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Chemistry of Mesitylgallium(III) Derivatives as Arene Ligands in Metal Carbonyl Complexes. Crystal and Molecular Structures of $[(CO)_3Mo(\eta^6\text{-}C_6Me_3H_2)]Ga(C_6Me_3H_2)_2$ and $[(CO)_3Mo(\eta^6\text{-}C_6Me_3H_2)]_2Ga(C_6Me_3H_2)$

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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 and characterized by elemental analyses, IR and ^1H NMR spectroscopy, and reactions with hydrogen chloride. X-ray structural studies have defined the nature of $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ in the solid state. Both complexes can be described as $GaMes_3$ molecules with either one or two $Mo(CO)_3$ units bonded in η^6 fashion to mesityl rings. The yellow crystal of $[(CO)_3MoMes]GaMes_2$ that 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) Å, $b = 12.702$ (2) Å, $c = 14.649$ (3) Å, $\alpha = 81.16$ (2)°, $\beta = 79.03$ (1)°, $\gamma = 109.82$ (1)°, $V = 1531.3$ (5) Å^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) Å, $b = 12.186$ (2) Å, $c = 15.497$ (3) Å, $V = 3321.4$ (11) Å^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, $Cr(CO)_5[PPh_2B(NMe_2)_2]$,[2] was prepared from $Cr(CO)_5(THF)$ and $(Me_2N)_2BPPh_2$ in THF solution. Similarly, the reaction between $Cr(CO)_5(NMe_3)$ and $(Me_3SiCH_2)_2AlPPh_2$ in benzene solution provided $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2\cdot NMe_3]$.[3] However, when $KCr(CO)_5PPh_2\cdot 2$dioxane was reacted with $Al(CH_2SiMe_3)_2Br$ in an attempt to develop a second synthetic route to transition-metal complexes of amphoteric ligands,[4] the observed product had the empirical formula $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$. The $(CH_2)_4O$ 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 $Et_2AlN(t\text{-}Bu)PPh_2$ 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 chemistry[5] when combined with $(C_5H_5)Fe(CO)_2Me$ or $HMn(CO)_5$. 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 $PhB(NMe_2)_2$,[6] $PhB(OMe)_2$,[6] $PhB(C_5H_{10})$,[6] and $PhB(CH_2CH(Me)C_2H_4)$.[6] An anionic arene–transition-metal carbonyl complex[8] is $[Me_4N][Ph_2B(\eta^6\text{-}PhM(CO)_3)_2]$ (M = Cr, W). When an attempt was made to prepare a molybdenum derivative, an inseparable mixture of products containing two, three, and possibly four $Mo(CO)_3$ units per BPh_4^- was observed.[8] The only aluminum-containing compounds are derivatives of ferrocene,[9–11] for example $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2Me_4Cl]$ and $[(\eta^5\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$.

In this paper, we report the results of our research that was designed to utilize the mesityl ring 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 $M(CO)_3$ unit (M = Cr, Mo). The new compounds $[(CO)_3MoMes]_2GaMes$, $[(CO)_3MoMes]GaMes_2\cdot nC_6H_6$, $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2DME$, and $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2DME$ (Mes = $C_6Me_3H_2$ = 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 $[(CO)_3MoMes]_2GaMes$ and

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$[(CO)_3MoMes]GaMes_2 \cdot nC_6H_6$.

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 $GaMes_2Cl$[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, NY. 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 tube were sealed under vacuum.

Reactions of Mesitylgallium Compounds with $M(CO)_6$ (M = Cr, 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 $M(CO)_6$. Finally, the product was recrystallized from an appropriate solvent system.

Synthesis of $[(CO)_3MoMes]_2GaMes$. The complex $[(CO)_3MoMes]_2GaMes$ 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 $Mo(CO)_6$ in 100 mL of DME for 24–28 h. Traces of $GaMes_3$ and $[(CO)_3MoMes]GaMes_2$ (~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 $[(CO)_3MoMes]_2GaMes$ 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 being left standing for 16 h at room temperature, the solution was decanted away from the crystals and the solvent was removed in vacuo. **$[(CO)_3MoMes]_2GaMes$**: yellow crystalline solid; mp decomposition begins ~140 °C; ^1H NMR (THF-d_8) 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, ν(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 $[(CO)_3MoMes]GaMes_2$. A reaction mixture of 0.628 g (1.47 mmol) of $GaMes_3$ and 0.380 g (1.44 mmol) of $Mo(CO)_6$ 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 $Mo(CO)_6$. The product was then extracted through a medium porosity frit with 50 mL of pentane (2×) into a 100-mL Schlenk flask. The pentane soluble product (0.254 g) was identified by ^1H NMR spectroscopy as a mixture of $[(CO)_3MoMes]GaMes_2$ 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 $[(CO)_3MoMes]GaMes_2$ (0.287 g 0.473 mmol, 32.8% based on $Mo(CO)_6$) was isolated as a yellow solid. The remaining pentane-insoluble material (0.182 g) was identified by ^1H NMR spectroscopy as predominantly $[(CO)_3MoMes]_2GaMes$ with a trace of $[(CO)_3MoMes]GaMes_2$. The product $[(CO)_3MoMes]GaMes_2$ 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. **$[(CO)_3MoMes]GaMes_2 \cdot n(C_6H_6)$**: yellow crystalline solid; mp decomposition begins ~205 °C; ^1H NMR (THF-d_8) 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, 3 H, Mo–arene), 2.20 (s, *o*-Me, 6 H, Mo–arene), 2.17 (s, *p*-Me, 6 H); ^1H NMR (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, ν(CO), cm^{-1}) 1970 (vs), 1961 (sh, vw), 1902 (vs), 1898 (vs); IR (DME, ν(CO), cm^{-1}) 1960 (sh, s), 1951 (vs), 1879 (vs). Anal. Calcd for $[(CO)_3MoMes]GaMes_2 \cdot {}^1/_2(C_6H_6)$: C, 61.33; H, 5.61. Found: C, 61.11; H, 5.80.

Synthesis of $[(CO)_3MoMes]_2GaCl \cdot {}^1/_2DME$. A reaction mixture of 0.404 g (1.18 mmol) of Mes_2GaCl and 0.649 g (2.46 mmol) of $Mo(CO)_6$ 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 the solution was left standing for 1 h at room temperature, the product $[(CO)_3MoMes]_2GaCl \cdot {}^1/_2DME$ 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 $[(CO)_3MoMes]_2GaCl \cdot {}^1/_2DME$ was isolated after evacuation at RT for several days to remove traces of benzene. **$[(CO)_3MoMes]_2GaCl \cdot {}^1/_2DME$**: yellow crystalline solid; mp decomposition begins ~200 °C; ^1H NMR (THF-d_8) δ 5.28 (s, *m*-H, 4 H), 3.39 (s, CH_2-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, ν(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 $[(CO)_3MoMes]GaCl_2 \cdot {}^1/_2DME$. The reagents $MesGaCl_2$ (0.623 g, 2.40 mmol) and $Mo(CO)_6$ (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 ~180 °C; ^1H NMR (THF-d_8) δ 5.34 (s, *m*-H, 2 H), 3.39 (s, CH_2-DME, 2 H), 3.25 (s, Me-DME, 3 H), 2.43 (s, *o*-Me, 6 H), 2.24 (s, *p*-Me, 3 H); IR (DME, ν(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

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after extracting the reaction product three times with 50 mL of pentane. The composition of the yellow solid was identified by ^{1}H NMR spectroscopy as 71.0% $GaMes_3$ and 2.90% $[(CO)_3CrMes]GaMes_2$. Attempts to separate a pure sample of $[(CO)_3CrMes]GaMes_2$ from $GaMes_3$ by recrystallization were unsuccessful. **$[(CO)_3CrMes]GaMes_2$ (impure)**: ^{1}H NMR (benzene-d_6) 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}, ν(CO), cm^{-1}) 1966 (vs), 1957 (sh, w), 1895 (vs), 1901 (vs).

Reaction of Mes_2GaCl with $Cr(CO)_6$. After 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 were combined, 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 the material was washed several times with benzene. The IR and ^{1}H NMR spectral data of this product were consistent with the formulation $[(CO)_3CrMes]GaCl_2\cdot{}^1/_2$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 ^{1}H NMR spectrum of this material indicated the presence of decomposition products. **$[(CO)_3CrMes]GaCl_2\cdot{}^1/_2$DME (impure)**: ^{1}H NMR (THF-d_8) δ 4.93 (s, *m*-H, 2 H), 2.37 (s, *o*-Me, 6 H), 2.15 (s, *p*-Me, 3 H); IR (DME, ν(CO), cm^{-1}) 1958 (sh, m), 1948 (vs), 1870 (vs). Anal. Calcd: C, 38.14; H, 3.66. Found: C, 40.09; H, 4.66.

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

Reaction of $[(CO)_3MoMes]_2GaMes$ with Anhydrous HCl. Reaction A. A 0.144-g (0.184-mmol) sample of $[(CO)_3MoMes]_2GaMes$ was placed into a reaction vessel that was connected to an NMR tube and ~3 mL of THF-d_8 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 ^{1}H 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 $[(CO)_3MoMes]_2GaCl\cdot$(THF-d_8). Traces of $HMesMo(CO)_3$, $[(CO)_3MoMes]_2GaMes$, and $[(CO)_3MoMes]GaMesCl$ were also observed in the spectrum. **^{1}H NMR data of reaction product mixture (THF-d_8)** (the asterisk indicates relative intensity of line): $[(CO)_3MoMes]_2GaCl\cdot$THF-d_8, 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*); $[(CO)_3MoMes]GaMesCl$, δ 6.74 (s, *m*-H, 1.4*), 2.47 (s, *o*-Me, 6.0*); $HMesMo(CO)_3$, δ 2.22 (s, Me, 10.4*); $[(CO)_3MoMe]_2GaMes$, 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 $[(CO)_3MoMes]_2GaMes$ in 25 mL of DME. After the reaction mixture was stirred 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 ^{1}H NMR spectroscopy as a mixture of HMes and $HMesMo(CO)_3$. The pentane-insoluble material was identified by ^{1}H NMR as a mixture of $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2$DME, $HMesMo(CO)_3$, and HMes. The compound HMes is volatile and can be vacuum distilled at room temperature. Therefore, the ^{1}H NMR spectra were not indicative of the relative amount of HMes produced during reaction. **^{1}H NMR data of reaction products (THF-d_8)**: $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2$DME, δ 5.36 (s, *m*-H, 2 H), 3.39 (s, CH_2-DME, 2 H), 3.23 (s, Me-DME, 3 H), 2.41 (s, *o*-Me, 6 H), 2.22 (s, *p*-Me, 3 H); $HMesMo(CO)_3$, 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 THF-d_8 was 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 min, and then a portion of the solution was decanted into the NMR tube and sealed under vacuum at −196 °C. The ^{1}H NMR spectrum of the reaction mixture identified $[(CO)_3MoMes]GaCl_2\cdot$THF-d_8 and HMes as products. ^{1}H NMR data of **reaction product mixture (THF-d_8)** (the asterisk indicates relative intensity of line): $[(CO)_3MoMes]GaCl_2\cdot$(THF-d_8), 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 the reaction mixture was stirred 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 were redissolved in 10 mL of DME, and the solution was layered with ~60 mL of pentane at room temperature. After the solution was left 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 $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2$DME by ^{1}H NMR spectroscopy. The orange viscous material had a ^{1}H NMR spectrum that was consistent with a mixture of $[(CO)_3MoMes]GaMes_2$, $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME, and $Mes_2GaCl\cdot$DME. On the basis of the chemical shifts of authenic samples of $[(CO)_3MoMes]GaMes_2$, $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME, and $Mes_2GaCl\cdot$DME, many lines in the spectrum were superimposed. Therefore, the relative amounts of individual products were ambiguous. However, the ortho-methyl line of $Mes_2GaCl\cdot$DME was definitively assigned as the major resonance in the spectrum. More detail is presented in the discussion. **^{1}H NMR data of reaction products (THF-d_8)** $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2$DME (yellow crystalline solid), 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 $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME with $KPPh_2$. Reaction A. A-0.509 g (0.679-mmol) sample of $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$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 $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME was added with stirring to $KPPh_2$. Upon mixing, all $KPPh_2$ dissolved and apparently reacted to form an orange solution. After the reaction mixture was stirred 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 ^{1}H 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 $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME was placed in a reaction flask, and 0.162 g (0.722 mmol) of $KPPh_2$ was contained in a connecting side-arm dumper. Then, 50 mL of benzene was vacuum distilled onto $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME, and a portion of the solvent was distilled onto the $KPPh_2$. The benzene-insoluble $KPPh_2$ was added with stirring at room temperature to the solution of $[(CO)_3MoMes]_2GaCl\cdot{}^1/_2$DME. Upon mixing, $KPPh_2$ 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 the precipitate was washed with benzene, 0.344 g of a light brown solid material was isolated. Multiple lines in the ^{1}H NMR spectrum of the brown material indicated a mixture of decomposition products.

Reaction of MesGaCl$_2$ with (C$_6$Me$_3$H$_3$)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$_6$Me$_3$H$_3$)Mo(CO)$_3$ in the drybox. Then, 15 mL of DME was vacuum distilled onto (C$_6$Me$_3$H$_3$)Mo(CO)$_3$. The solution of MesGaCl$_2$ was added at room temperature with stirring to the solution of (C$_6$Me$_3$H$_3$)Mo(CO)$_3$. After 13 h, the solvent was removed by vacuum distillation and a yellow solid remained. The compounds MesGaCl$_2$, (C$_6$Me$_3$H$_3$)Mo(CO)$_3$, [(CO)$_3$MoMes]GaCl$_2$·$^1/_2$DME and C$_6$Me$_3$H$_3$ were identified by the ^{1}H NMR spectrum (THF-d_8). After a period of 4 days, the spectrum indicated that an equilibrium between the starting materials MesGaCl$_2$ and (C$_6$Me$_3$H$_3$)Mo(CO)$_3$ and the reaction products [(CO)$_3$MoMes]GaCl$_2$·$^1/_2$DME and HMes had been established. **^{1}H NMR data of reaction mixture (THF-d_8)** (the asterisk indicates relative intensity of line): MesGaCl$_2$·$^1/_2$DME, δ 6.74 (s, *m*-H, 1.0*), 2.49 (s, *o*-Me, 4.3*); (C$_6$Me$_3$H$_3$)Mo(CO)$_3$, δ 5.36 (s, H), 2.23 (s, Me, 5.0*); [(CO)$_3$MoMes]GaCl$_2$·$^1/_2$DME: δ 5.36 (s, *m*-H), 2.42 (s, *o*-Me, 9.5*); C$_6$Me$_3$H$_3$, δ 6.69 (s, H, 1.4*), 2.20 (s, Me, 7.5*).

Collection of X-ray Diffraction Data for [(CO)$_3$MoMes]GaMes$_2$ and [(CO)$_3$MoMes]$_2$GaMes. A yellow single crystal of each complex was chosen for examination by X-ray diffraction procedures. The dimensions for the crystal of [(CO)$_3$MoMes]GaMes$_2$ were 0.10 × 0.15 × 0.31 mm and for [(CO)$_3$MoMes]$_2$GaMes were 0.19 × 0.20 × 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 P2$_1$ automated four-circle diffractometer. The crystal of [(CO)$_3$MoMes]GaMes$_2$ was found to be triclinic with no systematic absences suggesting the space group $P\bar{1}$, whereas [(CO)$_3$MoMes]$_2$GaMes 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 $2\theta-\theta$ 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)$_3$MoMes]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)$_3$MoMes]$_2$GaMes contained half a molecule with Ga, C(13), C(16), and C(18) fixed at x, z, and half occupancy on the twofold 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 = 0.95 Å, tetrahedral and trigonal angles and idealized thermal parameters with B = 1.0 Å^2 greater than the equivalent isotopic 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)$_3$MoMes]GaMes$_2$ and $R(F) = 0.046$, $R_w(F) = 0.045$, and GOF = 1.27 for 192 variables and 1254 reflections for [(CO)$_3$MoMes]$_2$GaMes.

Table I. Experimental Data for the X-ray Diffraction Studies of [(CO)$_3$MoMes]GaMes$_2$ and [(CO)$_3$MoMes]$_2$GaMes

	[(CO)$_3$MoMes]-GaMes$_2$	[(CO)$_3$MoMes]$_2$-GaMes
formula	MoGaC$_{30}$H$_{33}$O$_3$	Mo$_2$GaC$_{33}$H$_{33}$O$_6$
fw, amu	607.23	787.22
cryst 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)	
V, Å^3	1531.3 (5)	3321.4 (11)
Z	2	4
ρ(calcd), g cm^{-3}	1.40	1.57
cryst dimens, mm	0.10 × 0.15 × 0.31	0.19 × 0.20 × 0.25
cryst faces	(0, 0, 1), (0, 0, −1), (0, 1, 1), (0, −1, −1), (1, 0, 1), (−2, 1, −2)	(−1, −1, 0), (−2, 1, 0), (1, 1, 0), (2, −3, 0), (0, 0, −1), (0, 0, 1)
cryst vol, mm^3	5.08 × 10^{-3}	9.99 × 10^{-3}
diffractometer	Syntex P2	same as [(CO)$_3$MoMes]-GaMes$_2$
radiatn	Mo Kα (0.71073 Å)	
monochromator	graphite crystal	
temp, °C	23	
scan type	$2\theta-\theta$	
scan speed, deg min^{-1}	3.91	
bkgd scan	1.1°, below Kα_1 to 1.1° above Kα_2	
std reflctns	3 per 100 reflctns	
indices of std	(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
transmissn factors	0.7622–0.8885	0.6984–0.8011
2θ scan limits, deg	3.0–48.0	3.0–50.0
cryst 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 refctns scanned	5384 (189 standards)	3442 (108 standards)
unique refctns [$I \geq 3\theta(I)$]	2148	1254
average abs corr	0.9195	0.8694
final no. of variables	343	192
goodness of fit	1.21	1.27
$R(F)$ ($F_o^2 \geq 3\sigma(F_o)^2$)	0.047	0.046
$R_w(F)$ ($F_o^2 \geq 3\sigma(F_o)^2$)	0.045	0.045

Results and Discussion

The first examples of arene–group 6 metal tricarbonyl complexes which have gallium-containing substituents bonded to an arene ring, [(CO)$_3$MoMes]GaMes$_2$, [(CO)$_3$MoMes]$_2$GaMes, [(CO)$_3$MoMes]GaCl$_2$·$^1/_2$DME, and [(CO)$_3$MoMes]$_2$GaCl·$^1/_2$DME (Mes = C$_6$Me$_3$H$_2$, mesityl), have been prepared. These compounds have been fully characterized by elemental analyses, infrared and ^{1}H NMR spectroscopy, and reactions with hydrogen chloride. In addition, single-crystal X-ray diffraction studies of [(CO)$_3$MoMes]GaMes$_2$·nC$_6$H$_6$ and [(CO)$_3$MoMes]$_2$GaMes 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)$_3$MoMes]$_n$GaMes$_{3-n}$ (n = 1, 2) were readily prepared by reacting Mo(CO)$_6$ and

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(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(15) Main, P.; Fiske, S. J.; Hulls, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *Multan 80. A System of Computer Programmes for the Automatic Solution of Crystal Structures for X-Ray Diffraction Data*; University of York: York, England, University of Louvain: Louvain, Belgium.

(16) (a) Churchill, M. R. *Inorg. Chem.* **1983**, *12*, 1213. (b) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968; pp 63–66.

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

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

$GaMes_3$ in refluxing DME. When the ratio of $Mo(CO)_6$ to $GaMes_3$ was 1, 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 3 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 $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ are

Table III. Bond Angles (deg) 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)

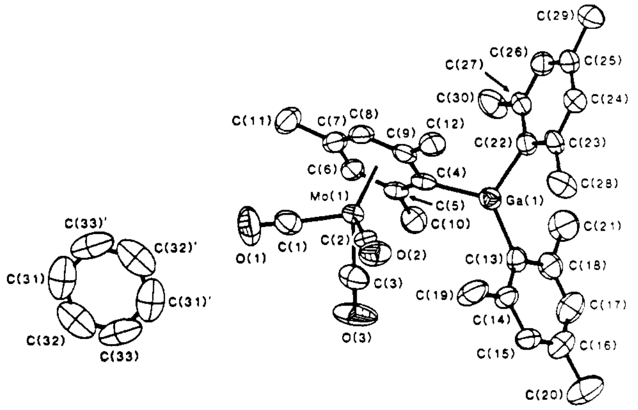

Figure 1. ORTEP drawing of the $[(CO)_3MoMes]GaMes_2$ molecule. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms have been omitted for clarity.

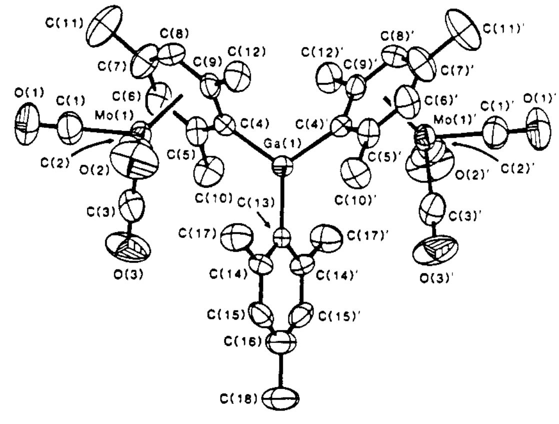

Figure 2. ORTEP drawing of the $[(CO)_3MoMes]_2GaMes$ molecule. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms have been omitted for clarity.

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 $[(CO)_3MoMes]GaMes_2$ is distorted from trigonal planar and lies 0.011 Å 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

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[17] Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* **1970**, 3362.

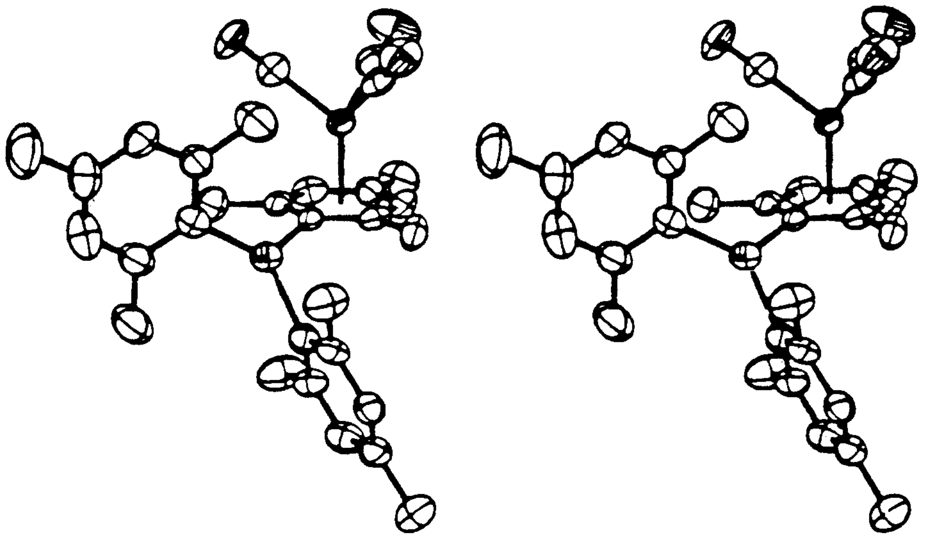

Figure 3. Stereoview of $[(CO)_3MoMes]GaMes_2$ showing the arrangement of the mesityl groups around the gallium atom.

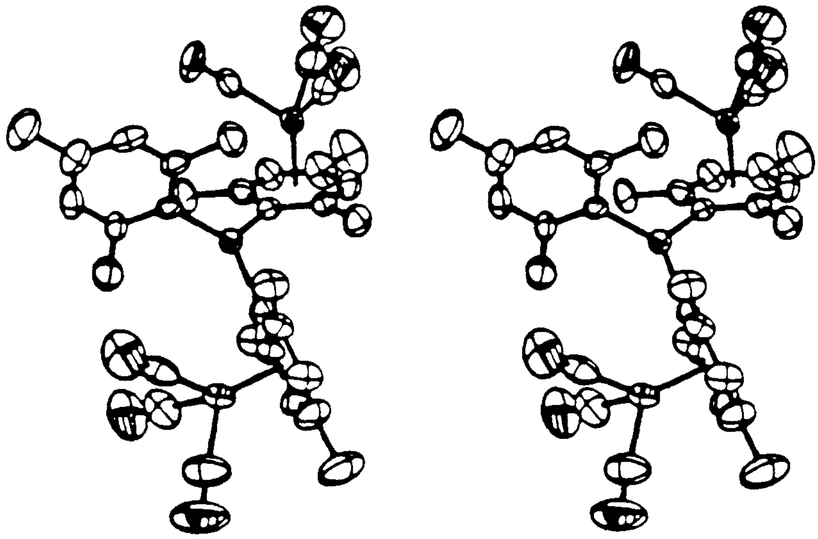

Figure 4. Stereoview of $[(CO)_3MoMes]_2GaMes$ showing the arrangement of the mesityl groups around the gallium atom.

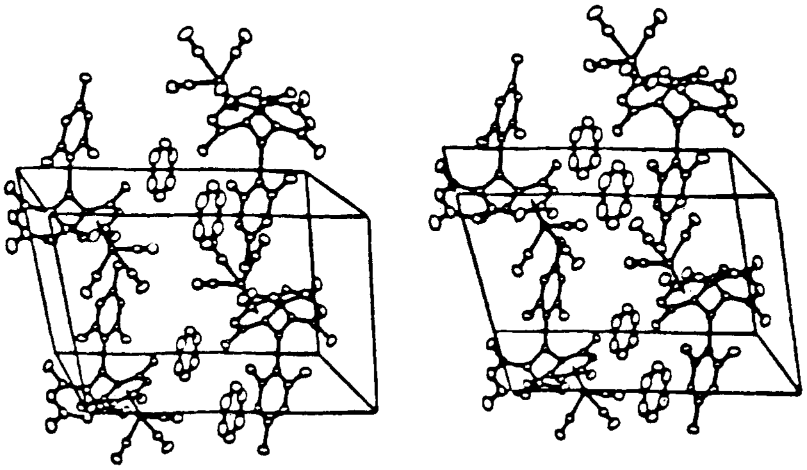

Figure 5. Stereoview showing the packing of molecules in crystalline $[(CO)_3MoMes]GaMes_2$.

C(13)-Ga-C(22) angle is 123.5 (4)°. The geometry of $[(CO)_3MoMes]_2GaMes$ is closer to trigonal planar than that of $[(CO)_3MoMes]GaMes_2$. 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 0.063 Å above the plane defined by the three bound carbon atoms and the C-Ga-C angles at 119.93 (16)°.[12]

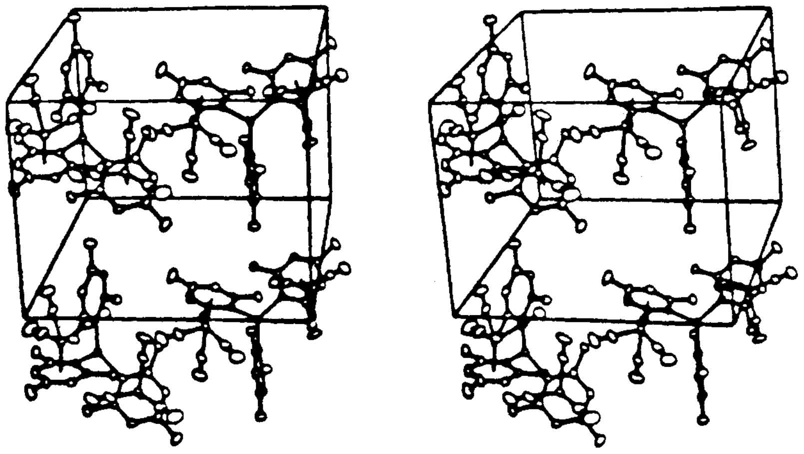

Figure 6. Stereoview showing the packing of molecules in crystalline $[(CO)_3MoMes]_2GaMes$.

As with other triarylgallium compounds,[12,17] the aromatic rings of $[(CO)_3MoMes]_nGaMes_{3-n}$ (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 $[(CO)_3MoMes]GaMes_2$; C(4), C(13), and C(4)′ of $[(CO)_3MoMes]_2GaMes$). For $[(CO)_3MoMes]GaMes_2$ 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 $Mo(CO)_3$ in $[(CO)_3MoMes]_2GaMes$ are equivalent due to the twofold axis at 51.60°. The free mesityl group of $[(CO)_3MoMes]_2GaMes$ which has no bonding interaction with either $Mo(CO)_3$ 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 $[(CO)_3MoMes]GaMes_2$, $[(CO)_3MoMes]_2GaMes$, 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 Å 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 $[(CO)_3MoMes]GaMes_2$ the effect is most pronounced with the bending being 0.3962 Å. The other two mesityl groups in this complex are also bent back (0.292 and 0.144 Å) with the greater distortion being exhibited by the uncomplexed mesityl group nearest to the $Mo(CO)_3$ 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 Å. The bending effect is not observed in the uncomplexed mesityl group since it lies on the twofold axis.

The mesityl rings of both molybdenum complexes are bound in a η^6 manner to the molybdenum atom. The structures of the $Mo(CO)_3Mes$ portions in both compounds are similar to that in 1,3,5-(trimethylbenzene)tricarbonylmolybdenum.[18] The average[18] Mo–C(ring) and Mo–C(carbonyl bond distances in $[(CO)_3MoMes]GaMes_2$ (2.359 (23), 1.948 (22) Å) and in $[(CO)_3MoMes]_2GaMes$ (2.355 (27), 1.951 (25) Å) are not significantly different from those of $(C_6Me_3H_3)Mo(CO)_3$ (2.372 (19), 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)° to 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), 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) Å, 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) Å) and of $[(CO)_3MoMes]_2GaMes$ (1.384 (16)–1.443 (13) Å, average = 1.41 (3) Å) are equivalent to those in $(C_6Me_3H_3)Mo(CO)_3$ which average 1.408 (14) Å.[18]

The elemental analysis as well as the ^1H NMR and infrared spectral data of bulk samples of $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ are consistent with the molecular structures identified by the X-ray structural studies. The ^1H NMR and infrared spectra of $[(CO)_3MoMes]GaMes_2$ in THF-d_8 solution are similar to but distinct from the corresponding spectra of $[(CO)_3MoMes]_2GaMes$. 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 $[(CO)_3MoMes]GaMes_2$. 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 $[(CO)_3MoMes]_2GaMes$ in THF-d_8 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

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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 $M(CO)_3$ unit (M = Cr, Mo, 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 $[(CO)_3MoMes]GaMes_2$ in pentane ($\nu(CO)$) showed a very weak shoulder at 1961 cm^{-1} and three very strong bands at 1970, 1902, and 1898 cm^{-1}, whereas $[(CO)_3MoMes]_2GaMes$ in DME exhibited a shoulder at 1960 cm^{-1} 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 π-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 THF-d_8 solutions of the resulting "air-exposed" solids were identical with 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 $Mo(CO)_3$ moiety on the reactivity of the gallium–mesityl carbon bond, the mono- and dimolybdenum complexes $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ were reacted with anhydrous HCl in either DME or THF-d_8 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 $[(CO)_3MoMes]GaMes_2$ and HCl in a 1:2 mol ratio in THF-d_8 solution indicated that the only reaction products were $[(CO)_3MoMes]GaCl_2\cdot THF\text{-}d_8$ and free mesitylene $C_6Me_3H_3$ (eq 1). When

$$[(CO)_3MoMes]GaMes_2 + 2HCl \xrightarrow{THF\text{-}d_8} [(CO)_3MoMes]GaCl_2\cdot THF\text{-}d_8 + 2C_6Me_3H_3 \quad (1)$$

the dimolybdenum complex $[(CO)_3MoMes]_2GaMes$ in THF-d_8 was reacted with HCl in a 1:1 mol ratio, the major reaction products were $[(CO)_3MoMes]_2GaCl\cdot THF\text{-}d_8$ and $C_6Me_3H_3$. In addition, the complex $(C_6Me_3H_3)Mo(CO)_3$ and a compound believed to be $[(CO)_3MoMes]GaMesCl\cdot THF\text{-}d_8$ were also present in trace amounts. When the amount of HCl was increased to a 1:2 mol ratio ($[(CO)_3MoMes]_2GaMes$/HCl), $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2DME$ was the predominate gallium-containing product (eq 2). The other products were $(C_6Me_3H_3)Mo(CO)_3$ and $C_6Me_3H_3$. The relative amounts of these products ob-

$$[(CO)_3MoMes]_2GaMes + 2HCl \xrightarrow{DME} [(CO)_3MoMes]GaCl_2\cdot{}^1/_2DME + (C_6Me_3H_3)Mo(CO)_3 + C_6Me_3H_3 \quad (2)$$

served in the NMR experiment were consistent with the balanced equation. The ^1H NMR spectra of $[(CO)_3MoMes]GaCl_2\cdot THF\text{-}d_8$, $[(CO)_3MoMes]_2GaCl\cdot THF\text{-}d_8$, $[(CO)_3MoMes]GaCl_2\cdot{}^1/_2DME$, $(C_6Me_3H_3)Mo(CO)_3$, and $(C_6Me_3H_3)$ obtained from these HCl reactions were identical with those observed for the pure compounds. The observation that the gallium–carbon bond to the uncomplexed mesityl ring in the arene complexes $[(CO)_3MoMes]GaMes_2$ and $[(CO)_3MoMes]_2GaMes$ was preferentially cleaved might be related to steric effects of the $Mo(CO)_3$ 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 $(C_6Me_3H_3)Mo(CO)_3$ 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 THF-d_8 solution identified the presence of $[(CO)_3MoMes]GaCl_2\cdot THF\text{-}d_8$ and $C_6Me_3H_3$ as reaction products, $(C_6Me_3H_3)Mo(CO)_3$ 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 (eq 3). The

$$(C_6Me_3H_3)Mo(CO)_3 + MesGaCl_2\cdot base \rightleftarrows [(CO)_3MoMes]GaCl_2\cdot base + C_6Me_3H_3 \quad (3)$$

spectral data suggest that $MesGaCl_2\cdot$base is apparently a better electron donating ligand to $Mo(CO)_3$ 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]

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Lewis bases significantly increase the rate of arene exchange.

The complex $[(CO)_3MoMes]_2GaMes$ also undergoes complex reactions with $MesGaCl_2$ in DME at room temperature to form $[(CO)_3MoMes]GaCl_2{\cdot}{}^1/_2DME$, Mes_2GaCl, $[(CO)_3Mo]GaMes_2$, and $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$. A reaction mixture of $[(CO)_3MoMes]_2GaMes$ 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 $[(CO)_3MoMes]GaCl_2{\cdot}{}^1/_2DME$ by ^1H NMR spectroscopy. The remaining viscous material was identified as a mixture of $Mes_2GaCl{\cdot}DME$, $[(CO)_3MoMes]GaMes_2$, and $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ according to ^1H NMR spectroscopy (THF-d_8 solution). The line with the highest relative intensity in the spectrum was assigned to $Mes_2GaCl{\cdot}DME$. Some of the lines of the other products were superimposed upon one another, a conclusion consistent with the spectra of authentic samples of $Mes_2GaCl{\cdot}DME$, $[(CO)_3MoMes]GaMes_2$, and $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$. The chemical shift of only one line (δ 2.32 ppm) in the spectrum of the viscous material was unassigned. The formation of $[(CO)_3MoMes]GaCl_2{\cdot}{}^1/_2DME$ and $[(CO)_3MoMes]GaMes_2$ is consistent with either a ligand redistribution reaction and/or an arene exchange reaction (eq 4). However, the products

$$[(CO)_3MoMes]_2GaMes + MesGaCl_2 \xrightarrow{DME} [(CO)_3MoMes]GaCl_2{\cdot}{}^1\!/_2DME + [(CO)_3MoMes]GaMes_2 \quad (4)$$

Mes_2GaCl and $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ would suggest only a ligand exchange reaction (eq 5).

$$[(CO)_3MoMes]_2GaMes + MesGaCl_2 \xrightarrow{DME} [(CO)_3MoMes]_2GaCl{\cdot}{}^1\!/_2DME + Mes_2GaCl \quad (5)$$

Attempts to replace the chlorine atom in $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ with the bulky phosphorus group PPh_2 to form a gallium–phosphorus bond were also investigated. When the complex $[(Co)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ 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 $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ 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 $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ 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 invisioned 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 $Cr(CO)_6$ and the group 13 compounds $GaMes_3$, Mes_2GaCl, and $MesGaCl_2$ were also investigated in attempts to prepare the arene complexes $[(CO)_3CrMes]GaMes_2$, $[(CO)_3CrMes]_2GaCl$, and $[(CO)_3CrMes]GaCl_2$. 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 cm^{-1} 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 THF-d_8 solution showed one *m*-H line at δ 4.93, one *o*-Me line at δ 2.37, and one *p*-Me line at δ 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 CH_2(DME) to *m*-H lines, respectively. The infrared spectrum of the benzene insoluble product in DME solution (ν(CO)) exhibited a shoulder at 1958 cm^{-1} and two very strong bands at 1948 and 1870 cm^{-1}. The elemental analyses indicated that the apparent product $[(CO)_3CrMes]GaCl_2{\cdot}{}^1/_2DME$ was impure. Trace contamination of $[(CO)_3CrMes]GaCl_2{\cdot}{}^1/_2DME$ by either $[(CO)_3CrMes]_2GaCl{\cdot}{}^1/_2DME$ or a slight excess of DME would be undetectable by spectroscopic techniques. The corresponding molybdenum complexes $[(CO)_3MoMes]GaCl_2{\cdot}{}^1/_2DME$ and $[(CO)_3MoMes]_2GaCl{\cdot}{}^1/_2DME$ cannot be distinguished by either ^1H NMR or infrared spectral data. When an attempt was made to prepare $[(CO)_3CrMes]GaCl^{2}{\cdot}{}^1/_2DME$ from $MesGaCl_2$ and $Cr(CO)_6$ in refluxing DME, only multiple decomposition products were observed.

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Registry No. $[(CO)_3MoMeS]_2GaMes$, 120085-50-9; GaMeS3, 60607-12-7; $Mo(CO)_6$, 13939-06-5; $[(CO)_3MoMeS]GaMeS_2$,

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120085-51-0; [(CO)$_3$MoMeS]GaMeS2·1/2(C$_6$H$_6$), 120085-52-1; [(CO)$_3$MoMeS]$_2$GaCl·1/2DME, 120085-53-2; MeS$_2$GaCl, 109391-13-1; [(CO)$_3$MoMeS]GaCl$_2$·1/2DME, 120085-54-3; MeSGaCl$_2$, 109391-14-2; Cr(CO)$_6$, 13007-92-6; [(CO)$_3$CrMeS]GaMeS$_2$, 120085-55-4; [(CO)$_3$CrMeS]GaCl2·1/2DME, 120085-56-5; HMeSMo(CO)$_3$, 12089-15-5; [(CO)$_3$MoMeS]GaMeSCl, 120085-57-6; [(CO)$_3$MoMeS]$_2$GaCl·(THF-d_8), 120085-58-7; [(CO)$_3$MoMeS]GaCl$_2$·(THF-d_8), 120085-59-8.

Supplementary Material Available: Tables of crystal data, atomic positional parameters, thermal parameters, bond lengths, and bond angles (11 pages); tables of indices with F_o vs F_c (17 pages). Ordering information is given on any current masthead page.

Structure of 2-Lithiobenzofuran–tmeda and 2-Lithiobenzothiophene–tmeda in the Solid State and in Solution

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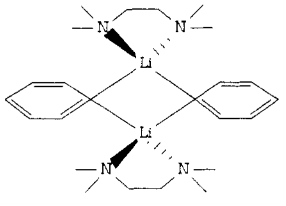
The solid-state structure of 2-lithiobenzofuran–tmeda, determined by single-crystal X-ray diffraction, consists of dimeric species in which benzofuryl rings bridge the lithium atoms and tmeda acts as chelating ligand. The oxygen atom of one of the benzofuryl rings shows an interaction with lithium. The X-ray structure of 2-lithiobenzothiophene–tmeda dimer also shows chelating tmeda ligands to be present, but no sulfur–lithium contacts. The distortion of the C(ipso)–Li–C(ipso)′–Li′ ring, which also is found for dimeric phenyllithium–tmeda, is explained by steric effects. In solution (toluene) both species are revealed by NMR to have dimeric structures with C_{2v} symmetry. NMR shows the same to be true for 2-lithiobenzoselenophene–tmeda in toluene.

Introduction

Dimeric organolithium compounds with chelating ligands, e.g. N,N,N',N'-tetramethylethylenediamine (tmeda), are well-known (1,[1] 2,[2] 3,[3] 4[4]) and have structures which are all of the same type: two bridging organic groups of which the C(ipso) atoms participate in three-center, two-electron bonds and a chelating ligand complete the fourfold coordination of the lithium atoms. Dimeric organolithium compounds derived from organic ring systems containing a heteroatom (e.g. N, O, S) are interesting because their structures may differ from this common type. For example, no bridging carbon atoms occur in the crystal structure of 2-lithio-2-methyl-1,3-dithiane (5[5]), but a sulfur atom of the second dithiane molecule occupies the fourth coordination site. The lithium atoms form part of a six-membered ring in the chair conformation. In our recently published crystal structure of bis[2-lithiophenyl *tert*-butyl sulfide]–tmeda (6[6]), the chelating property of tmeda is not used: one nitrogen atom is displaced by the StBu substituent and sulfur acts as a ligand instead.



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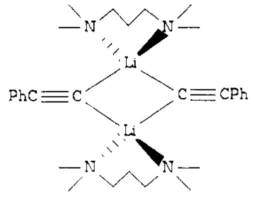

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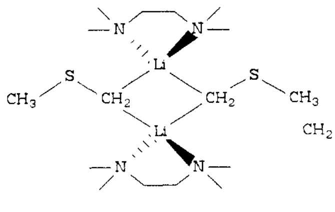

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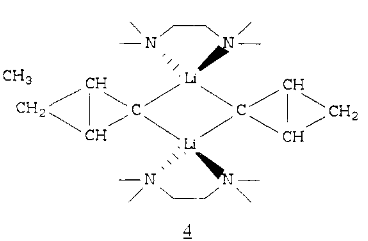

4

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