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 mesityl rings. The yellow crystal of $[(CO)_3MoMes]GaMes_2$ which cocrystallized with a
 benzene solvent molecule consisted of discrete molecules with no abnormally close inter-
 molecular interactions. The compound crystallized in the triclinic space group $P\bar{1}$ with
 $a = 9.171(1)$, $b = 12.702(2)$, $c = 14.649(3)\text{\AA}$, $\alpha = 81.16(2)$, $\beta = 79.03(1)$, $\gamma = 109.82(1)^\circ$,
 $V = 1531.3(5)\text{\AA}^3$ and $Z = 2$ (formula units). The structure was refined to $R(F) = 4.7\%$ for
 2148 reflections. The yellow compound $[(CO)_3MoMes]_2GaMes$ crystallized in the orthorhombic
 space group $Pbcn$ with $a = 17.587(3)$, $b = 12.186(2)$, $c = 15.497(3)\text{\AA}$, $V = 3321.4(11)\text{\AA}^3$ and
 $Z = 4$ (formula units). This structure refined to $R(F) = 4.6\%$ for 1254 reflections. These
 new arene complexes react with anhydrous HCl in either DME or THF solution. The gallium-
 mesityl carbon bond to the uncomplexed mesityl ring was preferentially cleaved.

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The Chemistry of Mesitylgallium(III) Derivatives as

Arene Ligands in Metal Carbonyl Complexes.

Crystal and Molecular Structures of $[(\text{CO})_3\text{Mo}(\eta^6\text{-C}_6\text{Me}_3\text{H}_2)]\text{Ga}(\text{C}_6\text{Me}_3\text{H}_2)_2$
and $[(\text{CO})_3\text{Mo}(\eta^6\text{-C}_6\text{Me}_3\text{H}_2)]_2\text{Ga}(\text{C}_6\text{Me}_3\text{H}_2)$

by

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Eugene A. Zarate and Claire A. Tessier-Youngs

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The Chemistry of Mesitylgallium(III) Derivatives as
Arene Ligands in Metal Carbonyl Complexes.

Crystal and Molecular Structures of $[(CO)_3Mo(\eta^6-C_6Me_3H_2)]Ga(C_6Me_3H_2)_2$
and $[(CO)_3Mo(\eta^6-C_6Me_3H_2)]_2Ga(C_6Me_3H_2)$

by

O. T. Beachley, Jr.*^{1a}, T. L. Royster, Jr.^{1a}, Wiley J. Youngs*^{1b},
Eugene A. Zarate^{1b} and Claire A. Tessier-Youngs^{1b}.

Abstract

The first examples of arene-group 6 metal tricarbonyl complexes which have gallium containing substituents bonded to an arene ring, $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$, $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$, $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2 \text{ DME}$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2 \text{ DME}$ (Mes = $\text{C}_6\text{Me}_3\text{H}_2$ = mesityl) have been prepared and characterized by elemental analyses, IR and ^1H NMR spectroscopy and reactions with hydrogen chloride. X-ray structural studies have defined the nature of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ in the solid state. Both complexes can be described as GaMes_3 molecules with either one or two $\text{Mo}(\text{CO})_3$ units bonded in η^6 fashion to mesityl rings. The yellow crystal of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ which cocrystallized with a benzene solvent molecule consisted of discrete molecules with no abnormally close intermolecular interactions. The compound crystallized in the triclinic space group $P\bar{1}$ with $a = 9.171(1)$, $b = 12.702(2)$, $c = 14.649(3)\text{\AA}$, $\alpha = 81.16(2)$, $\beta = 79.03(1)$, $\gamma = 109.82(1)^\circ$, $V = 1531.3(5)\text{\AA}^3$ and $Z = 2$ (formula units). The structure was refined to $R(F) = 4.7\%$ for 2148 reflections. The yellow compound $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ crystallized in the orthorhombic space group $Pbcn$ with $a = 17.587(3)$, $b = 12.186(2)$, $c = 15.497(3)\text{\AA}$, $V = 3321.4(11)\text{\AA}^3$ and $Z = 4$ (formula units). This structure refined to $R(F) = 4.6\%$ for 1254 reflections. These new arene complexes react with anhydrous HCl in either DME or THF solution. The gallium-mesityl carbon bond to the uncomplexed mesityl ring was preferentially cleaved.

Introduction

A variety of group 13 compounds which incorporate both Lewis acidic and basic moieties can react with transition metal complexes and be classified as amphoteric ligands. One of earliest examples of a compound with such a ligand $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{B}(\text{NMe}_2)_2]^2$, was prepared from $\text{Cr}(\text{CO})_5(\text{THF})$ and $(\text{Me}_2\text{N})_2\text{BPPH}_2$ in THF solution. Similarly, the reaction between $\text{Cr}(\text{CO})_5(\text{NMe}_3)$ and $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ in benzene solution provided $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]^3$. However, when $\text{KCr}(\text{CO})_5\text{PPh}_2\cdot 2$ dioxane was reacted with $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ in an attempt to develop a second synthetic route to transition metal complexes of amphoteric ligands⁴, the observed product had the empirical formula $\text{Cr}(\text{CO})_5[\text{PPh}_2(\text{CH}_2)_4\text{OAl}(\text{CH}_2\text{SiMe}_3)_2]$. The $(\text{CH}_2)_4\text{O}$ unit, which separated the phosphorus and aluminum atoms, arose from the cleavage of a THF solvent molecule. The Lewis acidity of the aluminum atom was clearly defined by an X-ray structural study which revealed dimeric molecules with four-membered Al_2O_2 rings. The compound $\text{Et}_2\text{AlN}(\text{t-Bu})\text{PPh}_2$ also has the Lewis acidic and basic sites separated by another atom, in this case nitrogen. This type of amphoteric ligand has been observed to initiate some unique reaction chemistry⁵ when combined with $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Me}$ or $\text{HMn}(\text{CO})_5$. A third type of amphoteric ligand utilizes a substituent on the group 13 element as a π -bonding (arene) ligand to a transition metal. To date only boron derivatives have been reported as arene ligands with neutral and anionic arylboron compounds being used to prepare group 6 transition metal tricarbonyl complexes.^{6,7} Some examples of useful neutral amphoteric ligands include $\text{PhB}(\text{NMe}_2)_2$, $\text{PhB}(\text{OMe})_2$, $\text{PhB}(\text{C}_5\text{H}_{10})^6$ and $\text{PhB}(\text{CH}_2\text{CH}(\text{Me})\text{C}_2\text{H}_4)^6$. An anionic arene-transition metal carbonyl complex⁸ is $[\text{Me}_4\text{N}][\text{Ph}_2\text{B}(\eta^6\text{-PhM}(\text{CO})_3)_2]$ ($\text{M} = \text{Cr}, \text{W}$). When an attempt was made to prepare a molybdenum derivative, an inseparable mixture of products containing two,

three and possibly four $\text{Mo}(\text{CO})_3$ units per BPh_4^- was observed⁸. The only aluminum containing compounds are derivatives of ferrocene⁹⁻¹¹, for example $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Al}_2\text{Me}_4\text{Cl})$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_3)\text{Al}_2\text{Me}_3\text{Cl}]_2$.

In this paper, we report the results of our research which was designed to utilize the mesityl ring ($\text{C}_6\text{Me}_3\text{H}_2\text{-Mes}$) on gallium(III) as a ligand in arene-transition metal tricarbonyl complexes and to understand which chemical properties of the group 13 moiety were affected by the electron withdrawing $\text{M}(\text{CO})_3$ unit ($\text{M} = \text{Cr}, \text{Mo}$). The new compounds, $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$, $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2 \cdot n\text{C}_6\text{H}_6$, $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ and $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ ($\text{Mes} = \text{C}_6\text{Me}_3\text{H}_2 = \text{mesityl group}$), have been isolated and characterized by elemental analyses, IR and ^1H NMR spectroscopy, solubility properties and reaction chemistry with hydrogen chloride and Lewis bases. Single crystal X-ray structural studies have also been used to characterize $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ and $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2 \cdot n\text{C}_6\text{H}_6$.

Experimental Section

General Data. All compounds described in this investigation were sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. Trimesitylgallium(III), GaMes_3^{12} , as well as $\text{GaMes}_2\text{Cl}^{13}$ (C_6H_6 solution) and GaMesCl_2^{13} were prepared as previously described. All solvents were purified before use. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra of solutions in appropriate solvents in 0.5 mm cells with NaCl plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with abbreviations w(weak), m(medium), s(strong), vs(very strong) and sh(shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to SiMe_4 as δ 0.00 and benzene as δ 7.13. All NMR tubes were sealed under vacuum.

Reactions of Mesityl-gallium Compounds with $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$). A typical procedure was employed for reactions of GaMes_3 , Mes_2GaCl and MesGaCl_2 with chromium or molybdenum hexacarbonyl. A specially designed apparatus was used to prevent oxidation of reaction products. The apparatus consisted of a 200 mL reaction flask equipped with a low hold-up Teflon valve which was in turn connected to a condenser with an adapter with a Teflon valve. In the drybox, the reactants were combined in the 200 mL reaction flask. The condenser was connected to reaction flask in the drybox by using silicone vacuum grease. The reaction solvent DME was vacuum distilled into the reaction flask. The adapter above the condenser was purged with argon for 15 min. Then, the valve was opened and the apparatus was filled with argon. Both Teflon valves in the apparatus remained opened to the bubbler of the argon source so that the CO produced in the reaction

could escape. The reaction flask was wrapped with aluminum foil and placed into a 110°C oil bath. After the reaction mixture was refluxed for the appropriate time, the valve on the reaction flask (not on top of the condenser) was closed and the oil bath removed. Unless otherwise specified, after the solution reached room temperature, the condenser was replaced with a medium porosity frit connected to a Schlenk flask. The apparatus was evacuated, the solution was filtered into the Schlenk flask and the solvent was removed in vacuo. The reaction product was evacuated for 16 h at 45°C to remove excess $\text{M}(\text{CO})_6$. Finally, the product was recrystallized from an appropriate solvent system.

Synthesis of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$. The complex $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ was prepared by refluxing a reaction mixture of 0.595 g (1.39 mmol) of GaMes_3 and 1.10 g (4.17 mmol) of $\text{Mo}(\text{CO})_6$ in 100 mL of DME for 24-28 h. Traces of GaMes_3 and $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ (~ 0.04 g) were removed from the crude product by washing several times with 50 mL portions of pentane. The product was then recrystallized from DME solution by slowly removing the solvent by vacuum distillation without stirring. When approximately 5 mL of DME remained, the yellow crystals were separated by filtration and then washed several times with the solvent. A yield of 0.723 g (0.918 mmol, 66.0% based on GaMes_3) of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ as a yellow crystalline product was isolated after the remaining solvent was removed in vacuo. Crystals suitable for an X-ray diffraction study were grown by layering a previously filtered saturated DME solution of the product with pentane. After standing for 16 h at room temperature, the solution was decanted away from the crystals and the solvent was removed in vacuo. **$[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$.** Yellow crystalline solid; mp decomposition begins ~ 140°C; ^1H NMR ($\text{d}^8\text{-THF}$) δ 6.82 (s, m-H, 2 H), 5.34 (s, m-H, 4 H, Mo-arene), 2.56 (s, p-Me, 6 H, Mo-arene),

2.29 (s, o-Me, 12 H, Mo-arene), 2.24 (s, o-Me, 6 H), 2.22 (s, p-Me, 3 H); IR (DME, $\nu(\text{CO})$, cm^{-1}) 1960 (sh, s), 1951 (vs), 1879 (vs). Anal. Calcd: C, 50.35; H, 4.22. Found: C, 50.56; H, 4.24.

Synthesis of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$. A reaction mixture of 0.628 g (1.47 mmol) of GaMes_3 and 0.380 g (1.44 mmol) of $\text{Mo}(\text{CO})_6$ in 100 mL of DME was refluxed for 24 h. After the reaction mixture was cooled to room temperature, the condenser was replaced with a glass elbow joint connected to a 250 mL Schlenk flask. The solution was poured into the Schlenk flask and the solvent was removed in vacuo. The remaining solid yellow product was evacuated for 6 h at 45°C to remove excess $\text{Mo}(\text{CO})_6$. The product was then extracted through a medium porosity frit with 50 mL of pentane (2x) into a 100 mL Schlenk flask. The pentane soluble product (0.254 g) was identified by ^1H NMR spectroscopy as a mixture of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and unreacted GaMes_3 . The remaining product was repeatedly extracted with 50 mL portions of pentane until all pentane soluble material was separated. The crude pentane soluble $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ (0.287 g 0.473 mmol, 32.8% based on $\text{Mo}(\text{CO})_6$) was isolated as a yellow solid. The remaining pentane insoluble material (0.182 g) was identified by ^1H NMR spectroscopy as predominantly $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ with a trace of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$. The product $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ was recrystallized by dissolving 0.287 g of the solid in 3 mL of benzene and layering the solution with 10 mL of pentane. Crystals suitable for an X-ray diffraction study were isolated after 16 h at 20°C. $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2 \cdot n(\text{C}_6\text{H}_6)$. Yellow crystalline solid; mp decomposition begins ~ 205°C; ^1H NMR (d^8 -THF) δ 6.76 (s, m-H, 4 H), 5.31 (s, m-H, 2 H, Mo-arene), 2.39 (s, o-Me, 12 H), 2.23 (s, p-Me, 3H, Mo-arene), 2.20 (s, o-Me, 6 H, Mo-arene), 2.17 (s, p-Me, 6H); (Benzene) δ 6.70 (s, m-H, 4 H), 4.38 (s, m-H, 2 H, Mo-arene), 2.41 (s, o-Me, 12 H), 2.11 (s, p-Me, 6 H),

1.97 (s, o-Me, 6 H, Mo-arene), 1.77 (s, p-Me, 3 H, Mo-arene); IR (pentane, $\nu(\text{CO})$, cm^{-1}) 1970 (vs), 1961 (sh, vw), 1902 (vs), 1898 (vs). (DME, $\nu(\text{CO})$, cm^{-1}) 1960 (sh, s), 1951 (vs), 1879 (vs). Anal. Calcd for $[(\text{CO})_3\text{MoMes}]_2\text{GaMe}_2 \cdot 1/2 (\text{C}_6\text{H}_6)$: C, 61.33; H, 5.61. Found: C, 61.11; H, 5.80.

Synthesis of $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2 \text{ DME}$. A reaction mixture of 0.404 g (1.18 mmol) of Mes_2GaCl and 0.649 g (2.46 mmol) of $\text{Mo}(\text{CO})_6$ in 50 mL of DME was refluxed for 20 h. In the drybox, a 100 mL Schlenk flask containing the crude product was connected to a 100 mL one-necked flask by using a medium porosity frit. Then, 10 mL of benzene was vacuum distilled onto the product. After standing for 1 h at room temperature, the product $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2 \text{ DME}$ crystallized from solution. The solution was decanted away from the yellow crystalline solid and the solvent was removed by vacuum distillation. A yield of 0.564 g (0.753 mmol, 64.0% based on Mes_2GaCl) of the purified product $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2 \text{ DME}$ was isolated after evacuation at RT for several days to remove traces of benzene.

$[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2 \text{ DME}$. Yellow crystalline solid; mp decomposition begins $\sim 200^\circ\text{C}$; ^1H NMR ($\text{d}^8\text{-THF}$) δ 5.28 (s, m-H, 4 H), 3.39 (s, $\text{CH}_2\text{-DME}$, 2 H), 3.23 (s, Me-DME, 3 H), 2.42 (s, o-Me, 12 H), 2.21 (s, p-Me, 6 H); IR (DME, $\nu(\text{CO})$, cm^{-1}) 1959 (sh, s), 1947 (vs), 1868 (vs). Anal. Calcd: C, 41.72; H, 3.64. Found: C, 41.39; H, 3.91.

Synthesis of $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}_2 \cdot 1/2 \text{ DME}$. The reagents MesGaCl_2 (0.623 g, 2.40 mmol) and $\text{Mo}(\text{CO})_6$ (0.635 g, 2.40 mmol) were combined in 50 mL of DME. Then, the reaction mixture was refluxed for 24 h. A 100 mL Schlenk flask containing the crude product was connected to another flask with a evacuated bulb containing pentane by using a glass elbow joint. Then, 25 mL of DME was vacuum distilled onto the reaction product. The solution was

poured into the other flask and layered with 40 mL of pentane. Within 16 h a brown oil separated from solution. The solution was decanted from the oil into the Schlenk flask and the solvent was removed by vacuum distillation. The crude yellow-orange solid $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$ was isolated from the Schlenk flask in a yield of 1.01 g (2.08 mmol, 86.4% based on $MesGaCl_2$). Crystals of $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$ were grown after a saturated DME solution of the product layered with pentane was permitted to stand for 16 h. $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$. Yellow crystalline solid; mp decomposition begins $\sim 180^\circ C$. 1H NMR (d^8 -THF) δ 5.34 (s, m-H, 2 H), 3.39 (s, CH_2 -DME, 2 H), 3.25 (s, Me-DME, 3H), 2.43 (s, o-Me, 6H), 2.24 (s, p-Me, 3H); IR (DME, $\nu(CO)$, cm^{-1}) 1960 (sh, s), 1948 (s), 1869 (s). Anal. Calcd: C, 34.68; H, 3.33. Found: C, 34.91; H, 3.57.

Reaction of $GaMes_3$ with $Cr(CO)_6$. A reaction mixture of 0.514 g (1.20 mmol) of $GaMes_3$ and 0.524 g (2.38 mmol) of $Cr(CO)_6$ in 100 mL of DME was refluxed for 13 h. Chromium metal formed during reflux. A yield of 0.464 g of a yellow solid was isolated after extracting the reaction product three times with 50 mL of pentane. The composition of the yellow solid was identified by 1H NMR spectroscopy as 71.0% $GaMes_3$ and 29.0% $[(CO)_3CrMes]GaMes_2$. Attempts to separate a pure sample of $[(CO)_3CrMes]GaMes_2$ from $GaMes_3$ by recrystallization were unsuccessful. **$[(CO)_3CrMes]GaMes_2$ (Impure).** 1H NMR (d^6 -benzene) δ 6.70 (s, m-H, 4 H), 4.11 (s, m-H, 2 H, Cr-arene), 2.37 (s, o-Me, 12 H), 2.10 (s, p-Me, 6 H), 1.92 (s, o-Me, 6 H, Cr-arene), 1.76 (s, p-Me, 3 H, Cr-arene). The lines of $GaMes_3$ have been omitted. IR (C_6H_{12} , $\nu(CO)$, cm^{-1}) 1966 (vs), 1957 (sh, w), 1895 (vs), 1901 (vs).

Reaction of Mes_2GaCl with $Cr(CO)_6$. After combining 0.420 g (1.22 mmol) of Mes_2GaCl and 0.541 g (2.46 mmol) of $Cr(CO)_6$ in 50 mL of DME, the

resulting reaction mixture was refluxed for a period of 8 days. (Insignificant reaction occurred during shorter reaction times.) The yellow glassy product was dissolved in benzene. After removal of the solvent by vacuum distillation, a yellow benzene insoluble powder was observed. A yield of 0.151 g of the benzene insoluble product was isolated after washing the material several times with benzene. The IR and ^1H NMR spectral data of this product were consistent with the formulation $[(\text{CO})_3\text{CrMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ but the carbon, hydrogen elemental analysis data were inconclusive. The yield of the unidentified dark orange benzene soluble solid was 0.337 g. The ^1H NMR spectrum of this material indicated the presence of decomposition products. $[(\text{CO})_3\text{CrMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ (Impure). ^1H NMR ($\text{d}^8\text{-THF}$) δ 4.93 (s, m-H, 2 H), 2.37 (s, o-Me, 6 H), 2.15 (s, p-Me, 3 H); IR (DME, $\nu(\text{CO})$, cm^{-1}) 1958 (sh, m), 1948 (vs), 1870 (vs). Anal. Calc: C, 38.14; H, 3.66. Found: C, 40.09; H, 4.66.

Reaction of MesGaCl_2 with $\text{Cr}(\text{CO})_6$. A reaction mixture of 0.360 g (1.39 mmol) of MesGaCl_2 and 0.317 g (1.44 mmol) of $\text{Cr}(\text{CO})_6$ in 50 mL of DME was refluxed for a period of 7 days. A yellow solid (0.230 g) was isolated after extracting the crude product with benzene. Very broad unresolved lines in the ^1H NMR spectrum of the product were indicative of decomposition.

Reaction of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ with Anhydrous HCl. Reaction (A): A 0.144 g (0.184 mmol) sample of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ was placed into a reaction vessel which was connected to an NMR tube and ~ 3 mL of $\text{d}^8\text{-THF}$ was added by vacuum distillation. Then, a 0.0052 g (0.14 mmol) sample of HCl was condensed into the reaction vessel at -196°C . The reaction mixture was warmed to room temperature and stirred for 10 min. A portion of the solution was decanted into the NMR tube and the NMR tube was sealed under

vacuum at -196°C . The ^1H NMR spectrum of the reaction mixture was recorded immediately upon warming the sample to room temperature. The major reaction products were identified as HMes and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot(\text{d}^8\text{-THF})$. A trace of $\text{HMesMo}(\text{CO})_3$, $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ and $[(\text{CO})_3\text{MoMes}]\text{GaMesCl}$ were also observed in the spectrum. ^1H NMR Data of Reaction Product Mixture ($\text{d}^8\text{-THF}$). (* - Relative Intensity of Line) $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot(\text{d}^8\text{-THF})$: δ 5.21 (s, m-H, 8.0*), 2.40 (s, o-Me, 17.0*). HMes: δ 6.69 (s, H, 5.0*), 2.19 (s, Me, 28.6*). $[(\text{CO})_3\text{MoMes}]\text{GaMesCl}$: δ 6.74 (s, m-H, 1.4*), 2.47 (s, o-Me, 6.0*). $\text{HMesMo}(\text{CO})_3$: δ 2.22 (s, Me, 10.4*). $[(\text{CO})_3\text{MoMe}]_2\text{GaMes}$: δ 6.80 (s, m-H, 1.0), 2.55 (s, p-Me, Mo-arene, 4.0*), 2.30 (s, o-Me, Mo-arene, 6.2*).

Reaction (B): A 0.0048 g (0.13 mmol) sample of HCl was vacuum distilled into a reaction flask containing 0.0521 g (0.0622 mmol) of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ in 25 ml of DME. After stirring the reaction mixture for 29 h at room temperature, the solvent was removed in vacuo to leave a yellow solid. The product was extracted several times with pentane in order to separate a pentane soluble product. The pentane soluble material was identified by ^1H NMR spectroscopy as a mixture of HMes and $\text{HMesMo}(\text{CO})_3$. The pentane insoluble material was identified by ^1H NMR as a mixture of $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2\cdot 1/2\text{DME}$, $\text{HMesMo}(\text{CO})_3$ and HMes. The compound HMes is volatile and can be vacuum distilled at room temperature. Therefore, the ^1H NMR spectra were not indicative of the relative amount of HMes produced during reaction. ^1H NMR data of Reaction Products ($\text{d}^8\text{-THF}$). $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2\cdot 1/2\text{DME}$: δ 5.36 (s, m-H, 2 H), 3.39 (s, $\text{CH}_2\text{-DME}$, 2 H), 3.23 (s, Me-DME, 3 H), 2.41 (s, o-Me, 6 H), 2.22 (s, p-Me, 3 H). $\text{HMesMo}(\text{CO})_3$: δ 5.34 (s, H, 3 H), 2.21 (s, Me, 9 H). HMes: δ 6.66 (s, H, 3 H), 2.19 (s, Me, 9 H).

Reaction of $[(CO)_3MoMes]GaMes_2$ with Anhydrous HCl. A 0.130 g (0.215 mmol) sample of $[(CO)_3MoMes]GaMes_2$ was placed into a reaction vessel with a connecting NMR tube and ~ 2 mL of d^8 -THF were added by vacuum distillation. Then, a 0.0147 g (0.403 mmol) sample of HCl was condensed into the reaction vessel. The reaction mixture was stirred at room temperature for 5 minutes and then a portion of the solution was decanted into the NMR tube and sealed under vacuum at $-196^\circ C$. The 1H NMR spectrum of the reaction mixture identified $[(CO)_3MoMes]GaCl_2 \cdot (d^8-THF)$ and HMes as products. 1H NMR data of Reaction Product Mixture (d^8 -THF). (* - Relative Intensity of Line)

$[(CO)_3MoMes]GaCl_2 \cdot (d^8-THF)$: 5.28 (s, m-H, 1*) 2.39 (s, o-Me, 3.2*). HMes: 6.68 (s, H, 2.5*) 2.22 (s, Me, 2.2*).

Reaction of $[(CO)_3MoMes]_2GaMes$ with $MesGaCl_2$. A 0.0816 g (0.314 mmol) sample of $MesGaCl_2$ was placed into a tube with a standard adapter and Teflon valve and 10 mL of DME was added by vacuum distillation. The tube was then connected to a reaction flask containing 0.248 g (0.315 mmol) of $[(CO)_3MoMes]_2GaMes$. Finally, ~ 40 mL of DME was vacuum distilled onto $[(CO)_3MoMes]_2GaMes$. The solution of $MesGaCl_2$ was added with stirring to the solution of $[(CO)_3MoMes]_2GaMes$ at room temperature. After stirring the reaction mixture for 4 days at room temperature, the orange solution was filtered through a medium porosity frit and the solvent was removed in vacuo. A dark orange viscous material remained in the reaction flask. The product was redissolved in 10 ml of DME and the solution was layered with ~ 60 mL of pentane at room temperature. After standing for 16 h, crystals separated from solution. The solution was decanted away from the crystals and the solvent was removed by vacuum distillation to leave an orange viscous material. The crystals (0.045 g) were identified as $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$ by 1H NMR spectroscopy. The orange viscous

material had a ^1H NMR spectrum which was consistent with a mixture of $[(\text{CO})_3\text{MoMes}]\text{GaMe}_2$, $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot 1/2\text{DME}$ and $\text{Me}_2\text{GaCl}\cdot\text{DME}$. Based upon the chemical shifts of authentic samples of $[(\text{CO})_3\text{MoMes}]\text{GaMe}_2$, $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot 1/2\text{DME}$ and $\text{Me}_2\text{GaCl}\cdot\text{DME}$, many lines in the spectrum were superimposed. Therefore, the relative amounts of individual products were ambiguous. However, the ortho-methyl line of $\text{Me}_2\text{GaCl}\cdot\text{DME}$ was definitively assigned as the major resonance in the spectrum. More detail is presented in the Discussion. ^1H NMR Data of Reaction Products ($\text{d}^8\text{-THF}$). Yellow crystalline solid. $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2\cdot 1/2\text{DME}$: δ 5.35 (s, m-H, 2 H), 2.45 (s, o-Me, 6 H), 2.25 (s, p-Me, 3 H). Orange viscous material. δ 6.75 (s, m-H,), 6.70 (s, m-H), 5.29 (s, m-H, Mo-arene), 2.45 (s, Me,), 2.40 (s, Me), 2.38 (s, Me), 2.32 (s, Me), 2.17 (s, Me).

Reaction of $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot 1/2\text{DME}$ with KPPH_2 . Reaction A: A 0.509 g (0.679 mmol) sample of $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot 1/2\text{DME}$ was placed into a tube equipped with a standard adapter and Teflon valve and ~ 10 mL of DME was added by vacuum distillation. The tube was connected to a flask that contained 0.160 g (0.714 mmol) of KPPH_2 and 20 mL of DME was vacuum distilled onto the KPPH_2 . The reaction flask was placed into a -57.0°C bath at which temperature KPPH_2 was insoluble. The solution of $[(\text{CO})_3\text{MoMes}]_2\text{GaCl}\cdot 1/2\text{DME}$ was added with stirring to KPPH_2 . Upon mixing, all KPPH_2 dissolved and apparently reacted to form an orange solution. After stirring the reaction mixture for 45 min., the temperature of the bath was slowly increased to 2°C and the solution turned dark orange. Within 16 h a brown precipitate formed. The temperature of the bath was increased to room temperature and the solvent was removed in vacuo. A red-brown viscous product was observed. The ^1H NMR spectrum of the material indicated the formation of an unknown mixture of products.

Reaction B: A 0.523 g (0.711 mmol) sample of $[(CO)_3MoMes]_2GaCl \cdot 1/2DME$ was placed in a reaction flask and 0.162 g (0.722 mmol) of KPh_2 was contained in a connecting side-arm dumper. Then, 50 mL of benzene was vacuum distilled onto $[(CO)_3MoMes]_2GaCl \cdot 1/2DME$ and a portion of the solvent was distilled onto the KPh_2 . The benzene insoluble KPh_2 was added with stirring at room temperature to the solution of $[(CO)_3MoMes]_2GaCl \cdot 1/2DME$. Upon mixing, KPh_2 dissolved (except for a trace amount) to form a bright orange solution. Within 3 h the solution turned dark brown and a light brown precipitate was observed. After washing the precipitate with benzene, 0.344 g of a light brown solid material was isolated. Multiple lines in the 1H NMR spectrum of the brown material indicated a mixture of decomposition products.

Reaction of $MesGaCl_2$ with $(C_6Me_3H_3)Mo(CO)_3$. After the reagent $MesGaCl_2$ (0.0647 g 0.249 mmol) was placed into a tube equipped with a standard adapter and Teflon valve, 5 mL of DME was added by vacuum distillation. The tube was connected to a reaction flask containing 0.0744 g (0.249 mmol) of $(C_6Me_3H_3)Mo(CO)_3$ in the drybox. Then, 15 mL of DME was vacuum distilled onto $(C_6Me_3H_3)Mo(CO)_3$. The solution of $MesGaCl_2$ was added at room temperature with stirring to the solution of $(C_6Me_3H_3)Mo(CO)_3$. After 13 h, the solvent was removed by vacuum distillation and a yellow solid remained. The compounds $MesGaCl_2$, $(C_6Me_3H_3)Mo(CO)_3$, $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$ and $C_6Me_3H_3$ were identified by the 1H NMR spectrum (d^8 -THF). After a period of 4 days, the spectrum indicated that an equilibrium between the starting materials $MesGaCl_2$ and $(C_6Me_3H_3)Mo(CO)_3$ and the reaction products $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$ and $HMes$ had been established. 1H NMR Data of Reaction Mixture (d^8 -THF). (* - Relative Intensity of Line)

$MesGaCl_2 \cdot 1/2DME$: δ 6.74 (s, m-H, 1.0*), 2.49 (s, o-Me, 4.3*)

$(C_6Me_3H_3)Mo(CO)_3$: δ 5.36 (s, H), 2.23 (s, Me, 5.0*).

$[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$: δ 5.36 (s, m-H), 2.42 (s, o-Me, 9.5*). $C_6Me_3H_3$:
 δ 6.69 (s, H, 1.4*), 2.20 (s, Me, 7.5*).

Collection of X-ray Diffraction Data for $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$. A yellow single crystal of each complex was chosen for examination by X-ray diffraction procedures. The dimensions for the crystal of $[(CO)_3MoMes]GaMes_2$ were 0.10 x 0.15 x 0.31 mm and for $[(CO)_3MoMes]_2GaMes$ were 0.19 x 0.20 x 0.25 mm. Each crystal was mounted in a thin walled glass capillary in an argon filled drybox. Diffraction measurements were made on a Syntex P2₁ automated four-circle diffractometer. The crystal of $[(CO)_3MoMes]GaMes_2$ was found to be triclinic with no systematic absences suggesting the space group $P\bar{1}$, whereas $[(CO)_3MoMes]_2GaMes$ was orthorhombic with systematic absences ($0kl$, $k=2n+1$; $h0l$, $l=2n+1$; $hk0$, $h+k=2n+1$) strongly indicative of the centrosymmetric space group $Pbcn$. Unit cell parameters and the orientation matrix were obtained and data collection was carried out by using a 2θ - θ scan. Data were corrected for Lorentz and polarization factors and reduced to $|F_o|$ values, experimental details appear in Table I.

Solution and Refinement of Structures. The analytical form of the scattering factors for neutral molybdenum, gallium, oxygen and carbon were used throughout the analysis.^{14a} The contributions of all non-hydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.^{14b} The positions of the molybdenum, gallium and several carbon atoms of each structure were found by direct methods.¹⁵ The remaining oxygen and carbon atoms in each were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. For $[(CO)_3MoMes]GaMes_2$, the asymmetric unit contained one molecule of the compound and one half of a benzene solvent molecule located around an

inversion center. The asymmetric unit of complex $[(CO)_3MoMes]_2GaMes$ contained half a molecule with Ga, C(13), C(16) and C(18) fixed at x, z and half occupancy on the two-fold axis. All hydrogen atoms whose approximate positions could be obtained from the electron density maps were placed in optimized positions, those remaining were included by calculation (all were based upon C-H = 0.95Å, tetrahedral and trigonal angles and idealized thermal parameters with B = 1.0Å² greater than the equivalent isotropic thermal parameter of the carbon to which the hydrogen is attached).¹⁶ Numerical absorption corrections were based on the indexed and measured faces of each crystal and the contents of each unit cell. Refinement was based on F and both structures involved only those reflections having $F_o^2 \geq 3\sigma(F_o^2)$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to final convergence with R(F) = 0.047, $R_w(F)$ = 0.045 and GOF = 1.21 for 343 variables and 2148 reflections for $[(CO)_3MoMes]GaMes_2$; and R(F) = 0.046, $R_w(F)$ = 0.045 and GOF = 1.27 for 192 variables and 1254 reflections for $[(CO)_3MoMes]_2GaMes$.

Results and Discussion

The first examples of arene-group 6 metal tricarbonyl complexes which have gallium containing substituents bonded to an arene ring, $[(CO)_3MoMes]GaMes_2$, $[(CO)_3MoMes]_2GaMes$, $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$ and $[(CO)_3MoMes]_2GaCl \cdot 1/2DME$ (Mes- $C_6Me_3H_2$, mesityl), have been prepared. These compounds have been fully characterized by elemental analyses, infrared and 1H NMR spectroscopy and reactions with hydrogen chloride. In addition, single crystal X-ray diffraction studies of $[(CO)_3MoMes]GaMes_2 \cdot nC_6H_6$ and $[(CO)_3MoMes]_2GaMes$ have provided the first structural data for simple compounds which have an aromatic ring bonded to a group 13 atom which in turn is directly bonded to a group 6 metal carbonyl moiety.

The molybdenum complexes $[(CO)_3MoMes]_nGaMes_{3-n}$ ($n=1,2$) were readily prepared by reacting $Mo(CO)_6$ and $GaMes_3$ in refluxing DME. When the ratio of $Mo(CO)_6$ to $GaMes_3$ was one, the monomolybdenum complex $[(CO)_3MoMes]GaMes_2$ was the primary product but it was isolated in only approximately 30% yield. The dimolybdenum complex was also observed as a product but in significantly lower yield. An increase in the $Mo(CO)_6$ to $GaMes_3$ ratio to three led to the formation of higher yields of the dimolybdenum complex, $[(CO)_3MoMes]_2GaMes$ (~ 65% as based on $GaMes_3$), but $[(CO)_3MoMes]GaMes_2$ was also isolated in trace amounts. The trimolybdenum complex, $Ga[MesMo(CO)_3]_3$, was never observed as a product, even when a large excess of $Mo(CO)_6$ was utilized in the preparative reaction.

The crystal structures of $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ consist of discrete molecules but a benzene solvent molecule cocrystallizes with $[(CO)_3MoMes]GaMes_2$. There are no abnormally close intermolecular interactions in either structure. These structures are consistent with the structure of the parent complex, $GaMes_3^{12}$, but are in contrast with the

structure of GaPh_3 ¹⁷. The new complexes can be described as GaMes_3 molecules with either one or two Mo(CO)_3 units bound in η^6 fashion to mesityl rings.

Important interatomic distances and angles and their standard deviations (esd's) for the structures of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ are shown in Tables II and III, respectively. The molecular structures and atom numbering schemes of these complexes are shown in Figures 1 and 2. Stereoscopic views of the complexes are shown in Figures 3 and 4 and packing diagrams are displayed in Figures 5 and 6.

The geometry around the central gallium atoms differs in the two complexes. The gallium atom in $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ is distorted from trigonal planar and lies 0.011Å above the plane defined by C(4), C(13) and C(22). Two of the angles about the gallium in the monomolybdenum complex deviate considerably from the ideal angle of 120°; the C(4)-Ga-C(13) angle at 127.2(4)° and the C(4)-Ga-C(22) angle at 109.3(4)°. The remaining C(13)-Ga-C(22) angle is 123.5(4)°. The geometry of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ is closer to trigonal planar than that of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$. In the dimolybdenum complex the gallium atom and its three bonded carbon atoms, C(4), C(4)' and C(13), exhibit the crystallographically imposed coplanar geometry. Steric hinderance between the Mo(CO)_3 groups and the mesityl ring to which they are not directly bound causes the C(4)-Ga-C(13) angle to be slightly larger than ideal at 124.0(3)° and the C(4)-Ga-C(4)' angle to be less than ideal at 112.1(6)°. For comparison, GaMes_3 exhibits a nearly ideal trigonal planar geometry with the gallium atom 0.063Å above the plane defined by the three bound carbon atoms and the C-Ga-C angles at 119.93(16)°.¹²

As with other triaryl gallium compounds,^{12,17} the aromatic rings of $[(\text{CO})_3\text{MoMes}]_n\text{GaMes}_{3-n}$ (n=1,2) are twisted from coplanarity and exhibit a

propeller-like arrangement. Specifically, the dihedral angles of the aromatic rings with the plane containing the gallium atom and the ipso carbons of each ring were calculated (C(4), C(13), and C(22) of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$; C(4), C(13) and C(4)' of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$). For $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ the dihedral angles range from 52.83° to 58.63° and are comparable to those of GaMes_3 at 55.90° .¹² The dihedral angles for the mesityl rings bound to $\text{Mo}(\text{CO})_3$ in $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ are equivalent due to the two-fold axis at 51.60° . The free mesityl group of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ which has no bonding interaction with either $\text{Mo}(\text{CO})_3$ has a dihedral angle of 77.08° . Due to steric interactions between the 2,6-methyl groups of adjacent mesityl substituents, the dihedral angles of the trimesitylgallium compounds $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$, $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ and GaMes_3 ¹² are considerably larger than those found in GaPh_3 (13.2° and 31.6°).¹⁷

In the structure of GaMes_3 the gallium atom is bent back by $0.214\text{\AA}$ from the mesityl plane.¹² A similar bending effect is observed in the structures of both mesitylgallium-molybdenum carbonyl complexes. For the mesityl group bound to molybdenum in $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ the effect is most pronounced with the bending being $0.3962\text{\AA}$. The other two mesityl groups in this complex are also bent back ($0.292\text{\AA}$ and $0.144\text{\AA}$) with the greater distortion being exhibited by the uncomplexed mesityl group nearest to the $\text{Mo}(\text{CO})_3$ fragment. In the mesityl groups bound to molybdenum of the dimolybdenum complex, the gallium atom is bent back from the mesityl plane by $0.141\text{\AA}$. The bending effect is not observed in the uncomplexed mesityl group since it lies on the two-fold axis.

The mesityl rings of both molybdenum complexes are bound in a η^6 manner to the molybdenum atom. The structures of the $\text{Mo}(\text{CO})_3\text{Mes}$ portions in both

compounds are similar to that in 1,3,5-trimethylbenzenetricarbonylmolybdenum.¹⁸ The average¹⁸ Mo-C(ring) and Mo-C(carbonyl) bond distances in $[(CO)_3MoMes]GaMes_2$ (2.359(23)Å, 1.948(22)Å) and in $[(CO)_3MoMes]_2GaMes$ (2.355(27)Å, 1.951(25)Å) are not significantly different from those of $(C_6Me_3H_3)Mo(CO)_3$ (2.372(19)Å, 1.964(8)Å). Like $(C_6Me_3H_3)Mo(CO)_3$, the carbonyl ligands in the new compounds are in an eclipsed configuration with respect to the methyl groups of the mesityl group to which the $Mo(CO)_3$ moiety is bound. The C(carbonyl)-Mo-C(carbonyl) angles for both $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ (85.2(5)°-88.0(6)°) indicate an octahedral arrangement around each molybdenum atom and are comparable to those of $(C_6Me_3H_3)Mo(CO)_3$ which range from 88.0(2)°-89.9(2)°. The C-O bond distances and the Mo-C(carbonyl)-O bond angles for the new compounds are equivalent within esd's to those of $(C_6Me_3H_3)Mo(CO)_3$.

The Ga-C distances for the free mesityl groups in $[(CO)_3MoMes]_nGaMes_{3-n}$ (n=1,2) which are not bound to molybdenum (Ga-C(13) = 1.958(10)Å and Ga-C(22) = 1.971(10)Å for $[(CO)_3MoMes]GaMes_2$ and Ga-C(10) = 1.955(14)Å for $[(CO)_3MoMes]_2GaMes$) are not significantly different from those of $GaMes_3$ (1.968(4)Å) and $GaPh_3$ (1.946(7)Å and 1.968(5)Å).^{12,18} The Ga-C distances to the mesityl groups bound to molybdenum are slightly longer at 2.002(10)Å for $[(CO)_3MoMes]GaMes_2$ and 1.991(10)Å for $[(CO)_3MoMes]_2GaMes$. The intra-ring C-C distances of the uncomplexed mesityl rings of $[(CO)_3MoMes]GaMes_2$ (1.357(14)-1.418(12)Å, average = 1.41(3)Å) and of $[(CO)_3MoMes]_2GaMes$ (1.374(14)-1.413(12)Å, average = 1.41(4)Å) are not significantly different than those of $GaMes_3$ (1.365(6)-1.399(6), average = 1.387(16)Å). The intra-ring C-C distances for the mesityl rings bound to molybdenum of $[(CO)_3MoMes]GaMes_2$ (1.393(13)-1.435(12)Å, average = 1.41(2))

and of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ (1.384(16)-1.443(13)Å, average = 1.41(3)Å) are equivalent to those in $(\text{C}_6\text{Me}_3\text{H}_3)\text{Mo}(\text{CO})_3$ which average 1.408(14)Å.¹⁸

The elemental analyses as well as the ^1H NMR and infrared spectral data of bulk samples of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ are consistent with the molecular structures identified by the X-ray structural studies. The ^1H NMR and infrared spectra of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ in d^8 -THF solution are similar to but distinct from the corresponding spectra of

$[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$. For example, two m-H lines were observed at δ 6.76 (uncomplexed ring) and 5.31 (Mo-bonded ring) with an integration ratio of 2:1 for $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$. Two o-Me lines were at δ 2.42 (uncomplexed ring) and 2.21 (Mo-bonded ring) with an intensity ratio of 2:1. The p-Me lines at δ 2.22 (Mo-bonded ring) and 2.19 (uncomplexed ring) also had the appropriate intensity ratios. Similarly, the ^1H NMR spectrum of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ in d^8 -THF solution exhibited two m-H lines at δ 6.82 (uncomplexed ring) and 5.34 (Mo-bonded ring) with an integration ratio of 1:2. Two p-Me lines were at δ 2.56 (Mo-bonded ring) and 2.22 (uncomplexed ring) with an intensity ratio of 2:1. The o-Me lines occurred at 2.29 (Mo-bonded ring) and 2.24 (uncomplexed ring) with an intensity ratio of 2:1. The m-H line assignments were based on the characteristic upfield shift observed for ring protons when the aromatic ring is bonded to a $\text{M}(\text{CO})_3$ unit ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$).²⁰ It is noteworthy that relative positions observed for the ortho and para methyl lines assigned to the Mo-bonded mesityl rings were reversed from that observed for the analogous groups in the spectrum of the uncomplexed ring. The infrared spectrum of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ in pentane (ν_{CO}) showed a very weak shoulder at 1961 and three very strong bands at 1970, 1902 and 1898 cm^{-1} , whereas $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ in DME exhibited a shoulder at 1960 and two very strong bands at 1951 and 1879 cm^{-1} . These

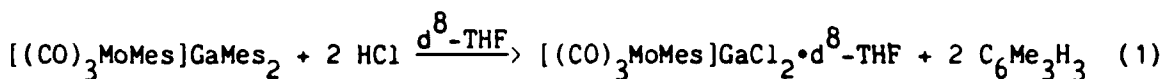
spectra are consistent with the pattern which is typically observed for arene-transition metal tricarbonyl complexes.²¹⁻²⁴ It is of interest that the asymmetric C-O stretching band of $[(CO)_3MoMes]GaMes_2$ is split, an indication of a loss in local symmetry of the molecule due to the $GaMes_2$ substituent.²⁵ The frequencies are slightly lower than those for $(C_6Me_3H_3)Mo(CO)_3$ (1977 and 1904 cm^{-1}). Since electron withdrawing groups or atoms bonded to the aromatic ring typically increase the frequencies of the carbonyl stretching bands^{22,23} and electron donating groups decrease the corresponding band frequencies,^{22,23} $-GaMes_2$ might be considered by some to be an electron donating group. If $-GaMes_2$ is indeed an electron donating group, one possible source of electron density is the pi-electron density of the free aryl groups.

An unusual feature of the chemistry of $[(CO)_3MoMes]_nGaMes_{3-n}$ ($n=1,2$) is their apparent stability in air for short periods of time. For example, solids samples of $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ were exposed to air for 1 h without any apparent changes. The 1H NMR spectra of d^8 -THF solutions of the resulting "air-exposed" solids were identical to typical spectra of the compounds. These observations suggest that the $Mo(CO)_3$ moiety hinders the approach of oxygen and water molecules to the gallium atom.

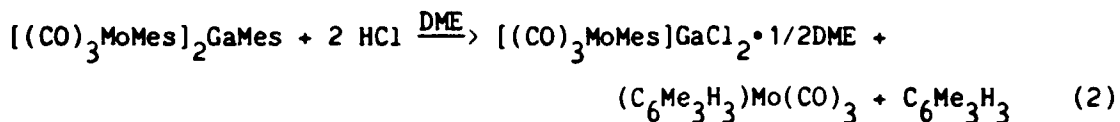
The chloromesitylgallium(III) compounds, Mes_nGaCl_{3-n} ($n=1,2$) have also been investigated as potential ligands to molybdenum. The compounds, $[(CO)_3MoMes]_2GaCl \cdot 1/2DME$ and $[(CO)_3MoMes]GaCl_2 \cdot 1/2DME$, were prepared in 64% and 87% yields, respectively, after the appropriate gallium compound and $Mo(CO)_6$ were combined in appropriate stoichiometric ratio in refluxing DME. Elemental analyses and 1H NMR spectral data confirmed the compositions of both compounds. Infrared spectral data supported the presence of $Mo(CO)_3$

units. The ^1H NMR spectra revealed that the DME bound to gallium was replaced by the stronger base, THF, and that slow decomposition was observed after approximately 16 h.

In an attempt to elucidate the effects of the $\text{Mo}(\text{CO})_3$ moiety on the reactivity of the gallium-mesityl carbon bond, the mono and di-molybdenum complexes $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ were reacted with anhydrous HCl in either DME or d^8 -THF solution. The experimental results demonstrate that the gallium-mesityl carbon bond to the uncomplexed mesityl ring was preferentially cleaved. The ^1H NMR spectrum of a reaction mixture prepared from $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and HCl in a 1:2 mol ratio in d^8 -THF solution indicated that the only reaction products were $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot d^8\text{-THF}$ and free mesitylene $\text{C}_6\text{Me}_3\text{H}_3$ (Equation 1). When the

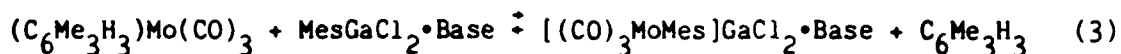


dimolybdenum complex $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ in d^8 -THF was reacted with HCl in a 1:1 mol ratio, the major reaction products were $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot d^8\text{-THF}$ and $\text{C}_6\text{Me}_3\text{H}_3$. In addition, the complex $(\text{C}_6\text{Me}_3\text{H}_3)\text{Mo}(\text{CO})_3$ and a compound believed to be $[(\text{CO})_3\text{MoMes}]\text{GaMesCl} \cdot d^8\text{-THF}$ were also present in trace amounts. When the amount of HCl was increased to a 1:2 mol ratio ($[(\text{CO})_3\text{MoMes}]_2\text{GaMes}/\text{HCl}$), $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ was the predominate gallium containing product (Equation 2). The other products were $(\text{C}_6\text{Me}_3\text{H}_3)\text{Mo}(\text{CO})_3$ and $\text{C}_6\text{Me}_3\text{H}_3$.



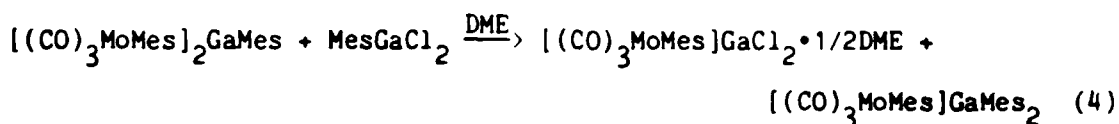
The relative amounts of these products observed in the NMR experiment were consistent with the balanced equation. The ^1H NMR spectra of $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot \text{d}^8\text{-THF}$, $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot \text{d}^8\text{-THF}$, $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$, $(\text{C}_6\text{Me}_3\text{H}_3)\text{Mo}(\text{CO})_3$ and $(\text{C}_6\text{Me}_3\text{H}_3)$ obtained from these HCl reactions were identical to those observed for the pure compounds. The observation, that the gallium-carbon bond to the uncomplexed mesityl ring in the arene complexes $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ was preferentially cleaved, might be related to steric effects of the $\text{Mo}(\text{CO})_3$ units. The site of preferential reaction should be the Ga-C bond which can most readily form a four-centered transition state. Previous kinetic studies have shown that elimination reactions in group 13 compounds are second order reactions.²⁶⁻²⁹ The Lewis acid and base must combine with the proper orientation and energy to form a four-centered transition state for elimination to occur.

The effects of the main-group metal moiety upon the chemical nature of the system can be seen from the results of arene exchange reactions. After a reaction mixture of $(\text{C}_6\text{Me}_3\text{H}_3)\text{Mo}(\text{CO})_3$ and MesGaCl_2 in a 1:1 mol ratio in DME solution was stirred for 16 h at room temperature, the ^1H NMR spectrum of the yellow crystalline product in $\text{d}^8\text{-THF}$ solution identified the presence of $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot \text{d}^8\text{-THF}$ and $\text{C}_6\text{Me}_3\text{H}_3$ as reaction products, $(\text{C}_6\text{Me}_3\text{H}_3)\text{Mo}(\text{CO})_3$ and MesGaCl_2 as reactants and DME (the reaction solvent) as a free base. After 4 days the spectrum indicated an equilibrium had been established in favor of the reaction products (Equation 3). The spectral data suggest that $\text{MesGaCl}_2 \cdot \text{Base}$ is apparently a better electron donating

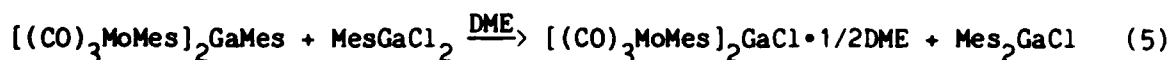


ligand to $\text{Mo}(\text{CO})_3$ than is mesitylene. The observed arene exchange reaction is consistent with other exchange reactions of arene molybdenum tricarbonyl complexes in the presence of Lewis bases.³⁰ Lewis bases significantly increase the rate of arene exchange.

The complex $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ also undergoes complex reactions with MesGaCl_2 in DME at room temperature to form $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$, Mes_2GaCl , $[(\text{CO})_3\text{Mo}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$. A reaction mixture of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ and MesGaCl_2 in a 1:1 mol ratio in DME produced an orange viscous material. The orange viscous product was dissolved in fresh DME and then the solution was layered with pentane. After the solution was allowed to stand at room temperature, a yellow crystalline precipitate was isolated and characterized as $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ by ^1H NMR spectroscopy. The remaining viscous material was identified as a mixture of $\text{Mes}_2\text{GaCl} \cdot \text{DME}$, $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ according to ^1H NMR spectroscopy (d^8 -THF solution). The line with the highest relative intensity in the spectrum was assigned to $\text{Mes}_2\text{GaCl} \cdot \text{DME}$. Some of the lines of the other products were superimposed upon one another, a conclusion consistent with the spectra of authentic samples of $\text{Mes}_2\text{GaCl} \cdot \text{DME}$, $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$. The chemical shift of only one line (δ 2.32 ppm) in the spectrum of the viscous material was unassigned. The formation of $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ and $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ is consistent with either a ligand redistribution reaction and/or an arene exchange reaction (Equation 4). However, the



products Mes_2GaCl and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2 \text{ DME}$ would suggest only a ligand exchange reaction (Equation 5).



Attempts to replace the chlorine atom in $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ with the bulky phosphorus group PPh_2 to form a gallium-phosphorus bond were also investigated. When the complex $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ was reacted with KPPH_2 in a 1:1 mol ratio in either DME or benzene, only an apparent mixture of decomposition products was isolated. Upon addition of a DME solution of $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ to KPPH_2 in DME at -57°C , the initially insoluble KPPH_2 apparently reacted as an orange solution was observed to form. As the temperature of the reaction mixture was slowly increased to 20°C , the solution turned brown with formation of a brown precipitate, an indication of decomposition. When KPPH_2 was added to $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ in benzene at room temperature, a bright orange solution was initially observed but within 3 h the solution turned brown with formation of a brown precipitate. The ^1H NMR spectra of the brown products from both reactions indicated that the material was an apparent mixture of unidentified decomposition products. Decomposition can be envisioned to occur if a phosphorus ligand either displaced the arene group on molybdenum or attacked the CO groups. Both types of reactions have been previously observed for other systems.^{32,33}

The reactions between $\text{Cr}(\text{CO})_6$ and the group 13 compounds GaMes_3 , Mes_2GaCl and MesGaCl_2 were also investigated in attempts to prepare the arene complexes $[(\text{CO})_3\text{CrMes}]\text{GaMes}_2$, $[(\text{CO})_3\text{CrMes}]_2\text{GaCl}$ and $[(\text{CO})_3\text{CrMes}]\text{GaCl}_2$. The chromium complexes might potentially be more inert in solution than the

corresponding molybdenum compounds.³⁴ The spectroscopic data indicate that $[(CO)_3CrMes]GaMes_2$ and $[(CO)_3CrMes]GaCl_2 \cdot 1/2DME$ were prepared but attempts to isolate pure samples of the compounds were unsuccessful.

The compound $GaMes_3$ reacted with $Cr(CO)_6$ in refluxing DME to yield the arene-chromium complex $[(CO)_3CrMes]GaMes_2$ as a pentane soluble compound and chromium metal as an insoluble product. The 1H NMR spectral data of the pentane soluble yellow material indicated the presence of approximately 29% $[(CO)_3CrMes]GaMes_2$ and 71% unreacted $GaMes_3$. A pure sample of the monochromium complex could not be separated from $GaMes_3$. The 1H NMR line at δ 4.11 has been assigned to the uncomplexed arene ring in $[(CO)_3CrMes]GaMes_2$. The two o-Me lines were exhibited at δ 2.37 (uncomplexed ring) and 1.92 (Cr-bonded ring) with an intensity ratio 2:1. The two p-Me lines occurred at 2.10 (uncomplexed ring) and 1.76 (Cr-bonded ring) with an intensity ratio of 2:1. The m-H line of $GaMes_3$ at δ 6.70 apparently masked the m-H line of the uncomplexed rings in $[(CO)_3CrMes]GaMes_2$. The ortho and para methyl groups of $GaMes_3$ had lines at 2.33 and 2.14 ppm. The infrared spectrum of $[(CO)_3CrMes]GaMes_2$ in C_6H_{12} solution (ν_{CO}) showed a weak shoulder at 1957 and three strong bands at 1966, 1901, and 1895 cm^{-1} .

The complex $[(CO)_3CrMes]GaCl_2 \cdot 1/2DME$ was produced in 28% yield by reacting Mes_2GaCl with $Cr(CO)_6$ in a 1:2 mol ratio in DME under reflux conditions. In addition to the yellow benzene insoluble product $[(CO)_3CrMes]GaCl_2 \cdot 1/2DME$ which was characterized by 1H NMR and infrared spectral data, a yellow benzene soluble decomposition product material was also observed. The apparent formation of $[(CO)_3CrMes]GaCl_2 \cdot 1/2DME$ instead of the desired product $[(CO)_3CrMes]_2GaCl \cdot 1/2DME$ was a surprising result. The 1H NMR spectrum of the compound in d^8 -THF solution showed one m-H line at δ 4.93, one o-Me line at 2.37 and one p-Me line at 2.15 with an

integration ratio of 1:3:1.5, respectively. The DME lines were exhibited at δ 3.39 and 3.25. An integration ratio of 1:1.6 was observed for the $\text{CH}_2(\text{DME})$ to m-H lines, respectively. The infrared spectrum of the benzene insoluble product in DME solution (ν_{CO}) exhibited a shoulder at 1958 and two very strong bands at 1948 and 1870 cm^{-1} . The elemental analyses indicated that the apparent product $[(\text{CO})_3\text{CrMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ was impure. Trace contamination of $[(\text{CO})_3\text{CrMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ by either $[(\text{CO})_3\text{CrMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ or a slight excess of DME would be undetectable by spectroscopic techniques. The corresponding molybdenum complexes $[(\text{CO})_3\text{MoMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ and $[(\text{CO})_3\text{MoMes}]_2\text{GaCl} \cdot 1/2\text{DME}$ cannot be distinguished by either ^1H NMR or infrared spectral data. When an attempt was made to prepare $[(\text{CO})_3\text{CrMes}]\text{GaCl}_2 \cdot 1/2\text{DME}$ from MesGaCl_2 and $\text{Cr}(\text{CO})_6$ in refluxing DME, only multiple decomposition products were observed.

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Supplementary material available: Atomic positional parameters, thermal parameters, complete tables of bond lengths and angles and tables of indices with $F(\text{obs})$ vs. $F(\text{Calcd})$. Ordering information is given on any current masthead page.

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Table I. Experimental Data for the X-ray Diffraction Studies of
 $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$.

Compound	$[(CO)_3MoMes]GaMes_2$	$[(CO)_3MoMes]_2GaMes$
formula	$MoGaC_{30}H_{33}O_3$	$Mo_2GaC_{33}H_{33}O_6$
formula weight, amu	607.25	787.22
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	Pbcn
a, Å	9.171(1)	17.587(3)
b, Å	12.702(2)	12.186(2)
c, Å	14.649(3)	15.497(3)
α , deg	81.16(2)	
β , deg	79.03(1)	
γ , deg	109.82(1)	
Volume, Å ³	1531.3(5)	3321.4(11)
Z	2	4
ρ (calc), g cm ⁻³	1.40	1.57
crystal dimension, mm	0.10 x 0.15 x 0.31	0.19 x 0.20 x 0.25
crystal faces	(0 0 1), (0 0 -1), (0 1 1), (0 -1 -1), (1 0 1), ($\bar{2}$ 1 -2)	(-1 -1 0), (-2 1 0), (1 1 0), (2 -3 0), (0 0 -1), (0 0 1)
crystal volume, mm ³	5.08 x 10 ⁻³	9.99 x 10 ⁻³
diffractometer	Syntex P2 ₁	
radiation	Mo K α (0.71073 Å)	
monochromator	graphite crystal	
temperature, °C	23	
scan type	2 θ - θ	same as $[(CO)_3MoMes]GaMes_2$
scan speed, ° min ⁻¹	3.91	
Background scan	1.1° below K α_1 to 1.1° above K α_2	
standard reflections	3 per 100 reflections	
indices of standards	(4 2 5), (5 -2 3), (3 3 1)	(1 0 10), (8 3 7), (6 4 2)
lin. abs. coeff., cm ⁻¹	13.048	15.679
transmission factors	0.7622 - 0.8885	0.6984 - 0.8011
2 θ scan limits, deg	3.0 - 48.0	3.0 - 50.0
crystal stability	The compounds are slightly air sensitive. The crystals were mounted in glass capillaries under argon. No indication of standard reflection decay during data collection was noted in either case.	
total refs. scanned	5384 (189 standards)	3442 (108 standards)
unique refs. I $\geq$ 3 σ (I)	2148	1254
average abs. corr.	0.9195	0.8694
final no. of variables	343	192
goodness of fit ₂	1.21	1.27
R(F) (F $\geq$ 3 σ F ₂)	0.047	0.046
R _w (F) (F $\geq$ 3 σ F _o)	0.045	0.045

Table II. Selected Interatomic Bond Distances (Å) for Molybdenum, Gallium, Oxygen, and Carbon in $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$.

Bond	$[(CO)_3MoMes]GaMes_2$	$[(CO)_3MoMes]_2GaMes$	Bond	$[(CO)_3MoMes]GaMes_2$	$[(CO)_3MoMes]_2GaMes$
(A) Mo-C(carbonyl) Distances			(E) C-C Distances		
Mo(1)-C(1)	1.949(13)	1.934(14)	C(4)-C(5)	1.435(12)	1.414(13)
Mo(1)-C(2)	1.953(12)	1.938(15)	C(4)-C(9)	1.422(13)	1.443(13)
Mo(1)-C(3)	1.942(13)	1.981(14)	C(5)-C(6)	1.419(13)	1.403(15)
(B) Mo-C(mesityl) Distances			C(6)-C(7)	1.405(14)	1.384(16)
Mo(1)-C(4)	2.390(9)	2.382(9)	C(7)-C(8)	1.404(14)	1.419(15)
Mo(1)-C(5)	2.347(9)	2.343(10)	C(8)-C(9)	1.393(13)	1.413(14)
Mo(1)-C(6)	2.348(10)	2.348(12)	C(13)-C(14)	1.418(12)	1.413(12)
Mo(1)-C(7)	2.367(10)	2.358(13)	C(14)-C(15)	1.389(13)	1.374(14)
Mo(1)-C(8)	2.348(10)	2.354(12)	C(15)-C(16)	1.394(14)	1.398(13)
Mo(1)-C(9)	2.352(9)	2.348(10)	(F) C(ring)-C(Me) Distances		
(C) Ga-C Distances			C(5)-C(10)	1.507(13)	1.519(13)
Ga(1)-C(4)	2.002(10)	1.991(10)	C(7)-C(11)	1.513(14)	1.521(16)
Ga(1)-C(13)	1.958(10)	1.955(14)	C(9)-C(12)	1.512(14)	1.507(14)
Ga(1)-C(22)	1.971(10)	-----	C(14)-C(17)	-----	1.523(14)
(D) C-O Distances			C(14)-C(19)	1.498(13)	-----
O(1)-C(1)	1.154(11)	1.175(14)	C(16)-C(18)	-----	1.530(21)
O(2)-C(2)	1.162(11)	1.164(14)	C(16)-C(20)	1.494(15)	-----
O(3)-C(3)	1.156(12)	1.134(13)			

Table III. Bond Angles (°) for Molybdenum, Gallium, Oxygen and Carbon in $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$.

Angle	$[(CO)_3MoMes]GaMes_2$	$[(CO)_3MoMes]_2GaMes$
(A) C-Mo-C Angles		
C(1)-Mo(1)-C(2)	88.0(4)	88.0(6)
C(1)-Mo(1)-C(3)	87.8(5)	88.0(6)
C(2)-Mo(1)-C(3)	87.0(5)	85.2(5)
(B) C-Ga-C Angles		
C(4)-Ga(1)-C(4)'	-----	112.1(6)
C(4)-Ga(1)-C(13)	127.2(4)	124.0(3)
C(4)-Ga(1)-C(22)	109.3(4)	-----
C(13)-Ga(1)-C(22)	123.5(4)	-----
(C) Mo-C-O Angles		
Mo(1)-C(1)-O(1)	176.9(10)	178.3(16)
Mo(1)-C(2)-O(2)	177.1(9)	177.0(13)
Mo(1)-C(3)-O(3)	178.7(11)	177.8(12)

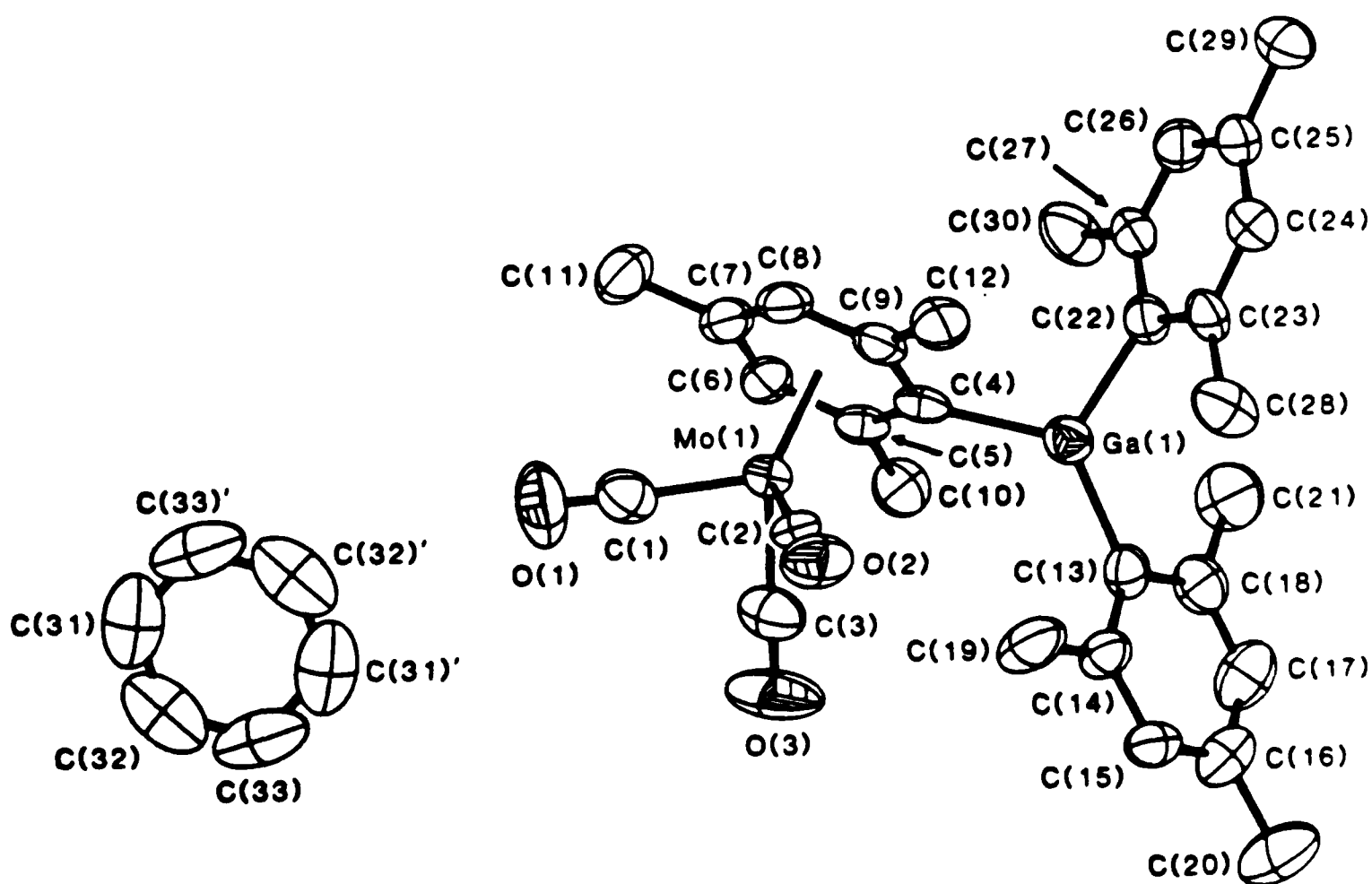


Figure 1. ORTEP drawing of the $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ molecule. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms have been omitted for clarity.

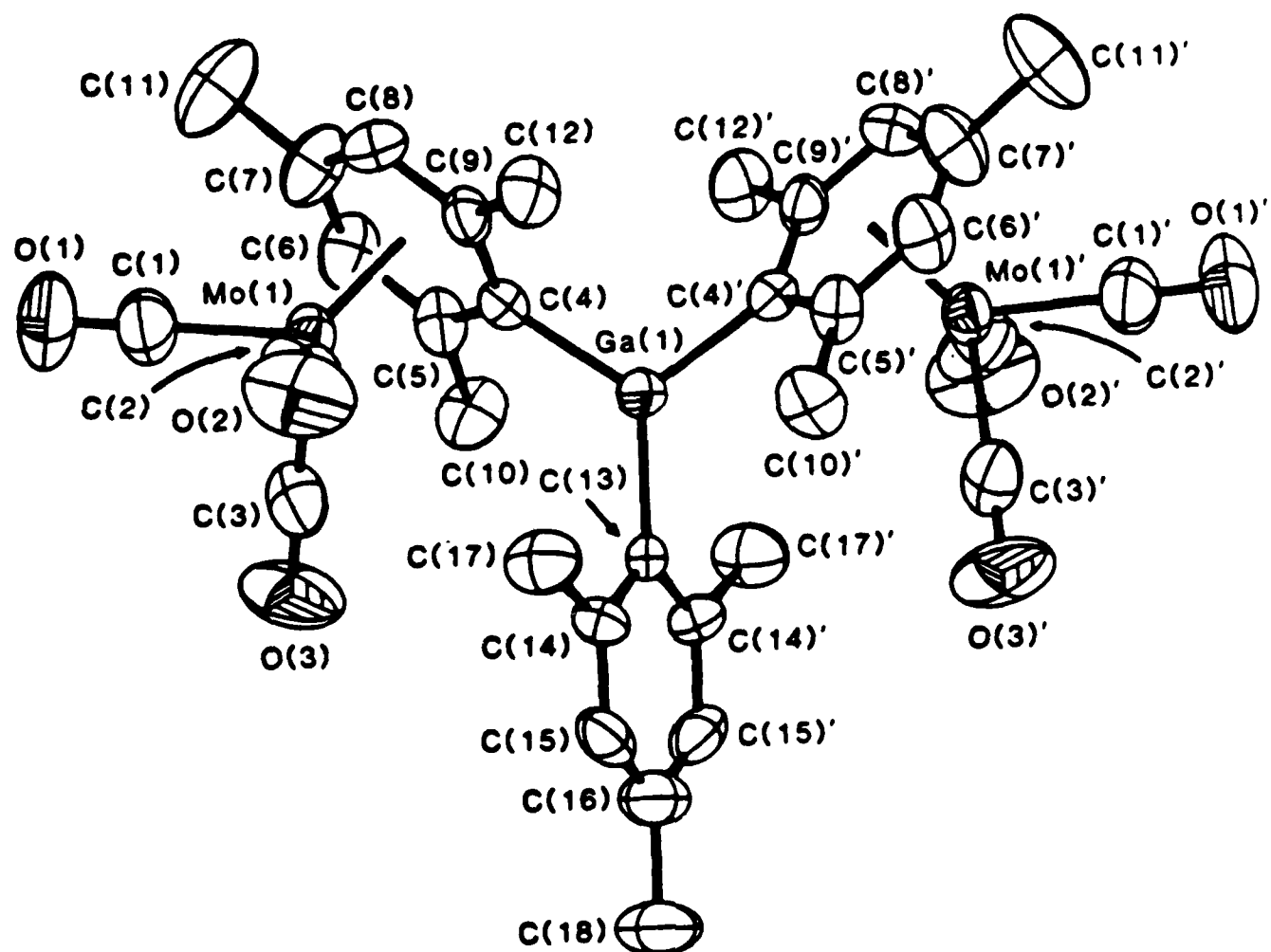


Figure 2. ORTEP drawing of the $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ molecule. The thermal ellipsoids are at the 50% probability level.² The hydrogen atoms have been omitted for clarity.

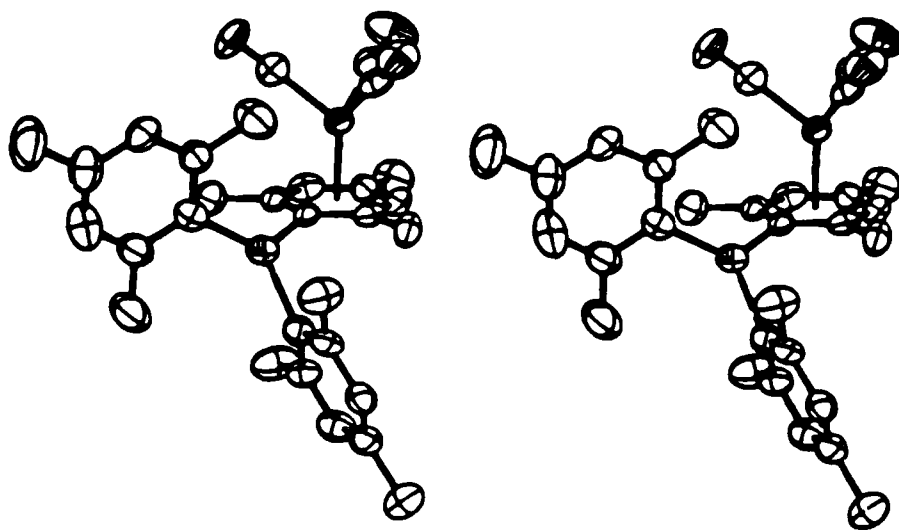


Figure 3. Stereoview of $[(\text{CO})_3\text{MoMes}]\text{GaMes}_2$ showing the arrangement of the mesityl groups around the gallium atom.

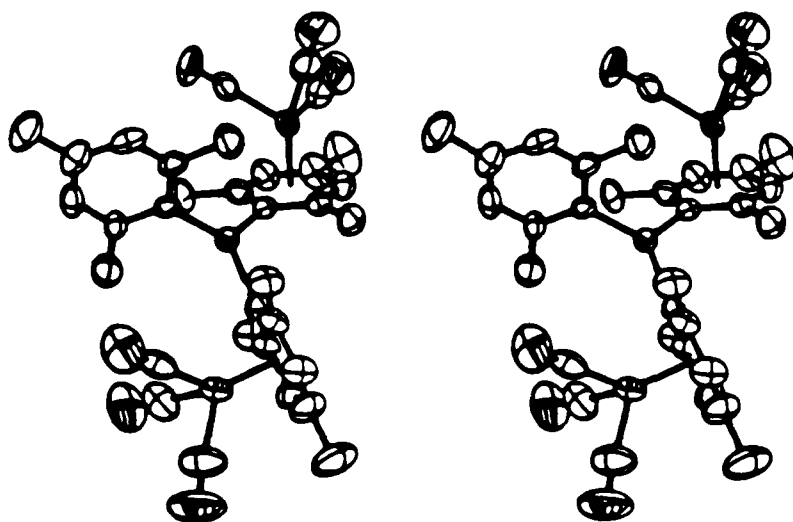


Figure 4. Stereoview of $[(\text{CO})_3\text{MoMes}]_2\text{GaMes}$ showing the arrangement of the mesityl groups around the gallium atom.

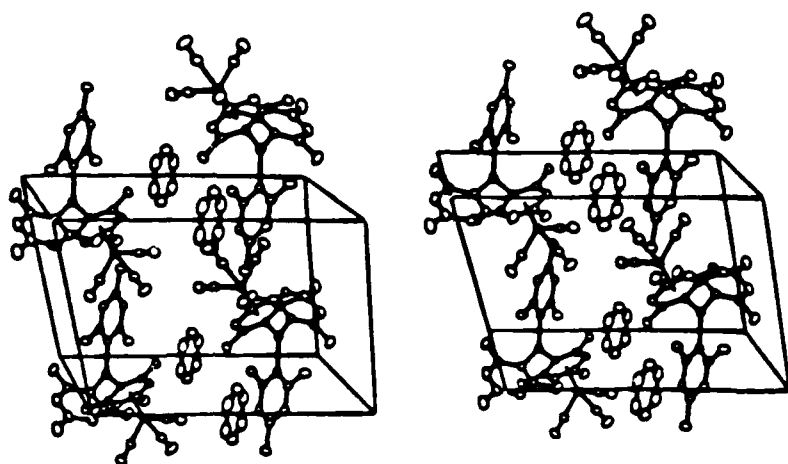


Figure 5. Stereoview showing the packing of molecules in crystalline $[(CO)_3MoMes]GaMes_2$

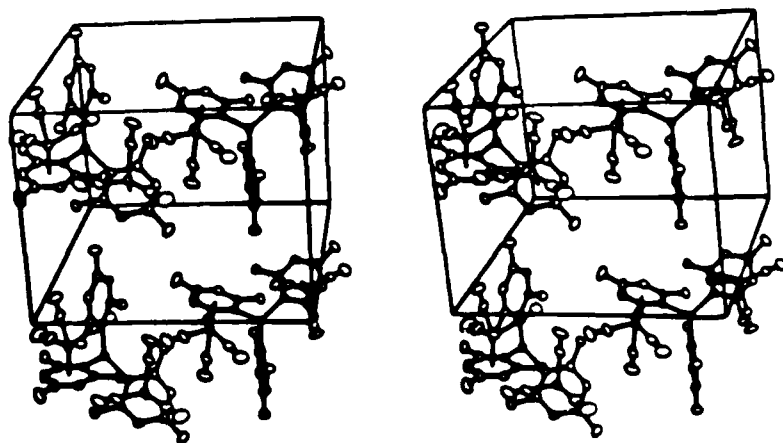


Figure 6. Stereoview showing the packing of molecules in crystalline $[(CO)_3MoMes]_2GaMes$

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