Main Group Compounds as Amphoteric Ligands to Transition Metals. Synthesis and Molecular Structure of $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$

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Received July 8, 1996[⊗]

The reactivities of the group 13 compounds, $R_2MCH_2PPh_2$ and R_2MPPh_2, as amphoteric ligands to transition metals have been investigated. The ligands $R_2MCH_2PPh_2$ ($R = CH_2CMe_3$, CH_2SiMe_3; $M = Ga$, In) reacted readily with $Cr(CO)_5NMe_3$ in benzene solution to form $Cr(CO)_5[PPh_2CH_2MR_2{\cdot}NMe_3]$, whereas for ligands of the type R_2MPPh_2 ($R = CH_2CMe_3$, CH_2SiMe_3; $M = Al$, Ga, In), only the two aluminum compounds and $(Me_3CCH_2)_2GaPPh_2$ formed isolable products of the type $Cr(CO)_5[PPh_2MR_2{\cdot}NMe_3]$. However, the gallium and indium ligands with (trimethylsilyl)methyl substituents $(Me_3SiCH_2)_2MPPh_2$ reacted with $NEt_4M_T(CO)_5Cl$ ($M_T = Cr$, Mo, W) to form products of the type $NEt_4M_T(CO)_5[PPh_2MR_2Cl]$. All new compounds were characterized by their physical properties, C and H analyses, and ^1H and ^{31}P NMR and IR spectral properties. The identity of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ was further confirmed by the subsequent identification of products from reactions with anhydrous HCl and with MeI. In addition, $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$ was characterized by an X-ray structural study.

Compounds of the type $R_2MER'_2$ (M = group 13 element, E = group 15 element) are amphoteric and have the potential to be ligands to transition metals. The goal of such a compound[1] was realized when $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$ was prepared from $Cr(CO)_5NMe_3$ and$(Me_3SiCH_2)_2AlPPh_2$ in benzene and was fully characterized. The preparative reaction was surprisingly slow at room temperature, as significant quantities of product were not observed by NMR spectroscopy until after approximately 9 h of reaction time had elapsed after 2 M solutions of reactants had been combined. When the potential amphoteric ligand was Et_2AlPPh_2, no transition metal derivative was formed.[1] The difference in reactivity between the two amphoteric ligands was attributed to their different degrees of association in solution. The compound $(Me_3SiCH_2)_2AlPPh_2$ exists as a monomer−dimer equilibrium mixture[2] in benzene solution, whereas Et_2AlPPh_2 is a dimer.[2,3] As more examples of aluminum−, gallium−, and indium−phosphorus derivatives with different degrees of association and with different types of bonding are now available, additional reactions with $Cr(CO)_5NMe_3$ have been investigated. These main group amphoteric compounds have also been reacted with $NEt_4M_T(CO)_5X$ ($M_T = Cr$, Mo,W; X = Cl, Br) in benzene in order to learn more about their reactivity patterns.

The potential ligands with the empirical formulas $(Me_3CCH_2)_2AlPPh_2$,[4] $(Me_3SiCH_2)_2GaPPh_2$,[5] $(Me_3CCH_2)_2GaPPh_2$,[5] $(Me_3SiCH_2)_2InPPh_2$,[6] and $(Me_3CCH_2)_2InPPh_2$[5,6] were combined with $Cr(CO)_5NMe_3$ in benzene. However, only two of these compounds reacted to form the isolable products, $Cr(CO)_5[PPh_2Al(CH_2CMe_3)_2{\cdot}NMe_3]$ and $Cr(CO)_5[PPh_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$. These two

$$\tfrac{1}{2}[(Me_3CCH_2)_2MPPh_2]_2 + Cr(CO)_5NMe_3 \rightarrow Cr(CO)_5[PPh_2M(CH_2CMe_3)_2{\cdot}NMe_3] \quad (1)$$
$$(M = Al,\ Ga)$$

new transition metal derivatives were characterized by their physical properties, C and H analyses, and their ^1H and ^{31}P NMR and IR spectra. A comparison of the spectral data for these new compounds with those previously observed for $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$, a compound which had been characterized by X-ray crystallography,[1] confirmed the identity of the new products. It is noteworthy that, even though $(Me_3CCH_2)_2AlPPh_2$ exists as a dimer in benzene solution[4] according to cryoscopic molecular weight studies, it is significantly more reactive with $Cr(CO)_5NMe_3$ than is $(Me_3SiCH_2)_2AlPPh_2$, a monomer−dimer equilibrium mixture.[2] Furthermore, $(Me_3CCH_2)_2GaPPh_2$ is also a dimer[5] and is reactive with $Cr(CO)_5NMe_3$, while $(Me_3SiCH_2)_2GaPPh_2$,[5] $(Me_3CCH_2)_2InPPh_2$,[5,6] and $(Me_3SiCH_2)_2InPPh_2$[6] are monomer−dimer equilibrium mixtures in benzene solutions and are unreactive. These observations suggest that the Lewis acidity of the main group moiety is more important than the degree of association. The group 13 moiety apparently ties up the trimethylamine so that the phosphorus can react with the transition metal.

Another class of group 13−15 compounds which we have previously prepared and fully characterized and

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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S0276-7333(96)00547-X CCC: $12.00

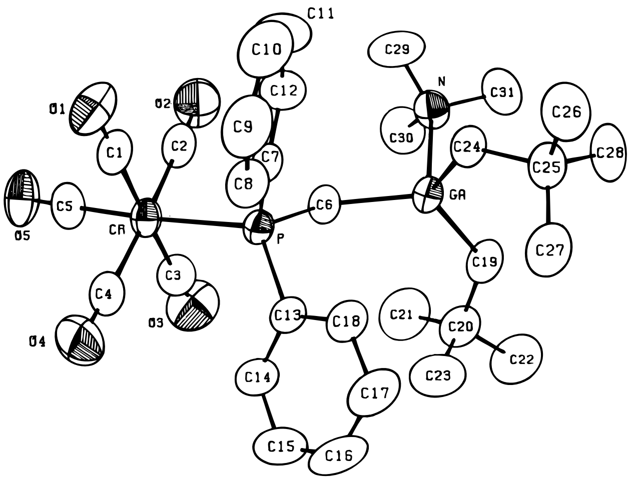

Figure 1. Molecular geometry of $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2 \cdot NMe_3]$. ORTEP diagram for non-hydrogen atoms and with hydrogen atoms omitted for clarity.

which can function as an amphoteric ligand to a transition metal is $R_2MCH_2PPh_2$. All four of the compounds which were investigated (M = Ga, In; R = CH_2CMe_3, CH_2SiMe_3)[7] reacted readily with $Cr(CO)_5NMe_3$ to form compounds of the type $Cr(CO)_5[PPh_2CH_2MR_2 \cdot NMe_3]$. Even though these potential ligands are dimers in benzene solution, all were more reactive than $(Me_3CCH_2)_2GaPPh_2$. For example, when $[(Me_3CCH_2)_2GaCH_2PPh_2]_2$ was combined with excess $Cr(CO)_5NMe_3$ in benzene at 20 °C, reaction was complete in 30 h, whereas when the reactant was $(Me_3CCH_2)_2GaPPh_2$, the ratio of product to reactant was estimated by ^1H NMR spectroscopy to be only 4.5:1 after 47 h. The general trend for the reactivity of the $R_2MCH_2PPh_2$ species follows the relative Lewis acidity of the group 13 moiety, with $(Me_3CCH_2)_2GaCH_2PPh_2$ being the most reactive of the four compounds studied, whereas $(Me_3SiCH_2)_2InCH_2PPh_2$ was least reactive. There are two possible reasons for the increased Lewis acidity and, in turn, the increased reactivity of $R_2MCH_2PPh_2$ in comparison with that for R_2MPPh_2. The insertion of the methylene group between the group 13 metal and phosphorus reduces the steric bulk around both the Lewis acid and base sites in the ligand and also eliminates any possibility for π-bonding between the group 13 metal and phosphorus.

Table 1. Important Interatomic Distances (Å) and Angles (deg) for $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2) \cdot NMe_3]$

(A) Bond Distances (Å)

atoms	distance	atoms	distance
Ga−N	2.235(3)	Ga−C(6)	2.027(3)
Ga−C(19)	2.005(3)	Ga−C(24)	1.993(3)
Cr−P	2.409(1)	Cr−C(1)	1.889(4)
Cr−C(2)	1.854(4)	Cr−C(3)	1.888(5)
Cr−C(4)	1.903(4)	Cr−C(5)	1.843(4)
P−C(6)	1.812(3)	P−C(7)	1.815(3)
P−C(13)	1.835(3)	O(1)−C(1)	1.134(4)
O(2)−C(2)	1.150(4)	O(3)−C(3)	1.136(5)
O(4)−C(4)	1.137(4)	O(5)−C(5)	1.147(4)
N−C(29)	1.476(5)	N−C(30)	1.462(5)
N−C(31)	1.462(5)		

(B) Bond Angles (deg)

atoms	angle	atoms	angle
N−Ga−C(6)	95.1(1)	Ga−C(6)−P	129.8(2)
C(6)−Ga−C(19)	118.8(1)	P−C(7)−C(12)	120.3(3)
C(6)−Ga−C(24)	115.2(1)	N−Ga−C(19)	99.3(1)
P−Cr−C(1)	90.7(1)	N−Ga−C(24)	100.4(1)
C(1)−Cr−C(2)	88.3(2)	C(19)−Ga−C(24)	119.8(1)
C(1)−Cr−C(3)	178.0(2)	P−Cr−C(2)	87.5(1)
P−Cr−C(4)	93.5(1)	P−Cr−C(3)	88.9(1)
C(2)−Cr−C(4)	177.5(2)	C(2)−Cr−C(3)	89.7(2)
P−Cr−C(5)	175.9(1)	C(1)−Cr−C(4)	89.4(2)
C(2)−Cr−C(5)	88.4(2)	C(3)−Cr−C(4)	92.7(2)
C(4)−Cr−C(5)	90.6(2)	C(1)−Cr−C(5)	89.0(2)
Cr−P−C(7)	109.1(1)	C(3)−Cr−C(5)	91.4(2)
Cr−P−C(13)	118.6(1)	Cr−P−C(6)	113.7(1)
C(7)−P−C(13)	103.3(2)	C(6)−P−C(7)	106.8(2)
Ga−N−C(30)	110.5(2)	C(6)−P−C(13)	104.2(2)
Ga−N−C(31)	108.7(2)	Ga−N−C(29)	112.2(2)
C(30)−N−C(31)	108.7(3)	C(29)−N−C(30)	108.3(3)
Cr−C(2)−O(2)	178.6(4)	C(29)−N−C(31)	108.3(3)
Cr−C(4)−O(4)	176.8(4)		

Recrystallization of $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2 \cdot NMe_3]$ from a saturated pentane solution at −25 °C afforded crystallographic quality crystals. The crystal consisted of discrete molecular units. There were no abnormally close contacts in the unit cell. The labeling of the atoms is given in Figure 1, and the significant interatomic bond distances and angles are listed in Table 1. The Cr−P bond distance is 2.409(1) Å, which is shorter than the corresponding distances in $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$[1] of 2.482(1) Å and in $Cr(CO)_5PPh_3$[8] of 2.422(1) Å but longer than the distance in $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2 \cdot NMe_3]$[9] of 2.383(6) Å. The Ga−N distance of 2.235(3) Å is similar to that observed for the trineopentylgallium−amine adduct,[10] $Ga(CH_2CMe_3)_3 \cdot NMe_2C_2H_4NMe_2 \cdot Ga(CH_2CMe_3)_3$ (2.241(9) Å), but longer than the distances observed for other trimethylgallium−amine adducts, 2.139(17) and 2.138(9) Å for the trimethylgallium−utropine adducts[11] $Me_3Ga \cdot C_6H_{12}N_4$ and $(Me_3Ga)_2 \cdot C_6H_{12}N_4$, respectively, and 2.012(4) Å for $Me_3Ga \cdot NH_2$(t-Bu).[12] Another noteworthy feature of the structure of $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2 \cdot NMe_3]$ relates to the angular relationship between the three carbon atoms and the nitrogen atom bonded to gallium. The two α-carbon atoms of the two neopentyl groups and the methylene carbon atom bonded to phosphorus have angles which are representative of distorted trigonal planar geometry rather than tetrahedral, as C(6)−Ga−C(24) = 115.2(1)°, C(6)−Ga−C(19) = 118.8(1)°, and C(19)−Ga−C(24) = 119.8(1)°. The carbon−gallium−nitrogen angles are, in turn, smaller than the normal tetrahedral angle, with N−Ga−C(6) = 95.1(1)°, N−Ga−C(19) = 99.3(1)°, and N−Ga−C(24) = 100.4(1)°. The angles between the six ligands around chromium are typical of a slightly distorted octahedral complex.

The reactions of $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$ with a different transition metal derivative, $NEt_4M_T(CO)_5Cl$ (M_T = Cr, Mo, W), in benzene were also investigated, and compounds of the type $NEt_4M_T(CO)_5[PPh_2M(CH_2SiMe_3)_2Cl]$ were readily formed. Each

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of the reactions appeared to be complete within minutes of mixing the reagents, as indicated by the disappearance of the initially insoluble transition metal reagent. Products were typically isolated as waxy solids or viscous oils, with the exception of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$, which was obtained as a light yellow crystalline powder in ~80% yield. The formation of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ is fully supported by C and H elemental analyses as well as by ^1H, ^{31}P, and ^{13}C NMR and IR spectral data. Further confirmation of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ with a bond between chromium and phosphorus was obtained by investigating its reaction chemistry with HCl and MeI. When $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ was reacted with anhydrous HCl in a 1:2 mole ratio, respectively, the isolated products were $Cr(CO)_5PPh_2H$ and $SiMe_4$ (eq 2).

$$NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl] + 2HCl \rightarrow 2SiMe_4 + Cr(CO)_5PPh_2H + \text{“}NEt_4InCl_4\text{”} \quad (2)$$

The product $Cr(CO)_5PPh_2H$ was formed in near quantitative yield as based on ^{31}P NMR spectral data but was isolated in only 69% yield. The isolated sample of $Cr(CO)_5PPh_2H$ was identified by comparing its melting point and IR spectrum with the literature values.[13] The $SiMe_4$ was isolated in 82% yield and was identified by its ^1H NMR spectrum. No attempt was made to isolate an indium-containing product. When $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ was reacted with MeI (eq 3), the only phosphorus-containing product was $Cr(CO)_5PPh_2Me$[14] according to the ^{31}P NMR spectrum of the product mixture.

$$NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl] + MeI \rightarrow Cr(CO)_5PPh_2Me + \text{“}NEt_4In(CH_2SiMe_3)_2(Cl)(I)\text{”} \quad (3)$$

However, the isolated product which was thought to be $Cr(CO)_5PPh_2Me$ was not pure. The IR spectrum of the isolated product exhibited all absorption bands expected for $Cr(CO)_5PPh_2Me$[14] but also had an extra band at 2035 cm^{-1}, a band observed in the IR spectrum of the starting compound, $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$. No attempt was made to isolate and characterize an indium-containing product from the reaction. It is noteworthy that a cryoscopic molecular weight study of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ in benzene suggested the existence of an equilibrium between very highly associated species. When the calculated concentration of the solution as based on the empirical formula was 0.0990 *m*, the observed degree of association was 5.99, whereas when the solution was 0.0342 *m*, the association was 2.69. These unusual degrees of association might serve to provide an explanation for the very large, unsolvable unit cell which was determined by the preliminary X-ray structural study of the molecule.

Experimental Section

All of the compounds which contain group 13 elements were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. All starting group 13−15 compounds and all transition metal reactants were prepared according to literature methods. Solvents were dried according to conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. The ^1H NMR spectra were recorded at 400 MHz by using a Varian VXR-400 spectrometer or at 90 MHz by using a Varian Model 390 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 and C_6H_6 at δ 7.15. The ^{31}P NMR spectra were recorded at 161.9 MHz by using either a Varian VXR-400 spectrometer or at 109.16 MHz by using a JEOL Model FX 270 spectrometer. Chemical shifts are referenced to 85% H_3PO_4 at δ 0.00. Standard abbreviations are used to report the multiplicities of the lines. All samples for NMR spectra were contained in flame-sealed NMR tubes. Infrared spectra were recorded as solutions by using 0.5 mm matched cells with NaCl windows or as Nujol mulls between KBr plates with a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with standard abbreviations. Melting points were observed in sealed capillaries and are uncorrected.

Synthesis of $Cr(CO)_5[PPh_2Al(CH_2CMe_3)_2\cdot NMe_3]$. A flask equipped with Solv-Seal joints and a Teflon valve was charged with 0.260 g (1.04 mmol) of $Cr(CO)_5NMe_3$,[15] 0.332 g (0.937 mmol) of $(Me_3CCH_2)_2AlPPh_2$, and 15 mL of benzene. The resulting solution was initially yellow-orange and then lightened to pale yellow after being stirred for 48 h. The benzene was then removed by vacuum distillation to leave a fluffy light yellow solid. This solid was recrystallized from a 5:1 pentane/benzene mixture to give 0.100 g (0.165 mmol, 17.6% yield based on $Cr(CO)_5NMe_3$) of $Cr(CO)_5[PPh_2Al(CH_2CMe_3)_2\cdot NMe_3]$ as a yellow, crystalline solid: mp 116−117 °C dec; ^1H NMR (C_6H_6) δ 1.59 (s, 9H, NMe), 1.19 (s, 9H, CMe), 0.86 (s, 4H, CH_2); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −27.9 (s); IR (ν_{CO}, cm^{-1}, Nujol mull) 2052 (m), 1980 (m), 1945 (m, sh), 1935 (vs), 1920 (s). Anal. Calcd: C, 59.50; H, 6.82. Found: C, 59.43; H, 6.99. The compound contained in a sealed vial under vacuum decomposed at room temperature over time (4 months).

Synthesis of $Cr(CO)_5[PPh_2Ga(CH_2CMe_3)_2\cdot NMe_3]$. A 5 mm NMR tube was charged with 0.137 g (0.344 mmol) of $(Me_3CCH_2)_2GaPPh_2$, 0.310 g (0.520 mmol) of $Cr(CO)_5NMe_3$, and ~0.7 mL of benzene. After the mixture was warmed to ambient temperature, an orange solution was present. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded prior to and after heating the reaction mixture at 55 °C for 5 h. After 5 h at 55 °C, a yellow solution was present. Cooling of this solution to ambient temperature afforded yellow crystals of $Cr(CO)_5[PPh_2Ga(CH_2CMe_3)_2\cdot NMe_3]$: mp 132−138 °C (glass transition), 146−148 °C dec; IR (ν_{CO}, cm^{-1}, pentane) 2063 (w), 1997 (vw), 1953 (vs), 1945 (s), 1917 (vw); initial NMR spectrum prior to heating, ^1H NMR (C_6H_6) δ 1.04 (s, 18H, CMe_3), 1.22 (s, 0.7H), 1.33 (t, $^3J_{PGaCH} = 3.6$ Hz, 3.2H, CH_2), 1.80 (s, 10H, $CrNMe_3$), 1.94 (s, 0.70H, $GaNMe_3$), and $^{31}P\{^1H\}$ NMR (C_6H_6) δ 30.7 (s, 1.0), −26.0 (s, 42.7, $(Me_3CCH_2)_2GaPPh_2$); 1 h, 40 min at 55 °C, ^1H NMR (C_6H_6) δ 1.06 (s, 2.4H, CH_2), 1.13 (s, 18H), 1.22 (s), 1.72 (s, 7.9H, $CrNMe_3$), 1.80 (s, 2.0H, $GaNMe_3$), and $^{31}P\{^1H\}$ NMR (C_6H_6) δ 30.7 (s, 0.59), −18.3 (s, 15.8, $Cr(CO)_5[PPh_2Ga(CH_2CMe_3)_2\cdot NMe_3]$, −26.0 (s, 1.0, $(Me_3CCH_2)_2GaPPh_2$) [Additional ^{31}P NMR resonances of very low intensity at 0.5, 27.9, 30.7, 33.2 and 43.3 ppm were observed but could not be identified. The ratio of the intensity of the most intense line at 30.7 ppm relative to the lines at −18.3 and −26.0 ppm was 1.00:1.7:26.9, respectively.]; 5 h at 55 °C, ^1H NMR (C_6H_6) δ 1.05 (s, 2.1H, CH_2), 1.13 (s, 18H), 1.23 (s), 1.70 (s, 7.8H, $CrNMe_3$), 1.80 (s, 2.5H, $GaNMe_3$), and $^{31}P\{^1H\}$ NMR (C_6H_6) δ 30.7 (s, 0.04), −18.3 (s, 22.8, $Cr(CO)_5[PPh_2Ga(CH_2CMe_3)_2\cdot NMe_3]$) [The low-intensity resonances at 0.5, 27.9, 30.7, 33.2, and 43.3 ppm were still present but with little change in intensity from the previous spectrum.].

Synthesis of $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2\cdot NMe_3]$. A flask equipped with a Teflon valve was charged with 0.576

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g (1.26 mmol) of $(Me_3CCH_2)_2GaCH_2PPh_2$, 0.456 g (1.82 mmol) of $Cr(CO)_5NMe_3$, and 15 mL of benzene. The initial mixture, an orange solution with a colorless precipitate, was heated at 60 °C with stirring for 3.5 h to form a clear yellow solution. The benzene was removed by vacuum distillation to leave a light-yellow oil. This oil was heated at 60 °C for 15 h with continuous evacuation and then 30 mL pentane was added by vacuum distillation. The resulting light yellow solution was stirred for ~30 min, and the pentane was removed by vacuum distillation and discarded. This procedure of adding and removing pentane was repeated 3 times until a pale yellow solid with only a trace of oil remained. Evacuation for another 18 h was followed by the addition of 45 mL of pentane and heating with a warm water bath. The resulting mixture was filtered with a coarse frit to remove a colorless precipitate and leave a yellow solution. Cooling of the solution to −25 °C afforded pale yellow crystals of $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$ (0.330 g, 0.498 mmol, 39.4% yield based on $(Me_3CCH_2)_2GaCH_2PPh_2$). These crystals were suitable for the X-ray structural study: mp 95.0−96.5 °C; ^1H NMR (C_6H_6) δ 0.55 (s, 4H, $-CH_2-$), 0.96 (s, 18H, CMe_3), 1.58 (s, 6H, NMe_3), 1.71 (s, 2H, $-CH_2P-$); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 48.2 (s); IR (pentane, ν_{CO}, cm^{-1}) 2060 (s), 1989 (sh), 1980 (s), 1969 (vs), 1956 (sh). Anal. Calcd: C, 56.21; H, 6.54; P, 4.68. Found: C, 55.87; H, 6.72; P, 4.99.

Synthesis of $Cr(CO)_5[PPh_2CH_2In(CH_2CMe_3)_2{\cdot}NMe_3]$. The synthesis of the compound was achieved by using 0.536 g (1.10 mmol) of $(Me_3CCH_2)_2InCH_2PPh_2$, 0.439g (1.75 mmol) of $Cr(CO)_5NMe_3$, and 20 mL of benzene and the procedure described for the previous compound. Pale yellow crystals of $Cr(CO)_5[PPh_2CH_2In(CH_2CMe_3)_2{\cdot}NMe_3]$ (0.156g, 0.211 mmol, 19.2% based on $(Me_3CCH_2)_2InCH_2PPh_2$) were obtained upon cooling a saturated pentane solution to −30 °C: mp 120−122 °C; ^1H NMR (C_6H_6) δ 0.64 (s, 4H, $-CH_2-$), 1.03 (s, 18H, $-CMe_3$), 1.43 (d, $J = 4.5$ Hz, 2H, $-CH_2P-$), 1.68 (s, 9H, NMe_3) [In addition, there were low-intensity lines at 0.86 and 1.26 ppm which are consistent with a pentane impurity, but these lines were not conclusively identified.]; IR (pentane, ν_{CO}, cm^{-1}) 2058 (m), 1990 (w), 1980 (w), 1955 (sh), 1943 (vs), 1935 (vs), 1870 (w, br). Anal. Calcd: C, 52.63; H, 6.13. Found: C, 52.24; H, 5.43.

Reaction of $R_2MCH_2PPh_2$ with $Cr(CO)_5NMe_3$ (M = Ga, R = CH_2CMe_3, CH_2SiMe_3; M = In, R = CH_2SiMe_3) As Monitored by ^{31}P NMR Spectroscopy. All reactions were carried out in 10 mm NMR tubes using the following procedure. Weighed quantities of reactants were added to the tube, and then ~1.9 mL of benzene was added by vacuum distillation. The tube was sealed by fusion, and the ^{31}P NMR spectrum recorded after the sample was held at room temperature for the time indicated.

$(Me_3CCH_2)_2GaCH_2PPh_2$ (0.0402 g, 0.0907 mmol), $Cr(CO)_5NMe_3$ (0.0260 g, 0.104 mmol): 20 min, −10.2 (s, $(Me_3CCH_2)_2GaCH_2PPh_2$); 38 h, −10.1 (s, 4.6, $(Me_3CCH_2)_2GaCH_2PPh_2$), 48.1 (s, 1.0, $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$.

$(Me_3SiCH_2)_2GaCH_2PPh_2$ (0.0509 g, 0.118 mmol), $Cr(CO)_5NMe_3$ (0.0297 g, 0.118 mmol): 37 h, −10.2 (s, 4.7, $(Me_3SiCH_2)_2GaCH_2PPh_2$), 46.3 (s, 1.0, $Cr(CO)_5[PPh_2CH_2Ga(CH_2SiMe_3)_2{\cdot}NMe_3]$).

$(Me_3SiCH_2)_2InCH_2PPh_2$ (0.0596 g, 0.122 mmol), $Cr(CO)_5NMe_3$ (0.0319 g, 0.127 mmol): 38 h, −9.8 (s, 8.1, $(Me_3SiCH_2)_2InCH_2PPh_2$), 47.5 (s, 1.0, $Cr(CO)_5[PPh_2CH_2In(CH_2SiMe_3)_2{\cdot}NMe_3]$).

X-ray Data Collection, Structure Determination, and Refinement for $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$. A yellow fragment of a single crystal of the title compound was mounted under argon in a thin-walled glass capillary and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure were carried out in the centric space group $P\bar{1}$. A summary of data collection parameters is given in Table 2.

Table 2. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $Cr(CO)_5[PPh_2CH_2Ga(CH_2CMe_3)_2{\cdot}NMe_3]$

molecular formula	$CrGaPNC_{31}H_{43}O_5$
color/shape	yellow/irregular
MW	662.4
crystal system	triclinic
space group	$P\bar{1}$
temp, °C	20
a, Å	10.768(8)
b, Å	10.875(8)
c, Å	15.155(8)
α, deg	90.65(5)
β, deg	104.66(6)
γ, deg	90.38(6)
V, Å^3	1716.8
Z	2
D_{calc}, cm^{-1}	1.28
μ_{calc}, cm^{-1}	11.2
diffractometer/scan	Enraf-Nonius Cad4/$\theta - 2\theta$
range of relative transm factors, %	88/100
radiation, graphite monochromator	Mo Kα ($\lambda = 0.710\ 73$)
max. crystal dimensions, mm	0.30 × 0.40 × 0.55
reflections measured	6002
2θ range, deg	$2 \le 2\theta \le 50$
range of h,k,l	+12,±12,±18
reflections observed [$F_o \ge 5\sigma(F_o)$]	4638
computer programs	SHELX[17]
structure solution	MULTAN[18]
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.038
R_w	0.039
largest feature final diff map	0.5 e$^-$ Å^{-3}

Least-squares refinement with isothermal parameters led to $R = 0.095$. The phenyl and methylene hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atoms and allowed to ride on that atom, with B fixed at 5.5 Å^2. The methyl hydrogen atoms were located from a difference Fourier map and included with fixed contributions ($B = 5.5$ Å^2). Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.038$ and $R_w = 0.039$.

Synthesis of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$. A flask was charged with 0.530 g (1.12 mmol) of $(Me_3SiCH_2)_2InPPh_2$ and 0.400 g (1.12 mmol) of $NEt_4Cr(CO)_5Cl$.[16−18] After 30 mL of benzene was transferred to the flask by vacuum distillation, the contents were warmed to room temperature, and a light yellow solution formed within approximately 10 min. The mixture was stirred for 12 h, and then the benzene was removed by vacuum distillation to leave a material which was a mixture of a light yellow oil and light yellow solid. This material was washed 4 times with 20 mL of pentane. After the pentane was removed by vacuum distillation, the product was evacuated for 1 h to give a light yellow solid, 0.755 g (0.907 mmol, 80.9% yield) of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$: mp 102−105 °C (glass), 110−120 °C (becomes translucent), 140−160 °C dec (yellow to red glass); cryoscopic molecular weight, fw 832 (obsd molality, obsd mol wt, association): 0.0165, 4983, 5.99; 0.0142, 3652, 4.39; 0.0130, 2904, 3.49; 0.0177, 3536, 4.25; 0.0140, 2796, 3.36; 0.0127, 2238, 2.69; ^1H NMR (C_6H_6) δ 2.15 (q, 8H, NCH_2), 0.44 (t, 12H, NCH_2CH_3), 0.36 (s, 18H, $SiCH_3$), 0.13 (t, 4H, $InCH_2$); ^{13}C NMR (C_6H_6) δ 226.14 (d, $J = 7$ Hz, *trans*-CO), 220.21 (d, $J = 8.8$ Hz, *cis*-CO), 54.01 (t, NCH_2CH_3), 8.66 (s, NCH_2CH_3), 4.61 (s, $SiCH_3$), $InCH_2$ not observed; ^{31}P NMR (C_6H_6) δ −18.3 (s); IR (ν_{CO}, THF solution) 2065 (w), 2050 (m), 2035 (w, sh, impurity), 1937 (s, sh), 1927 (vs), 1890 (m, sh). Anal. Calcd: C, 47.63; H, 6.30. Found: C, 47.53; H, 6.33.

Reaction of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ with MeI. A 100 mL flask was charged with 0.555 g (0.667 mmol)

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(18) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368.

of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$, and then excess MeI (15 mL) was added by vacuum distillation. The resulting solution was stirred for 2.5 h at room temperature, and then all volatile components were removed by vacuum distillation to leave a sticky, yellow solid. The sticky nature of this solid made it impossible to weigh the product. Thus, the solid was dissolved in benzene for spectroscopic characterization; ^{31}P NMR δ 36.0 (lit.[14] $Cr(CO)_5PPh_2Me$, ^{31}P NMR δ 35.0 ppm); IR (ν, cm^{-1}, THF) 2064 (m), 2035 (w), 1980 (w), 1947 (s, sh), 1940 (vs) 1885 (w) (lit.[14] $Cr(CO)_5PPh_2Me$ IR (ν, cm^{-1}, THF) 2064 (s), 1981 (vw), 1947 (sh), 1939 (vs)).

Reaction of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ with HCl. A flask was charged with 0.833 g (1.00 mmol) of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ and 25 mL of benzene. Anhydrous HCl (2.04 mmol) was then condensed into the flask by using a liquid N_2 bath. The flask was warmed to room temperature, and the resulting solution was stirred for 0.5 h. The $SiMe_4$ was separated by fractionation through two −78 °C traps and collected in a −196 °C trap. The amount of $SiMe_4$ was calculated from PVT measurements (1.64 mmol, 82% based on $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$). The remaining solid was extracted 8 times with 20 mL of pentane to give 0.260 g of $Cr(CO)_5PPh_2H$ (0.687 mmol, 68.7% based on $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$): mp 56−59 °C (lit.[13] 55−65 °C); IR (ν, cm^{-1}, Nujol mull) 2330 (w), 2060 (s), 1982 (m), 1907 (s) (lit.[13] IR (ν, cm^{-1}, Nujol mull) 2325 (w), 2068 (m), 1979 (m), 1937 (vs), 1900 (sh)).

Synthesis of $NEt_4M_T(CO)_5[PPh_2M(CH_2SiMe_3)_2Cl]$ (M_T = Cr, Mo, W; M = Ga; M_T = Mo, W; M = In). All compounds were prepared according to the following procedure. A flask was charged with 1.0 mmol of the transition metal carbonyl chloride, 1.0 mmol of the main group metal phosphide and 15 mL of benzene. A clear solution formed approximately 10 min after the benzene was added to the reactants. After the solution was stirred for 24 h, the benzene was removed by vacuum distillation to leave a thick viscous oil or waxy solid which was resistant to crystallization. Some purification was achieved by dissolving the product in 20 mL of benzene and then adding 10 mL of pentane. This mixture was stirred for 1 h and then allowed to settle into two layers, a dark brown lower layer and a light yellow upper layer. The light yellow upper layer was removed in the drybox by using a syringe, whereas the brown lower layer was discarded without further study. The solvent was removed by vacuum distillation to leave a viscous oil, which turned into a sticky, waxy yellow material after continuous evacuation for 12 h. This product was characterized by IR and ^{31}P NMR spectroscopy. The sticky nature of the products precluded a reliable estimate of mass and percent yield. Attempts to purify these compounds by thin-layer or column chromatography resulted in apparent hydrolysis with formation of $M_T(CO)_5PPh_2H$[13] (M_T = Cr, Mo, W).

$NEt_4M_T(CO)_5[PPh_2M(CH_2SiMe_3)_2Cl]$ (M_T, M). Cr, Ga: ^{31}P NMR δ −14.9; IR (ν, cm^{-1}, C_6H_6) 2060 (w), 2042 (w), 1940 (m), 1920 (vs), 1890 (s); IR (ν, cm^{-1}, THF) 2060 (w), 2040 (w), 1940 (m), 1925 (vs), 1905 (s), 1895 (s, sh). Mo, Ga: ^{31}P NMR δ −25.8; IR (ν, cm^{-1}, THF) 2075 (w), 2057 (m), 1950 (m, sh), 1930 (vs), 1893 (s). W, Ga: ^{31}P NMR δ −42.4 (J_{W-P} = 156 Hz); IR (ν, cm^{-1}, THF) 2070 (w), 2058 (m), 1940 (vs), 1925 (s, sh), 1908 (s), 1870 (m, sh). Mo, In: ^{31}P NMR δ −31.3; IR (ν, cm^{-1}, THF) 2075 (w), 2060 (m), 1950 (m, sh), 1932 (vs), 1895 (m). In, W: ^{31}P NMR δ −49.0 (J_{W-P} = 166 Hz); IR (ν, cm^{-1}, THF) 2070 (w), 2058 (m), 1940 (m, sh), 1920 (vs), 1890 (m).

Acknowledgment. This work was supported in part by the Office of Naval Research (O.T.B.). The extensive efforts by Professor Melvyn R. Churchill to determine the structure of $NEt_4Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$ by X-ray crystallography were greatly appreciated.

Supporting Information Available: Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms (5 pages). Ordering information is given on any current masthead page.

OM960547F