (m), 2023 (w), 1977 (m), 1930 (vs), 1898 (s, sh). Similar results were obtained by varying the reaction time and temperature (110–140 °C).

Reaction of $Cr(CO)_5(THF)$ with Et_2AlPPh_2. A solution of 0.710 g (3.23 mmol) of $Cr(CO)_6$ in 40 mL of THF was irradiated undr argon for 34 h. The resultant orange solution (under argon) was poured into a two-neck flask. A solution of 0.881 g (3.26 mmol) of Et_2AlPPh_2 in 5 mL of THF was prepared in a tube with a Teflon stopcock, and the tube was attached to the flask containing $Cr(CO)_5(THF)$. The reaction vessel was evacuated, and then the Et_2AlPPh_2 solution was added to the stirred $Cr(CO)_5(THF)$ solution. After 14 h the solvent was removed by vacuum distillation. The resultant brown-yellow oil was dissolved in 8 mL of toluene, and the solution was filtered from unreacted $Cr(CO)_6$ and a small amount of black solid. The volatile components were removed under high vacuum for 18 h. Attempts to crystallize the brown-yellow oil from toluene/hexane or hexane were unsuccessful. ^1H NMR (toluene-d_8): τ 2.61 (m, Ph), 2.98 (m, Ph), 6.39 (m, OCH_2), 7.59 (m, b, PCH_2), 8.66 (m, CH_2), 8.76 (m, $AlCH_2CH_3$), ~9.96 (m, $AlCH_2$). IR (neat, cm^{-1}): ν_{CO} 2076 (m), 1972 (m), 1908 (vs, vb).

Results and Discussion

The first example of the new class of compounds in which a diphenylphosphido group bridges a transition metal and a main-group metal has been prepared and fully characterized. An apparent substitution of $Cr(CO)_5NMe_3$ by $(Me_3SiCH_2)_2AlPPh_2$ occurs readily at room temperature in benzene solution to give good yields of the new compound $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$, a light yellow crystalline solid (eq 1). The identity of the new compound with

$$Cr(CO)_5NMe_3 + (Me_3SiCH_2)_2AlPPh_2 \rightarrow Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3] \quad (1)$$

a Cr–P–Al atom sequence has been determined by elemental analyses, infrared and ^1H NMR spectral data, reaction chemistry, and an X-ray structural study. Other combinations of reagents did not lead to the formation of isolable compounds with the desired Cr–P–Al atom sequence. Either reactions did not occur or a ligand on chromium reacted with the aluminum phosphide. For example, no reaction occurs between $Cr(CO)_5NMe_3$ and Et_2AlPPh_2 in toluene at room temperature for 12 h. Heating of this reaction mixture to 70 °C results in decomposition; $Cr(CO)_6$ and Et_2AlPPh_2 are isolated. The difference in reactivity at 25 °C between $(Me_3SiCH_2)_2AlPPh_2$ and Et_2AlPPh_2 can be attributed to the observed association of the aluminum–phosphorus compounds in aromatic solvents. The successful reaction was observed for $(Me_3SiCH_2)_2AlPPh_2$, a monomer–dimer equilibrium mixture.[4] In contrast, Et_2AlPPh_2 is a dimer in benzene solution[6] and both the aluminum and phosphorus atoms are coordinatively saturated and unavailable for reaction. The reactions of $Cr(CO)_6$, $Cr(CO)_5(CH_3CN)$, and $Cr(CO)_5(THF)$ with organoaluminum phosphides do not give the desired compounds with a Cr–P–Al atom sequence. Instead, the labile ligand on chromium has been apparently attacked by the aluminum–phosphorus compound at the conditions required for reaction.

The X-ray structural study demonstrates that the crystal consists of discrete isolated molecules of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$, separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. Interatomic distances with their estimated standard deviations (esd's) are given in Table III; angles appear in Table IV, while least-squares planes are defined in Table VI-S (supplementary data). Figure 1 shows the scheme used in labeling the atoms, while Figure 2 provides a stereoscopic view of the molecule.

The $(OC)_5Cr–P$ portion of the structure has approximate C_{4v} symmetry, and the $(OC)_5Cr–PPh_2$ system lends itself to comparison with parameters obtained for $(OC)_5Cr(PPh_3)$.[15]

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[15] Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

Table III. Selected Interatomic Distances (Å) with Esd's for $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$[a]

(A) Distances in the $Cr(CO)_5$ System			
Cr–C(1)	1.894 (4)	C(1)–O(1)	1.147 (5)
Cr–C(2)	1.890 (4)	C(2)–O(2)	1.142 (5)
Cr–C(3)	1.847 (4)	C(3)–O(3)	1.147 (5)
Cr–C(4)	1.888 (4)	C(4)–O(4)	1.145 (5)
Cr–C(5)	1.879 (4)	C(5)–O(5)	1.144 (5)
(B) Distances in the Cr–P–Al System			
Cr–P	2.482 (1)	P–Al	2.485 (1)
(C) Phosphorus–Carbon (Phenyl) Distances			
P–C(11)	1.844 (3)	P–C(21)	1.848 (3)
(D) Aluminum–Carbon and Aluminum–Nitrogen Distances			
Al–C(1a)	1.963 (4)	Al–N	2.049 (3)
Al–C(1b)	1.966 (4)		
(E) Silicon–Carbon Distances			
Si(1)–C(1a)	1.865 (4)	Si(2)–C(1b)	1.851 (4)
Si(1)–C(27)	1.860 (5)	Si(2)–C(30)	1.858 (4)
Si(1)–C(28)	1.852 (5)	Si(2)–C(31)	1.868 (5)
Si(1)–C(29)	1.862 (5)	Si(2)–C(32)	1.857 (4)
(F) Nitrogen–Carbon (Methyl) Distances			
N–C(2a)	1.477 (5)	N–C(2c)	1.473 (6)
N–C(2b)	1.474 (5)		

[a] Carbon–carbon distances appear in the supplementary data (Table IV-S).

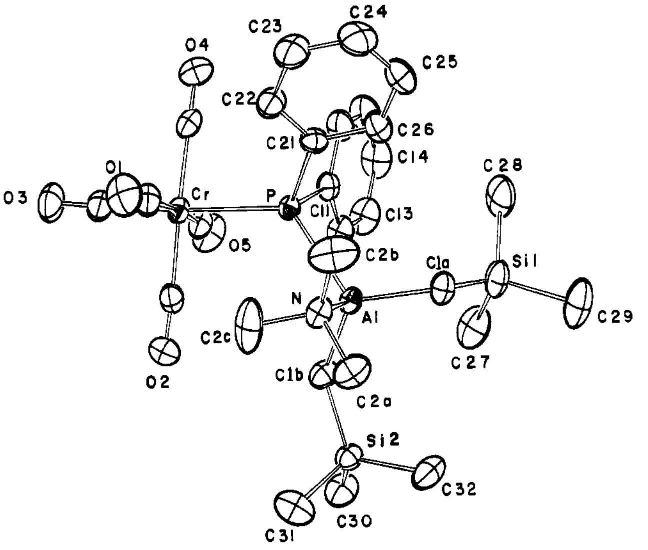

Figure 1. Labeling of atoms in the $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$ molecule (ORTEP-II diagram; 30% ellipsoids; hydrogen atoms omitted).

Table IV. Selected Angles (deg) within the $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$ Molecule[a]

(A) Angles around the Chromium Atom			
C(1)–Cr–C(2)	90.33 (16)	C(2)–Cr–P	94.90 (12)
C(1)–Cr–C(3)	88.11 (16)	C(3)–Cr–C(4)	91.27 (16)
C(1)–Cr–C(4)	93.73 (16)	C(3)–Cr–C(5)	86.78 (16)
C(1)–Cr–C(5)	173.86 (16)	C(3)–Cr–P	174.20 (12)
C(1)–Cr–P	95.38 (12)	C(4)–Cr–C(5)	89.78 (16)
C(2)–Cr–C(3)	89.70 (17)	C(4)–Cr–P	83.90 (11)
C(2)–Cr–C(4)	175.86 (16)	C(5)–Cr–P	90.00 (11)
C(2)–Cr–C(5)	86.26 (16)		
(B) Angles around the Phosphorus Atom			
Cr–P–Al	124.64 (4)	Al–P–C(11)	104.00 (11)
Cr–P–C(11)	105.99 (11)	Al–P–C(21)	103.40 (11)
Cr–P–C(21)	115.00 (11)	C(11)–P–C(21)	100.84 (15)
(C) Angles around the Aluminum Atom			
P–Al–N	101.98 (9)	N–Al–C(1a)	104.21 (13)
P–Al–C(1a)	116.58 (11)	N–Al–C(1b)	107.77 (13)
P–Al–C(1b)	108.21 (11)	C(1a)–Al–C(1b)	116.62 (15)
(D) Angles at the Methylene Carbon Atoms			
Al–C(1a)–Si(1)	126.52 (19)	Al–C(1b)–Si(2)	130.24 (20)
(E) Angles around the Silicon Atoms			
C(27)–Si(1)–C(28)	108.85 (23)	C(30)–Si(2)–C(31)	107.38 (20)
C(27)–Si(1)–C(29)	107.04 (24)	C(30)–Si(2)–C(32)	108.06 (19)
C(27)–Si(1)–C(1a)	112.44 (20)	C(30)–Si(2)–C(1b)	108.50 (18)
C(28)–Si(1)–C(29)	107.32 (23)	C(31)–Si(2)–C(32)	106.56 (20)
C(28)–Si(1)–C(1a)	111.17 (20)	C(31)–Si(2)–C(1b)	111.99 (19)
C(29)–Si(1)–C(1a)	109.81 (20)	C(32)–Si(2)–C(1b)	114.07 (18)
(F) Angles around the Nitrogen Atom			
Al–N–C(2a)	109.06 (21)	C(2a)–N–C(2b)	106.96 (29)
Al–N–C(2b)	113.34 (24)	C(2a)–N–C(2c)	107.06 (30)
Al–N–C(2c)	110.21 (24)	C(2b)–N–C(2c)	109.96 (32)
(G) Chromium–Carbon–Oxygen Angles			
Cr–C(1)–O(1)	175.92 (34)	Cr–C(4)–O(4)	177.10 (32)
Cr–C(2)–O(2)	175.53 (34)	Cr–C(5)–O(5)	175.28 (33)
Cr–C(3)–O(3)	178.15 (34)		
(H) Phosphorus Carbon–Carbon Angles			
P–C(11)–C(12)	119.71 (25)	P–C(21)–C(22)	122.90 (25)
P–C(11)–C(16)	122.35 (26)	P–C(21)–C(26)	119.59 (25)

[a] C–C–C angles appear as supplementary data (Table V-S).

The equatorial Cr–CO linkages in the present complex range from 1.879 (4) to 1.894 (4) Å averaging 1.888 [6] Å[16] —some 0.041 Å longer than the axial Cr–CO linkage of 1.847 (4) Å. [Analogous bond lengths in $(OC)_5Cr(PPh_3)$ are Cr–CO (equatorial) = 1.867 (4) – 1.894 (4) Å (average 1.880 [11] Å) and Cr–CO (axial) = 1.845 (4) Å.] These results are all consistent with the accepted model for metal–carbonyl bonding; the longer Cr–CO (equatorial) bonds reflect the greater competition for d_π-electron density between the mutually trans pairs of equatorial ligands. Similar results are found in such molecules as $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.[17] The Cr–P bond length in $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$ is 2.482 (1) Å, which is significantly longer than that of 2.422 (1) Å found in $(OC)_5Cr(PPh_3)$.

The P–Cr–CO (equatorial) angles in $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$ are P–Cr–C(1) = 95.38 (12)°, P–Cr–C(2) = 94.90 (12)°, P–Cr–C(4) = 83.90 (11)°, and P–Cr–C(5) = 90.00 (11)°; similar irregularities appear in $(OC)_5Cr(PPh_3)$, where individual P–Cr–CO (equatorial) angles are 94.3 (1), 96.2 (1), 88.4 (1), and 87.5 (1)°.

The geometry about the tetrahedrally coordinated phosphorus atom is decidedly irregular: the Cr–P–Al angle is increased to 124.64 (4)°, the two Cr–P–C angles are inequivalent [Cr–P–C(21) = 115.00 (11)° and Cr–P–C(11) = 105.99 (11)°], the Al–P–C angles are close to equivalent [Al–P–C(11) = 104.00 (11)° and Al–P–C(21) = 103.40 (11)°], and the C(11)–P–C(21) angle is reduced to 100.84 (15)°. The phosphorus–carbon bond lengths [P–C(11) = 1.844 (3) Å and P–C(21) = 1.848 (3) Å (average 1.846 [3] Å)] are slightly longer than those observed in triphenylphosphine (1.822–1.831 Å)[18] or in $(OC)_5Cr(PPh_3)$ (1.821 (3)–1.834 (4) Å).[15] However, this is not general for derivatives of the diphenylphosphido ligand [e.g., P–C = 1.822 (5)–1.831 (5) Å in $Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}PPh_2)$[19] and P–C = 1.826 (5)–1.839 (6) Å in $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$].[20]

The aluminum atom is in a rather distorted tetrahedral environment being bonding to the phosphido ligand, two alkyl

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(16) Esd's on average distances etc. are enclosed in square brackets. They are calculated via the "scatter formula"

$$\sigma = [\sum_{i=1}^{i=N}(d_i - \bar{d})^2/(N-1)]^{1/2}$$

(17) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

(18) Daly, J. J. *J. Chem. Soc.* **1964**, 3799.

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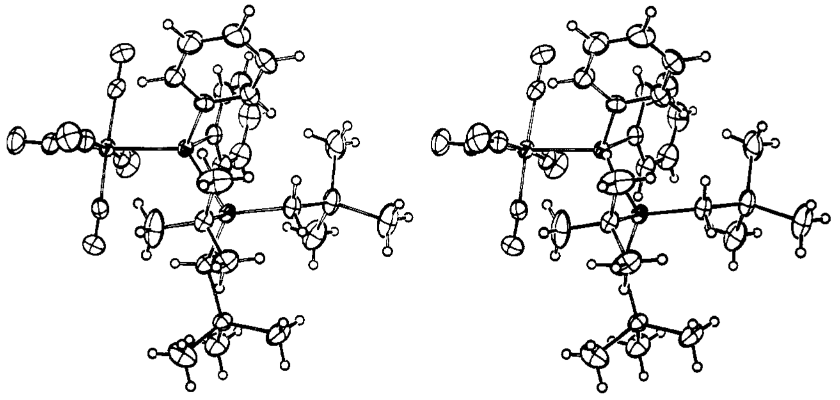

Figure 2. Stereoscopic view of the $(OC)_5Cr[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ molecule, with all hydrogen atoms included (ORTEP-II diagram).

ligands, and an amine ligand. Two interligand angles are expanded from the regular tetrahedral value—P-Al-C(1a) = 116.58 (11)° and C(1a)-Al-C(1b) = 116.62 (15)°; other angles (in decreasing order) are P-Al-C(1b) = 108.21 (11)°, N-Al-C(1b) = 107.77 (13)°, N-Al-C(1a) = 104.21 (13)°, and P-Al-N = 101.98 (9)°. The aluminum-alkyl distances ($Al-CH_2SiMe_3$) are Al-C(1a) = 1.963 (4) Å and Al-C(1b) = 1.966 (4) Å; the average Al-C(sp^3) distance is 1.965 [2] Å, in good agreement with terminal aluminum-alkyl bond lengths reported previously.[21a] This suggests a covalent radius of ~1.19 Å for aluminum (cf. the accepted value of 1.18 Å).[21b] The observed Al-P distance of 2.485 (1) Å seems anomalously long when compared to the value predicted from radii ~2.29 Å, based on *r*(Al) = 1.19 Å and *r*(P) = 1.10 Å.[22] An X-ray study[23] of aluminum phosphide (AlP) provided an average Al-P bond distance of 2.367 Å (zinc blende type of structure), whereas the electron diffraction study[24] of the adduct Me_3AlPMe_3 suggests a long donor-acceptor Al-P bond distance of 2.53 (4) Å. Thus, the comparison of these bond distances suggests that the Al-P bond in $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ might be best considered as a donor-acceptor or a dative bond. The Al-N bond distance of 2.049 (3) Å also seems to be consistent with a donor-acceptor bond as expected. All other distances and angles in the molecule (cf. Table III and IV) seem normal.

The isolation of the trimethylamine adduct $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ might be unexpected in view of results obtained by other researchers. The organoaluminum phosphide Me_2AlPPh_2 reacts with NMe_3 to give the adduct $Ph_2PAlMe_2{\cdot}NMe_3$.[5] However, the amine can be removed by heating to 65 °C under vacuum. The ethyl-substituted compound Et_2AlPPh_2 does not form a stable adduct with NMe_3.[6] This has been rationalized as a consequence of steric interaction as weaker but less sterically hindered bases such as OEt_2, THF, and acridine reportedly produce adducts. We have tried to repeat several of these experiments[4] and find that the adduct $Ph_2PAlEt_2{\cdot}OEt_2$ is not stable at room temperature under vacuum. Furthermore, the material claimed to be $Ph_2PAlEt_2{\cdot}THF$ is not a true adduct but contains a cleaved THF molecule. The isolation of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ indicates that steric considerations cannot be the only reason that $Ph_2PAlEt_2{\cdot}NMe_3$ has not been isolated. Until these and other inconsistencies in the literature are resolved, it is difficult to make any useful comparisons between the properties of oligomeric organaluminum phosphides and $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$.

The reaction of a benzene solution of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ with HBr is consistent with the proposed structure with the long aluminum-phosphorus bond. When 3 mol of HBr is consumed, the products include $Cr(CO)_5PPh_2H$,[23] Br_3AlNMe_3, and $SiMe_4$. The HBr probably reacts initially at the long Al-P bond to form $Cr(CO)_5PPh_2H$ and $Br(Me_3SiCH_2)_2AlNMe_3$. Then the remaining 2 mol of HBr serve to cleave CH_2SiMe_3 groups and form the observed products. Another possible site of initial reaction would be at the Al-N bond to form $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2]$ and $NMe_3H^+Br^-$. Subsequent reaction would produce $Cr(CO)_5[PPh_2AlBr(CH_2SiMe_3)_2{\cdot}NMe_3]$ and $SiMe_4$. Consecutive reactions using this type of path could lead to the observed products. However, this latter path seems unlikely. There is no evidence for the intermediate formation of an insoluble ammonium salt at any stage during reaction. Furthermore, kinetic studies suggest that elimination reactions of organoaluminum compounds with Lewis bases with acidic protons are second-order reactions and require prior dissociation of preformed adducts.[26,27] Consequently, since NMe_3 is tightly bound and cannot be removed from $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ under high vacuum with gentle heating, reaction should occur preferentially by the dissociation of the abnormally long Al-P bond.

The reaction between $(Me_3SiCH_2)_2AlPPh_2$ and $Cr(CO)_5NMe_3$ to form $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ in benzene solution is apparently slow on the NMR time scale. The extent of reaction can be easily followed by monitoring the ^1H NMR spectrum of a reaction mixture at the normal operating temperature of the instrument as a function of time. Significant quantities of products were not observed until approximately 9 h of reaction time and elapsed for a reaction mixture, which had initial concentrations of approximately 2 M. The initial spectrum of the reaction mixture in benzene-d_6 was observed less than 5 min after combining the reagents and exhibited the patterns of the pure reagents. The chemical shifts of the reagents in the reaction mixture were only slightly shifted from those of the pure reagents. After 2 h, new low-intensity lines, suggestive of an intermediate or a secondary product but not the primary product, appeared in the regions expected for the N-methyl and Al-alkyl resonances. There was no apparent change in the phenyl region of the spectrum to suggest that the phosphorus was complexing the chromium.[28] After 9.5 h the reaction mixture had lightened considerably in color and the spectrum showed that a significant amount of product had formed. However, the reactants had

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(21) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235–271: (a) Table II on p 240; (b) Table I on p 238; (c) Table IV on p 249.

(22) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. See Table 7-2 on p 224.

(23) Wang, C. C.; Zaheeruddin, M.; Spinar, L. H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 326.

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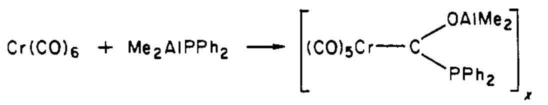
not been entirely consumed. Only after 25.5 h were the major absorptions in the spectrum those which corresponded to the final product. Furthermore, the reaction mixture was very pale yellow, almost colorless. The spectrum after 72 h showed that reaction was essentially complete. There are at least two possible substitution mechanisms that can be used to account for the surprisingly slow formation of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$. In one scheme, the dissociation of amine from $Cr(CO)_5NMe_3$ would be followed by the rapid addition of the organoaluminum phosphide. This overall process might be expected to lead to the relatively rapid formation of product. An alterative scheme could involve the initial formation of complex between the Lewis acid end of the organoaluminum phosphide with a bonded carbonyl. A dissociative reaction followed by a substitution reaction at chromium, analogous to that proposed for the reactions of the metathesis catalysts[29] $W(CO)_5PPh_3$ and $W(CO)_5P(n\text{-}Bu)_3$ activated by $AlBr_3$, could lead to the product. However, a rearrangement of the initial Lewis acid–carbonyl complex can also be envisioned to give the product. The definition of the reaction mechanism will have to await more detailed kinetic studies of the system.

The reactions of $Cr(CO)_6$, $Cr(CO)_5(CH_3CN)$, and $Cr(CO)_5(THF)$ with organoaluminum phosphides give rise to complexes in which attack of the labile ligand had occurred. The reaction of $Cr(CO)_6$ with Me_2AlPPh_2 in toluene requires high temperatures (>110 °C). The major product is a dark brown insoluble material, which has not been characterized. In addition, a very small quantity of a sticky yellow material is obtained. The infrared and ^1H NMR spectra of this material suggest the formulation $Cr(CO)_5[PPh_2AlMe_2]$. All attempts to vary the reaction conditions to favor this substitution product have been unsuccessful. The small amount of the desired yellow compound in comparison to the large quantity of the brown material, the relatively small amount of CO generated during reaction, and the fact that all Me_2AlPPh_2 was consumed suggest that processes other than substitution occur. Addition reactions of Me_2AlPPh_2 across the carbonyl ligand, as depicted in eq 2, seem likely. The resulting product may have polymerized or decomposed at the temperature for reaction. Similar addition reactions have been observed for $LiPMe_2$[30] and $Al(NMe_2)_3$[31] with transition-metal carbonyl complexes. The reactions of $Cr(CO)_5(CH_3CN)$ with Me_2AlPPh_2 or Et_2AlPPh_2 in diethyl ether yield products in which the organoaluminum phosphide has added across the triple bond of the acetonitrile. This reaction course is suggested by the presence of an infrared band at about 1600 cm^{-1} ($\nu_{C=N}$) in the products. In addition, the product from the Et_2AlPPh_2–$Cr(CO)_5(CH_3CN)$ reaction has an infrared band at 2156 cm^{-1}, which suggests that a nitrile adduct is also formed. The product from the reaction of $Cr(CO)_5(THF)$ with Et_2AlPPh_2 has the simplest formula $Cr(CO)_5(THF)(Et_2AlPPh_2)$. However, spectral data suggest that the THF has been cleaved. The ease with which these reactions of $Cr(CO)_5(CH_3CN)$ or $Cr(CO)_5(THF)$ with organoaluminum phosphides occur, i.e. room temperature, raised the question whether the chromium was somehow activating the organoaluminum phosphide by coordination. We have found that this is not necessarily the case. Organoaluminum phosphides react with CH_3CN and THF at room temperature to form products with spectral features analogous to those previously described.[4] The combination of data suggests that the products from the $Cr(CO)_5(CH_3CN)$ reactions are probably $Cr(CO)_5[PPh_2C(CH_3){=}NAlR_2]$ (R = Me, Et) and $Cr(CO)_5[PPh_2AlEt_2{\cdot}NCCH_3]$. The product from the $Cr(CO)_5(THF)$ reaction is $Cr(CO)_5[PPh_2(CH_2)_4OAlEt_2]$. This latter compound has also been obtained by a completely different pathway, and a congener $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$, has been fully characterized, including an X-ray structural study.[32]



(2)

The reaction of $Cr(CO)_5NMe_3$ and $(Me_3SiCH_2)_2AlPPh_2$ indicates that monomeric organoaluminum phosphides have sufficient basicity to bind to chromium and replace NMe_3. The reactions of $Cr(CO)_6$, $Cr(CO)_5(CH_3CN)$, and $Cr(CO)_5(THF)$ with organoaluminum phosphides suggest that the aluminum–phosphorus bond has a high propensity to undergo reactions with compounds that allow the Al–P bond to be replaced by the stronger bonds of aluminum and phosphorus to first-row elements. We plan to continue our efforts to clarify earlier work on organoaluminum phosphides and to investigate other possible routes for synthesizing their transition-metal derivatives. The extension of this work to the related gallium and indium derivatives is also in progress.

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Registry No. $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$, 84558-22-5; $(Me_3SiCH_2)_2AlPPh_2$, 84537-82-6; $Cr(CO)_5NMe_3$, 15228-26-9; Cr, 7440-47-3; P, 7723-14-0; Al, 7429-90-5.

Supplementary Material Available: Tables I-S–VI-S, showing observed and calculated structure factor amplitudes, calculated hydrogen atom positions, anisotropic thermal parameters, carbon–carbon distances, C–C–C angles, and least-squares planes (33 pages). Ordering information is given on any current masthead page.

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