Organometallic Clusters with Face-Capping Arene Ligands. 4.[†] Tris(cyclopentadienylcobalt) Clusters with μ_3-Alkenyl- and μ_3-Alkylbenzenes

Hubert Wadepohl,* Klaus Büchner, Michael Herrmann, and Hans Pritzkow

*Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270,
D-6900 Heidelberg, Federal Republic of Germany*

The $(CpCo)_3(\mu_3\text{-}(1\text{-alkenyl})benzene)$ clusters **5a,b** and **6a,b** are prepared from $CpCo(C_2H_4)_2$ **(3)** and α-methylstyrene, β-methylstyrene, 1,1-diphenylethylene, and stilbene. From **3** and 4-methoxystilbene a mixture of the coordination isomers of $(CpCo)_3(\mu_3\text{-}4\text{-methoxystilbene})$ **(7a,b)** is obtained. $(CpCo)_3(\mu_3\text{-}1,1\text{-diphenylpropene})$ **(10)** is formed from 1,1-diphenylpropene and $CpCo(C_6Me_6)$ **(4)**. Styrene and **3** do not give a μ_3-styrene cluster, but $(CpCo)_3(\mu_3\text{-}4\text{-methylstyrene})$ **(8)** and $(CpCo)_3(\mu_3\text{-}4\text{-methoxystyrene})$ **(9)** are isolated in good yield from the reaction of **3** and the corresponding substituted styrenes. Allylbenzene, 4-methoxy(allyl)benzene, and 4-phenyl-1-butene are catalytically rearranged by **3** or **4** to the (1-alkenyl)benzene derivatives. By reaction of the further ligands with 3 molar equiv of **3** the $(CpCo)_3(\mu_3\text{-}(1\text{-alkenyl})arene)$ complexes **5b**, **11**, and **12** are formed. The X-ray crystal structures of **5b** and **6a** have been determined. Crystal data: **5b**, monoclinic, $P2_1$, $a = 8.725$ (5) Å, $b = 7.542$ (5) Å, $c = 15.151$ (6) Å, $\beta = 103.17$ (4)°, $Z = 2$, $R = 0.026$, $R_w = 0.027$ $(w = \sigma^{-2}(F))$ with 2893 reflections; **6a·0.5C$_7$H$_8$**, triclinic, $P\bar{1}$, $a = 8.734$ (4) Å, $b = 11.470$ (5) Å, $c = 12.791$ (6) Å, $\alpha = 85.37$ (3)°, $\beta = 83.81$ (3)°, $\gamma = 83.52$ (3)°, $Z = 2$, $R = 0.043$, $R_w = 0.038$ $(w = \sigma^{-2}(F))$ with 5795 reflections. The face-capping arene rings in both compounds are coplanar with the $(CpCo)_3$ triangles and adopt a staggered orientation. Bond length alternation within the μ_3-η^2:η^2:η^2-coordinated arene rings is only slight, with a mean difference of 0.03 Å between longer and shorter carbon–carbon bonds. In solution rotation of the arenes on top of the $(CpCo)_3$ triangles takes place, which can be frozen out at low temperature. The chemical reactivity of the title compounds is low. The μ_3-arene ligands cannot be displaced by other arenes or by two-electron donors. Bromination, hydrosilylation, and cyclopropanation of the exocyclic alkenyl group of **5b** cannot be achieved. However, catalytic hydrogenation of **5b** to give $(CpCo)_3(\mu_3\text{-}n\text{-propylbenzene})$ **(18)** proceeds readily. The relationship of the μ_3-arene clusters to the metal surface adsorption states of benzene is discussed.

Molecular complexes containing arene ligands interacting with more than one transition-metal center are still rare. Bridging benzene molecules were found to be present in the polymeric silver perchlorate benzene adduct Ag·ClO_4·C_6H_6 as early as 1950.[1] The first example of a dinuclear molecular μ_2-benzene complex, $Pd_2(Al_2Cl_7)_2(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_6)_2$, was reported already in 1965.[2] However, only in the last few years have more dinuclear compounds with bridging arenes been prepared and structurally characterized.[3] A great variety of coordination modes of the bridging arenes ($\eta^2:\eta^2$,[3a–d] $\eta^3:\eta^3$,[3e] $\eta^4:\eta^4$,[3e,f] and $\eta^6:\eta^6$[3e,g–i]) was found in these complexes. Examples of cluster-bound arenes had been restricted to a few compounds with η^6 coordination of the organic ring to one metal center until 1985, when trimetal face-capping μ_3-$\eta^2:\eta^2:\eta^2$-benzene was shown to be present in $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)$ **(1)** and $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$ **(2)**.[4] The μ_3-benzene ligands were introduced into or respectively generated on the preformed *oligonuclear* metal clusters.

In a preliminary communication[5] we reported the one-pot synthesis of $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}(E)\text{-}\beta\text{-methylstyrene})$ **(5b)** from the alkenylbenzene ligand and the *mononuclear* Jonas reagent[6] $CpCo(C_2H_4)_2$ **(3)**. Using this route, we have subsequently prepared a considerable number of complexes $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-arene})$ **(5–12)**, where the arene is a ring-substituted and/or side-chain-substituted vinylbenzene.

In the present contribution this novel class of organometallic clusters with face-capping arene ligands is fully described in terms of syntheses, chemical properties, solid-state structure, and dynamic behavior in solution. We shall also address the relationship of the molecular clusters with μ_3-benzene ligands to the adsorption states

of arenes (benzene in particular) on close-packed metal surfaces.

Experimental Section

Materials and Methods. The preparations of the complexes described in this study were carried out under an atmosphere of purified nitrogen with use of Schlenk techniques. Solvents and liquid ligands were dried by standard methods and stored under

(1) Rundle, R. E.; Goring, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 5337. Smith, H. G.; Rundle, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 5075. [Cu(OS-O$_2$CF$_3$)]$_2$(C$_6$H$_6$) also has a polymeric layered structure with μ_2-η^2:η^2 coordination of the bridging benzene molecules: Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.

(2) Allegra, G.; Immirzi, A.; Porri, L. *J. Am. Chem. Soc.* **1965**, *87*, 1394. Allegra, G.; Tettamanti Casagrande, G.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289. Nardin, G.; Delise, P.; Allegra, G. *Gazz. Chim. Ital.* **1975**, *105*, 1047.

(3) (a) Harman, W. D., Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883; **1988**, *110*, 5725, 7555. Harman, W. D.; Gebhard, M.; Taube, H. *Inorg. Chem.* **1990**, *29*, 567. (b) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576. (c) Neithamer, D. R.; Párkányi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421. (d) Omori, H.; Suzuki, H.; Take, Y.; Moro-oka, Y. *Organometallics* **1989**, *8*, 2270. (e) Jonas, K.; Koepe, G.; Schieferstein, L.; Mynott, R.; Krüger, C. Tsai, Y.-H. *Angew. Chem.* **1983**, *95*, 637; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 620; *Angew. Chem. Suppl.* **1983**, 920. (f) Jonas, K.; Wiskamp, V.; Tsai, Y.-H.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480. (g) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H. J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. Angermund, K.; Claus, K. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1985**, *97*, 241; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 241. (h) Jonas, K.; Rüsseler, W.; Angermund, K.; Krüger, C. *Angew. Chem.* **1986**, *98*, 904; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 927. (i) Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096. Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583.

(4) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682.

(5) Wadepohl, H.; Büchner, K.; Pritzkow, H. *Angew. Chem.* **1987**, *99*, 1294; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1259.

(6) Jonas, K.; Krüger, C. *Angew. Chem.* **1980**, *92*, 513; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005.

nitrogen. The following ligands were prepared according to published procedures: allylbenzene,[7] 1,1-diphenylethene,[8] 1,1-diphenylpropene,[9] and 4-phenyl-1-butene.[10] All other ligands were obtained from commercial sources. $CpCo(C_2H_4)_2$ (3) and $CpCo(C_6Me_6)$ (4) were prepared as described by Jonas et al.[6] Instruments used were as follows: NMR spectra (at ambient temperature if not stated otherwise), Bruker AC 200 (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C); mass spectra, Finnigan MAT 8230 (electron impact ionization (EI) mode (70 eV) or chemical ionization (CI) with isobutane). Multiplicities of the ^{13}C NMR signals were generally determined by using the standard ^{1}H gated decoupled, DEPT, or J-modulated spin echo techniques. Elemental analyses were performed at the analytical laboratory of the Chemische Institute, Universität Heidelberg. Petroleum ether refers to the fraction with a boiling range of 40–60 °C.

(CpCo)₃(μ₃-alkenylbenzene). General Procedure. The arene ligand (maximum 50 mmol) was added to a solution of $CpCo(C_2H_4)_2$ (3; maximum 30 mmol) in 100–150 mL of petroleum ether at room temperature. The mixture was stirred at 40–45 °C, and the progress of the reaction was monitored by ^{1}H NMR analysis. If no $H(CpCo)_4(CCH_3)$ (13) was apparent after 3–4 h, the temperature was raised to 60 °C for a further 1 h. Otherwise, the reaction was brought to completion at 30–40 °C for another 3–4 h.

Product Workup. Method 1. The solvent was removed from the reaction mixture in vacuo, and the dry residue was redissolved in the minimum amount of toluene. The toluene solution was then chromatographed on $Al_2O_3/5\%$ H_2O (3 × 30 cm column).

Method 2. The precipitate was removed from the reaction mixture by filtration and redissolved in petroleum ether/toluene (1:1), and this solution was filtered through a short (5–10 cm) column of $Al_2O_3/5\%$ H_2O. The products could be crystallized directly from the brown eluates at +5 to –20 °C.

(CpCo)₃(μ₃-η²:η²:η²-α-methylstyrene) (5a). From 0.96 g (5.33 mmol) of $CpCo(C_2H_4)_2$ (3) and 1.26 g (10.68 mmol) of α-methylstyrene 0.63 g (73% yield) of 5a was obtained (method 1): mp 168 °C dec; ^{1}H NMR (toluene-d_8) δ 5.05 (dd, J_{HH} = 1.3, 0.7 Hz, 1 H, olefin H), 4.54 ("s", 18 H, Cp, arene H, olefin H), 4.19 (m, 3 H, arene H), 1.60 (d, J_{HH} = 0.7 Hz, 3 H, CH_3); ^{1}H NMR (CD₂Cl₂, 220 K) δ 5.03 (s, 1 H, olefin H), 4.89 (s, 5 H, Cp), 4.80 (s, 6 H, Cp and olefin H), 4.66 (s, 5 H, Cp), 4.42 (br m, 5 H, arene H), 1.70 (s, 3 H, CH_3); ^{13}C NMR (toluene-d_8) δ 149.7 (s, C-α), 104.7 (t, C-β), 82.6 (br d, Cp), 59.3 (s, arene C_{ipso}), 41.1 (d, arene CH), 40.1 (br d, arene CH), 39.6 (d, arene CH), 21.7 (q, CH_3); ^{13}C{^{1}H} NMR (CD₂Cl₂, 200 K) δ 149.0 (C-α), 102.5 (br, C-β), 83.37 (Cp), 81.82 (Cp), 81.79 (Cp), 58.3 (arene C_{ipso}), 43.0 (arene CH), 40.5 (arene CH), 40.1 (arene CH), 39.2 (arene CH), 38.2 (arene CH), 21.4 (CH_3); EI-MS m/z 490 (22% relative intensity, M⁺), 370 (83, [(CpCo)₃ – 2H]⁺), 301 (12), 247 (23, [(CpCo)₂ – H]⁺), 189 (100, [Cp₂Co]⁺), 124 (51, [CpCo]⁺), 119 (37, [C₉H₁₁]⁺), 118 (25, [C₉H₁₀]⁺), 117 (16, [C₉H₉]⁺), 115 (14), 103 (15), 92 (16, [C₇H₈]⁺), 91 (34, [C₇H₇]⁺), 78 (16, [C₆H₆]⁺), 77 (20, [C₆H₅]⁺), 66 (32, [C₅H₆]⁺), 65 (21, [C₅H₅]⁺), 63 (13), 59 (26, Co⁺), 41 (12), 40 (10), 39 (43, [C₃H₃]⁺), 32 (10). Anal. Calcd for $C_{24}H_{25}Co_3$: C, 58.80; H, 5.14. Found: C, 58.62; H, 5.25.

(CpCo)₃(μ₃-η²:η²:η²-(E)-β-methylstyrene) (5b). From 3.00 g (16.67 mmol) of $CpCo(C_2H_4)_2$ (3) and 3.94 g (33.39 mmol) of β-methylstyrene 2.28 g (84% yield) of 5b was obtained (method 2). Likewise, 1.18 g (6.56 mmol) of 3 and 0.93 g (7.88 mmol) of allylbenzene gave 0.91 g (85% yield) of 5b (method 2): mp 182 °C; ^{1}H NMR (toluene-d_8) δ 5.76 (dq, J_{HH} = 15.6, 1.5 Hz, 1 H, olefin H), 5.44 (dq, J_{HH} = 15.6, 6.5 Hz, 1 H, olefin H), 4.58 (s, 15 H, Cp), 4.4 (m, 2 H, arene H), 4.2 (m, 3 H, arene H), 1.57 (dd, J_{HH} = 6.5, 1.5 Hz, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 140.1 (d, olefin C), 116.4 (d, olefin C), 82.7 (d, Cp), 56.1 (s, arene C_{ipso}), 41.8 (d, arene CH), 40.9 (d, arene CH), 39.2 (d, arene CH), 18.4 (q, CH_3); ^{13}C{^{1}H} NMR (THF-d_8, 200 K) δ 139.9 (olefin C), 115.4 (olefin C), 83.5 (Cp), 83.0 (Cp), 56.1 (arene C_{ipso}), 45.3 (arene CH), 41.0 (arene CH), 39.5 (arene CH), 38.7 (arene CH), 38.6 (arene CH), 19.1 (CH_3); DCI-MS m/z 490 (43% relative intensity, M⁺, 370 (100, [(CpCo)₃ – 2H]⁺), 247 (20, [(CpCo)₂ – H]⁺), 207 (22), 189 (87, [Cp₂Co]⁺),

124 (28, [CpCo]⁺), 118 (15, [PhC₃H₅]⁺), 117 (19, [PhC₃H₄]⁺), 91 (8, [C₇H₇]⁺), 59 (15, Co⁺), 44 (19). Anal. Calcd for $C_{24}H_{25}Co_3$: C, 58.80; H, 5.14. Found: C, 58.45; H, 5.16.

(CpCo)₃(μ₃-η²:η²:η²-1,1-diphenylethylene) (6a). From 1.70 g (9.44 mmol) of $CpCo(C_2H_4)_2$ (3) and 0.64 g (3.56 mmol) of 1,1-diphenylethylene 1.55 g (89% yield) of 6a was obtained (method 2); mp 188–190 °C. The product crystallized from toluene with ¹/₂ molar equiv of toluene as a solvent of crystallization: ^{1}H NMR (toluene-d_8) δ 7.33–6.92 (m, Ph* (Ph* = noncoordinated phenyl)), 5.25 (d, J_{HH} = 1.2 Hz, 1 H, olefin H), 5.03 (d, J_{HH} = 1.1 Hz, 1 H, olefin H), 4.58 (s, br, 17 H, Cp and coordinated arene H), 4.18 (m, 3 H, coordinated arene H); ^{13}C{^{1}H} NMR (C_6D_6) δ 156.7 (olefin C), 141.8 (Ph* C_{ipso}), 129.5 (Ph* CH), 127.79 (Ph* CH), 127.75 (Ph* CH), 107.9 (CH_2), 82.9 (br, Cp), 54.7 (arene C_{ipso}), 42.2 (br, arene CH), 41.3 (arene CH), 39.8 (arene CH); EI-MS m/z 552 (1% relative intensity, M⁺), 372 (1, [(CpCo)₃]⁺), 282 (9), 233 (19), 232 (100), 215 (14), 180 (7, L⁺), 154 (11), 153 (12), 141 (34), 128 (22), 115 (17), 92 (12, [C₇H₈]⁺), 91 (47, [C₇H₇]⁺) (L = 1,1-diphenylethylene). Anal. Calcd for $C_{29}H_{27}Co_3·0.5C_7H_8$: C, 65.23; H, 5.32. Found: C, 65.25; H, 5.22.

(CpCo)₃(μ₃-η²:η²:η²-(E)-stilbene) (6b). A 1.02-g (5.67-mmol) amount of $CpCo(C_2H_4)_2$ (3) and 1.02 g (5.67 mmol) of (E)-stilbene gave 0.89 g (85% yield) of 6b (method 1). The same product (0.59 g, 85% yield) was obtained from 0.68 g (3.78 mmol) of 3 and 0.25 g (1.39 mmol) of (Z)-stilbene (method 1): dec pt above 180 °C; ^{1}H NMR (CD₂Cl₂) δ 7.41–7.14 (m, 5 H, Ph* (Ph* – noncoordinated phenyl)), 6.68 and 6.44 (AB system, J_{AB} = 16.0 Hz, 2 H, H-α, H-β), 4.89 (s, 15 H, Cp), 4.76 (m, 2 H, arene H), 4.50 (m, 3 H, arene H); ^{1}H NMR (CD₂Cl₂, 190 K) δ 7.37–7.06 (m, 5 H, Ph*), 6.63 and 6.32 (AB system, J_{AB} = 15.5 Hz, 2 H, H-α, H-β), 4.93 (s, 5 H, Cp), 4.80 (s, 5 H, Cp), 4.78 (s, 5 H, Cp), 4.46 (m, 5 H, arene H); ^{13}C{^{1}H} NMR (CD₂Cl₂) δ 139.0 (Ph* C_{ipso}), 138.4 (C-α), 129.0 (Ph* CH), 126.4 (Ph* CH), 125.5 (Ph* CH), 120.1 (C-β), 82.8 (Cp), 55.5 (arene C_{ipso}), 42.3 (arene CH), 41.5 (arene CH), 39.7 (arene CH); EI-MS m/z 552 (1% relative intensity, M⁺), 370 (4, [(CpCo)₃ – 2H]⁺), 189 (100, [Cp₂Co]⁺, 180 (65, [C₁₄H₁₂]⁺), 179 (41, [C₁₄H₁₁]⁺, 178 (22, [C₁₄H₁₀]⁺, 165 (17), 124 (33, [CpCo]⁺), 89 (11, [C₇H₅]⁺), 59 (24, Co⁺), 44 (13), 39 (12, [C₃H₃]⁺), 32 (17). Anal. Calcd for $C_{29}H_{27}Co_3$: C, 63.06; H, 4.93. Found: C, 62.99; H, 5.21.

(CpCo)₃(μ₃-η²:η²:η²-4-methoxy-(E)-stilbene) (Mixture of Isomers; 7a,b). From 1.05 g (5.86 mmol) of $CpCo(C_2H_4)_2$ (3) and 0.45 g (2.14 mmol) of 4-methoxy-(E)-stilbene 0.78 g (69% yield) of an inseparable mixture of 7a,b was obtained (method 1). The isomeric ratio was 7a:7b = 2.3:1 (by ^{1}H NMR analysis): ^{1}H NMR (CD₂Cl₂) δ 7.4 to 6.8 (several overlapping signals, arene H*,†,‡ (* = noncoordinated ring, † = compound 7a, ‡ = compound 7b)), thereof 7.31 (m) and 6.82 (m) ((AB)₂ system, arene H*,†), 6.68 and 6.46 (AB system, J_{HH} = 16 Hz, olefin H‡), 6.52 and 6.41 (AB system, J_{HH} = 16 Hz, olefin H†), 4.88 (br s, Cp†,‡), 4.76 (m, arene H†,‡), 4.48 (m, arene H†,‡), 3.77 (s, OCH₃†), 3.36 (s, OCH₃‡); ^{1}H NMR (toluene-d_8, 320 K) δ 7.3–6.9 (several overlapping signals, arene H*,†,‡), thereof 7.24 (m) and 6.72 (m) ((AB)₂ system, arene H*,†), 6.57 (m, olefin H‡), 6.51 and 6.47 (AB system, J_{HH} = 16.0 Hz, olefin H†), 4.68 (s, Cp‡), 4.67 (s, Cp†), 4.58 (m, arene H†,‡), 4.31 (m, arene H†,‡), 3.37 (s, OCH₃†), 3.09 (s, OCH₃‡); ^{13}C{^{1}H} NMR (CD₂Cl₂) δ 158.7 (COCH₃*,†), 138.9 (C), 137.9 (CH), 136.2 (CH), 131.7 (C), 129.0 (CH), 126.6 (CH), 126.4 (CH), 125.5 (CH), 120.2 (CH), 119.8 (CH), 114.5 (CH) (arene C*,†,‡ CH*,†,‡ olefin CH†,‡), 105.2 (arene COCH₃‡), 83.3 (Cp‡), 82.8 (Cp†), 56.0 (arene C_{ipso}), 55.9 (OCH₃‡), 55.6 (OCH₃†), 53.5 (arene C_{ipso}), 41.9 (br), 41.4 (arene CH), 39.6 (arene CH), 38.3 (arene CH), 32.7 (arene CH); EI-MS m/z 582 (35% relative intensity, M⁺), 456 (10), 393 (25, [M – Cp₂Co]⁺), 370 (65, [(CpCo)₃ – 2H]⁺), 210 (75, L⁺), 189 (100, [Cp₂Co]⁺), 167 (15), 165 (20), 152 (10), 124 (35, [CpCo]⁺) (L = 4-methoxystilbene). Anal. Calcd for $C_{30}H_{29}Co_3O$: C, 61.87; H, 5.02. Found: C, 62.01; H, 5.38.

(CpCo)₃(μ₃-η²:η²:η²-4-methylstyrene) (8). A 1.05-g (8.93-mmol) amount of 4-methylstyrene was added to a solution of 1.61 g (8.94 mmol) of $CpCo(C_2H_4)_2$ (3) in 60 mL of petroleum ether. The solution immediately turned deep red and was divided into two equal parts after 8 h at room temperature. All volaties were removed from the first half under reduced pressure; the residue was redissolved in 15 mL of toluene and the solution chromatographed on a $Al_2O_3/5\%$ H_2O column (3 × 25 cm). The main red fraction was identified as $CpCo(C_6H_6)$ by ^{1}H NMR analysis. The second half of the original reaction mixture was refluxed for

(7) Hershberg, E. B. *Helv. Chim. Acta* **1934**, *17*, 351.
(8) *Organikum*; VEB Verlag der Wissenschaften: Berlin, 1977.
(9) Klages, A. *Chem. Ber.* **1902**, *35*, 2649.
(10) Hurd, C. D.; Bollman, H. T. *J. Am. Chem. Soc.* **1934**, *56*, 447.

another 5 h and then worked up according to method 1. Recrystallization of the oily brown product from petroleum ether gave 0.5 g of 8 (extrapolated yield 68%): mp 179 °C; ^{1}H NMR (toluene-d_8) δ 6.00 (dd, J_{HH} = 17.3, 10.6 Hz, 1 H, H-α), 5.01 (dd, J_{HH} = 17.4, 1.3 Hz, 1 H, H-β), 4.74 (dd, J_{HH} = 10.6, 1.3 Hz, 1 H, H-β'), 4.55 (s, 15 H, Cp), 4.32 (m) and 4.10 (m) ((AB)$_2$ system, 4 H, arene H), 1.65 (s, 3 H, CH$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 310 K): δ 145.5 (C-α), 104.6 (C-β), 83.1 (Cp), 44.0 (arene CH), 40.2 (arene CH), 27.6 (CH$_3$) (quaternary carbons could not be detected unambiguously); EI-MS m/z 490 (6% relative intensity, M$^+$), 488 (5, [M – 2H]$^+$), 370 (13, [(CpCo)$_3$ – 2H]$^+$), 189 (73, [Cp$_2$Co]$^+$), 124 (20, [CpCo]$^+$), 120 (19, [L + 2H]$^+$), 118 (85, L$^+$), 117 (69, [L – H]$^+$), 115 (58), 106 (15), 105 (100, [C$_8$H$_9$]$^+$), 103 (13, [C$_8$H$_7$]$^+$), 91 (31, [C$_7$H$_7$]$^+$), 77 (12, [C$_6$H$_5$]$^+$), 63 (11), 59 (14, Co$^+$), 58 (28), 51 (13), 50 (18), 42 (27), 41 (17), 39 (35), 32 (22) (L = 4-methylstyrene). Anal. Calcd for C$_{24}$H$_{25}$Co$_3$: C, 58.80; H, 5.14. Found: C, 58.81; H, 5.06.

(CpCo)$_3$(μ_3-η^2:η^2:η^2-4-methoxystyrene) (9). From 1.10 g (6.11 mmol) of CpCo(C$_2$H$_4$)$_2$ (3) and 0.82 g (6.11 mmol) of 4-methoxystyrene 0.88 g (85% yield) of 9 was obtained (method 1): mp 166 °C; ^{1}H NMR (C$_6$D$_6$) δ 6.09 (dd, J_{HH} = 17.3, 10.7 Hz, 1 H, H-α), 5.10 (dd, J_{HH} = 17.3, 1.1 Hz, 1 H; H-β), 4.83 (dd, J_{HH} = 10.6, 1.2 Hz, 1 H, H-β'), 4.67 (s, 15 H, Cp), 4.55 (m) and 4.18 (m) ((AB)$_2$ system, 4 H, arene H), 3.00 (s, 3 H, OCH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 145.7 (C-α), 104.3 (C-β), 83.8 (Cp), 55.7 (OCH$_3$), 53.7 (arene C$_{ipso}$), 49.3 (arene C$_{ipso}$), 38.4 (arene CH), 33.1 (arene CH); high-resolution MS calcd for M (^{59}Co$_3$^{16}O^{12}C$_{24}$^{1}H$_{25}$) 505.990, measd 505.985. Anal. Calcd for C$_{24}$H$_{25}$Co$_3$O: C, 56.94; H, 4.98. Found: C, 56.07; H, 5.03. The carbon value was consistently low for several samples prepared and multiply recrystallized independently.

(CpCo)$_3$(μ_3-η^2:η^2:η^2-1,1-diphenylpropene) (10). A mixture of 0.42 g (1.47 mmol) of CpCo(C$_6$Me$_6$) (4) and 0.10 g (0.49 mmol) of 1,1-diphenylpropene in 50 mL of THF was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and C$_6$Me$_6$ was sublimed off from the residue at 10^{-3} mbar and 65 °C. The brown residue was extracted with toluene. The toluene solution was then chromatographed on Al$_2$O$_3$/5% H$_2$O (3 × 20 cm). After recrystallization of the brown fraction from toluene/petroleum ether 0.10 g (38% yield) of 10 was obtained. The crystals do not melt up to 300 °C: ^{1}H NMR (C$_6$D$_6$, 330 K) δ 7.25–7.10 (Ph* (Ph* = noncoordinated phenyl)), 5.89 (q, J_{HH} = 7.2 Hz, 1 H, olefin H), 4.69 (s, 15 H, Cp), 4.6 (m, 2 H, arene H), 4.25 (m, 3 H, arene H), 2.95 (d, J_{HH} = 7.2 Hz, 3 H, CH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 148.0 (C), 140.0 (C), 130.6 (Ph* CH), 127.9 (Ph* CH), 126.9 (Ph* CH), 118.3 (olefin CH), 83.1 (Cp), 58.6 (arene C$_{ipso}$), 42.9 (arene CH), 41.1 (arene CH), 39.5 (arene CH), 16.0 (CH$_3$); EI-MS m/z 566 (6% relative intensity, M$^+$), 370 (100, [(CpCo)$_3$ – 2H]$^+$), 368 (57), 311 (23), 189 (8, [Cp$_2$Co]$^+$), 124 (2, [CpCo]$^+$), 59 (2, Co$^+$). Anal. Calcd for C$_{30}$H$_{29}$Co$_3$: C, 63.62; H, 5.16. Found: C, 63.18; H, 5.39.

(CpCo)$_3$(μ_3-η^2:η^2:η^2-4-methoxy-(E)-β-methylstyrene) (11). From 0.46 g (2.56 mmol) of CpCo(C$_2$H$_4$)$_2$ (3) and 0.76 g (5.11 mmol) of 4-allylanisole a brown oil (100 mg) was obtained (method 1). Complete separation of 11 from 4-methoxy-(E)-β-methylstyrene was not possible: ^{1}H NMR (C$_6$D$_6$) δ 5.80 (m, 1 H, olefin H), 5.55 (m, 1 H, olefin H), 4.72 (br s, 15 H, Cp), 4.59 (m) and 4.23 (m) ((AB)$_2$ system, 4 H, arene H), 3.03 (s, 3 H, OCH$_3$), 1.62 (dd, 3 H, CH$_3$).

(CpCo)$_3$(μ_3-η^2:η^2:η^2-(E)-β-ethylstyrene) (12). From 1.64 g (9.11 mmol) of CpCo(C$_2$H$_4$)$_2$ (3) and 0.44 g (3.33 mmol) of 4-phenyl-1-butene 0.05 g (3% yield) of 12 was obtained (method 1): ^{1}H NMR (C$_6$D$_6$) δ 5.87 (d, J_{HH} = 15.7 Hz, 1 H, H-α), 5.58 (m, 1 H, H-β), 4.68 (s, 15 H, Cp), 4.53 (m, 2 H, arene H), 4.24 (m, 3 H, arene H), 1.99 (m, 2 H, CH$_2$), 0.98 (t, J_{HH} = 7.5 Hz, 3 H, CH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 137.4 (C-α), 123.5 (C-β), 82.7 (Cp), 56.0 (arene CH), 41.9 (arene CH), 40.9 (arene CH), 39.2 (arene CH), 26.4 (CH$_2$), 14.7 (CH$_3$); EI-MS m/z 504 (17% relative intensity, M$^+$), 370 (42, [(CpCo)$_3$ – 2H]$^+$), 207 (30), 189 (25, [Cp$_2$Co]$^+$), 132 (49, L$^+$), 131 (14, [L – H]$^+$), 117 (93, [C$_9$H$_9$]$^+$), 115 (22), 91 (26, [C$_7$H$_7$]$^+$), 66 (11, [C$_5$H$_6$]$^+$), 62 (12, [C$_5$H$_5$]$^+$), 51 (11, [C$_4$H$_3$]$^+$), 39 (14, [C$_3$H$_3$]$^+$) (L = 4-phenyl-1-butene).

(CpCo)$_3$(μ_3-η^2:η^2:η^2-n-propylbenzene) (18). In a 2-L round-bottom flask 0.21 g (0.43 mmol) of (CpCo)$_3$(μ_3-β-methylstyrene) (5b) was dissolved in 150 mL of toluene. A 50-mg amount of Pd (10%) on charcoal was added and the reaction flask flushed with 1 bar of H$_2$. The slurry was shaken mechanically for 48 h and

Table I. Details of the Crystal Structure Determinations of (CpCo)$_3$(μ_3-η^2:η^2:η^2-(E)-β-methylstyrene) (5b) and (CpCo)$_3$(μ_3-η^2:η^2:η^2-(E)-1,1-diphenylethene) (6a)

	5b	6a
mol formula	C$_{24}$H$_{25}$Co$_3$	C$_{29}$H$_{27}$Co$_3$·0.5C$_7$H$_8$
cryst habit, color	plate, deep brown	box-shaped, brown
cryst size, mm	0.08 × 0.31 × 0.86	0.26 × 0.50 × 0.58
cryst syst	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
a, Å	8.725 (5)	8.734 (4)
b, Å	7.542 (5)	11.470 (5)
c, Å	15.151 (6)	12.791 (6)
α, deg	90	85.37 (3)
β, deg	103.17 (4)	83.81 (3)
γ, deg	90	83.52 (3)
V, Å^3	970.7	1262.7
Z	2	2
M_r	490.26	598.40
d_c, g cm^{-3}	1.68	1.58
F_{000}	500	614
μ(Mo Kα), cm^{-1}	25.4	19.7
X-radiation; λ, Å	Mo Kα (graphite monochrom); 0.7107	
data collecn temp	ambient	
$2\theta_{min}$, $2\theta_{max}$, deg	6.5, 60	3, 60
hkl range	12,10,±21	±12,±16,18
no. of rflns measd	3030	7361
no. of unique rflns	3030	7361
no. of obsd rflns	2893 ($I \geq \sigma(I)$)	5795 ($I \geq 2\sigma(I)$)
abs cor	numerical	numerical
T_{max}, T_{min}	0.85. 0.58	0.64, 0.39
no. of parms refined	337	413
no. of R	0.026	0.043
R_w ($w = \sigma^{-2}(F)$)	0.027	0.038

filtered. The solvent was removed from the filtrate and the residue redissolved in petroleum ether. Chromatography on Al$_2$O$_3$/5% H$_2$O (2.5 × 15 cm) followed by recrystallization from toluene/petroleum ether gave 0.18 g (86% yield) of dark brown microcrystals of 18: mp 198 °C; ^{1}H NMR (C$_6$D$_6$) δ 4.70 (s, 15 H, Cp), 4.27 (m, 5 H, arene H), 1.93 (t, J_{HH} = 6.1 Hz, 2 H, CH$_2$), 1.70 (m, 2 H, CH$_2$), 1.05 (t, J_{HH} = 7.2 Hz, 3 H, CH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 82.5 (Cp), 62.0 (arene C$_{ipso}$), 45.0 (CH$_2$), 44.7 (arene CH), 40.4 (arene CH), 39.2 (arene CH), 26.3 (CH$_2$), 14.6 (CH$_3$); EI-MS m/z 492 (21% relative intensity, M$^+$), 370 (80, [(CpCo)$_3$ – 2H]$^+$), 247 (13, [(CpCo)$_2$ – H]$^+$), 189 (66, [Cp$_2$Co]$^+$), 124 (15, CpCo$^+$), 120 (24, L$^+$), 111 (12), 97 (17), 95 (11), 92 (13, [C$_7$H$_8$]$^+$), 91 (100, [C$_7$H$_7$]$^+$), 85 (13), 85 (13), 83 (14), 71 (20), 69 (17), 65 (12), 59 (11, Co$^+$), 57 (34), 55 (21), 43 (28), 41 (17) (L = n-propylbenzene). Anal. Calcd for C$_{24}$H$_{27}$Co$_3$: C, 58.56; H, 5.53. Found: C, 58.57; H, 5.53.

Crystal Structure Determinations. 5b crystallized from a toluene/petroleum ether (2:1) solution at 5 °C. Single crystals of 6a were obtained by allowing petroleum ether to diffuse by vapor transfer into a saturated toluene solution of 6a at room temperature over a period of 4 days. Crystallographic data are summarized in Table I. Intensity data were collected on a STOE STADI-2 two-circle Weissenberg diffractometer (compound 5b) and a Siemens/STOE four-circle diffractometer (compound 6b) and corrected for Lorentz, polarization, and absorption effects. The structure of 5b could only be solved in the noncentrosymmetric space group $P2_1$. For 6a intensity statistics strongly favored the centrosymmetric space group $P\bar{1}$. The structures were solved with the heavy-atom method and refined by blocked-matrix least squares. All non-hydrogen atoms were given anisotropic thermal parameters. All hydrogen atoms (except those of the methyl group in 5b, which was refined as a rigid group with hydrogen atoms at calculated positions) were located from difference Fourier maps and refined with isotropic thermal parameters. The unit cell of 6b was found to contain a molecule of toluene statistically disordered across a center of inversion. During refinement of this structure, the phenyl ring of the solvent of crystallization was constrained to a rigid regular hexagon with isotropic thermal parameters. The calculations were performed with use of the SHELX-76 program.[11] Scattering factors were those given by

(11) Sheldrick, G. M. SHELX-76: A Program for Crystal Structure Determination; University of Cambridge: Cambridge, U.K., 1976.
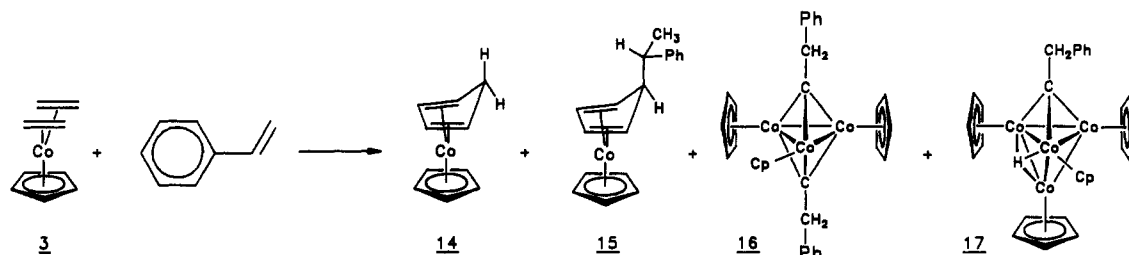
Scheme I

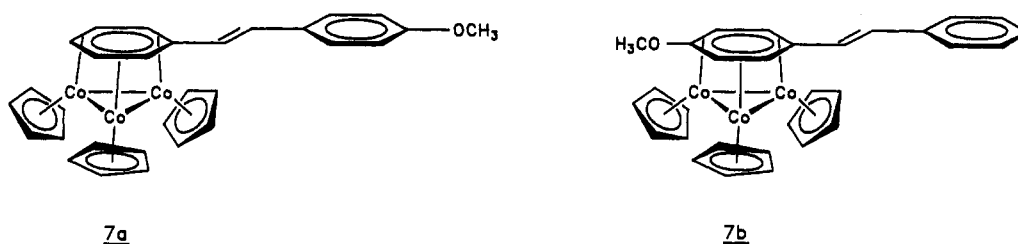## Scheme II

Chart I

7a

7b
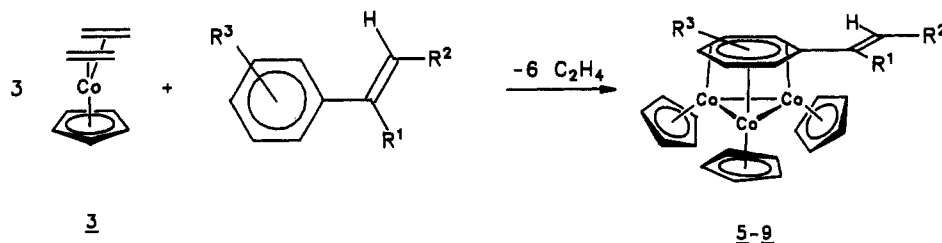
(12) Cromer, D. T.; Mann.[12] Anomalous dispersion factors were taken from ref 13. Graphical representations were drawn with the ORTEP II program.[14]

Results

Syntheses of (CpCo)$_3$(μ_3-η^2:η^2:η^2-arene) (arene = Alkenylbenzene). (a) From CpCo(C$_2$H$_4$)$_2$ (3) and 1-Alkenylbenzenes. Reaction of CpCo(C$_2$H$_4$)$_2$ (3)[6] with various ring-substituted and/or side-chain-substituted vinylbenzenes in hydrocarbon solutions resulted in the evolution of a gas and the formation of brown slurries. The complexes (CpCo)$_3$(μ_3-η^2:η^2:η^2-arene) (5–9; Scheme I) were isolated from the reaction mixtures by chromatography on deactivated alumina or recrystallization (Table II).

Regardless of the isomeric composition of the starting materials (*E*- or *Z*-configurated olefins or mixtures thereof) the products obtained from β-methylstyrene and stilbene always had an *E* configuration in the olefinic side chain. Careful control of temperature was crucial for the success of the reactions. If the reaction mixture was heated too quickly, H(CpCo)$_4$(μ_3-CCH$_3$) (13), the thermal decomposition product of 3,[15] was formed in addition to the μ_3-arene clusters. Chromatographic separation of 13 from the latter, although possible, was always accompanied by substantial product losses. In most cases a cleaner reaction was observed with CpCo(C$_6$Me$_6$)[6] (4) as a source of CpCo fragments. Reaction with 4 in THF generally took place at

(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A.* **1968**, *24*, 321.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV, p 149.

(14) Johnson, C. K. ORTEP: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations; Report No. ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(15) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1985**, *296*, C6. (b) Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *New J. Chem.* **1988**, *12*, 621.

Table II. Complexes of the Type (CpCo)$_3$(μ_3-η^2:η^2:η^2-arene) (arene = (R^{3}C$_6$H$_4$)[(*E*)-C(R^1)=C(H)R^2])

complex	complex no.	R^3	R^1	R^2	% yield
(CpCo)$_3$(α-methylstyrene)	5a	H	Me	H	75
(CpCo)$_3$(β-methylstyrene)	5b	H	H	Me	85
(CpCo)$_3$(1,1-diphenylethene)	6a	H	Ph	H	90
(CpCo)$_3$(stilbene)	6b	H	H	Ph	85
(CpCo)$_3$(4-methoxystilbene)	7a	H	H	4-anisyl	50
(CpCo)$_3$(4-methylstyrene)	7b	4-OMe	H	Ph	20
	8	4-Me	H	H	70
(CpCo)$_3$(4-methoxystyrene)	9	4-OMe	H	H	80
(CpCo)$_3$(1,1-diphenylpropene)	10	H	Ph	Me	37
(CpCo)$_3$[1-(4-anisyl)propene]	11	4-OMe	H	Me	~5[a]
(CpCo)$_3$(β-ethylstyrene)	12	H	H	Et	~5

[a] Not isolated.

room temperature and gave high product yields without contamination by 13. The cluster (CpCo)$_3$(μ_3-1,1-diphenylpropene) (10) was only obtained from 4 and 1,1-diphenylpropene. Reaction of 3 with 1,1-diphenylpropene resulted in virtually quantitative formation of 13.

4-Methoxystilbene and 3 gave an approximately 2:1 mixture of the two isomeric μ_3-arene clusters 7a,b (Chart I). This ratio was reproducible in several experiments worked up under somewhat different conditions.[16] Separation of these coordination isomers was not possible by
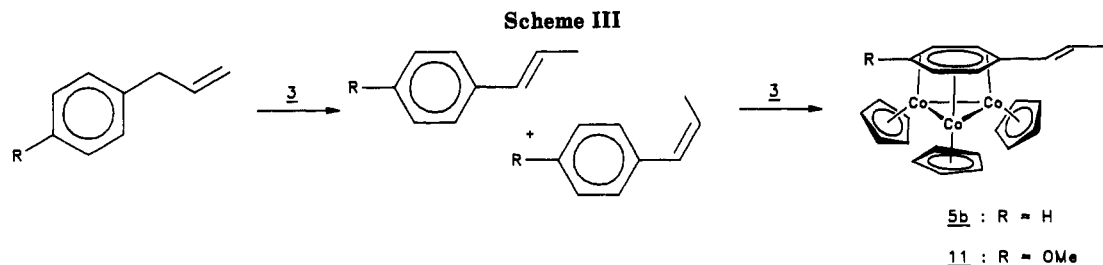
(16) On the basis of the observed inertness to arene displacement we rule out an equilibrium of 7a and 7b.

Scheme III

5b : R = H

11 : R = OMe

Table III. Selected Bond Distances (Å) and Angles (deg) for 5b

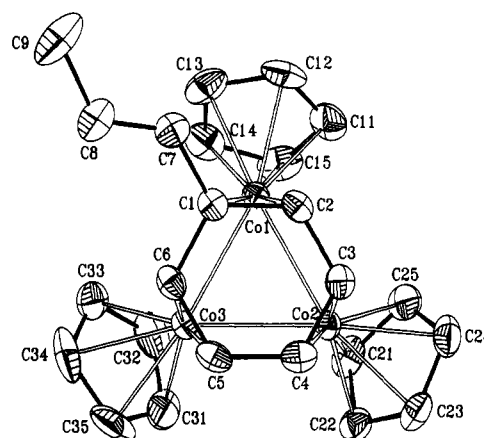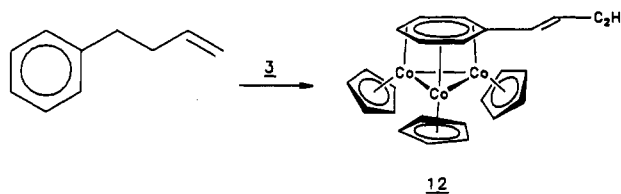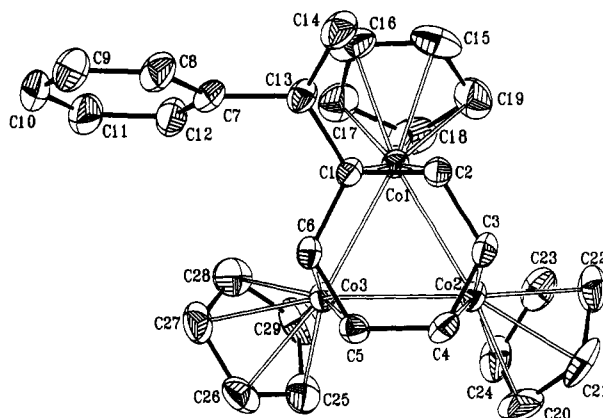|					
Co1–Co2	2.501 (1)	Co2–C4	2.027 (3)	C2–C3	1.435 (5)
Co1–Co3	2.503 (1)	Co3–C5	2.023 (3)	C3–C4	1.412 (4)
Co2–Co3	2.496 (1)	Co3–C6	2.017 (3)	C4–C5	1.438 (5)
Co1–C1	2.059 (3)	C1–C2	1.432 (4)	C5–C6	1.415 (5)
Co1–C2	2.019 (3)	C1–C6	1.466 (4)	C7–C8	1.317 (6)
Co2–C3	2.027 (3)	C1–C7	1.461 (5)	C8–C9	1.512 (8)
		Co1–(C11–C15)		2.085–2.135 (4)	
		Co2–(C21–C25)		2.087–2.137 (4)	
		Co3–(C31–C35)		2.081–2.115 (4)	
Co3–Co1–Co2	59.8 (0)	C7–C1–C2	119.7 (2)	C5–C4–C3	119.8 (3)
Co3–Co2–Co1	60.1 (0)	C7–C1–C6	120.3 (2)	C5–C6–C1	120.1 (2)
Co1–Co3–Co2	60.1 (0)	C3–C2–C1	121.6 (2)	C8–C7–C1	128.2 (3)
C6–C1–C2	117.7 (2)	C4–C3–C2	119.9 (2)	C9–C8–C7	124.2 (4)

chromatography or crystallization.

Styrene derivatives with less than two hydrogen substituents on the exocyclic double bond such as 1,1-diphenylpropene, 1-phenylisobutene, 2-phenyl-2-butene, and 2-phenyl-3-methyl-2-butene did not react with 3. In all cases, the tetracobalt ethylidyne cluster 13 was isolated in high yield.

From the reaction of styrene with 3 a number of mononuclear CpCo complexes, mainly CpCo(η^4-cyclopentadiene) (14) and the substituted cyclopentadiene complex CpCo[2-4-η-1-*exo*-(2-phenylethyl)-2,4-cyclopentadiene] (15), along with traces of the phenylethylidyne clusters (CpCo)$_3$(μ_3-CCH$_2$Ph)$_2$ (16) and H(CpCo)$_4$(μ_3-CCH$_2$Ph) (17), could be isolated (Scheme II).[17] In marked contrast, the (CpCo)$_3$(μ_3-arene) clusters 8 and 9 were obtained from the para-substituted styrene derivatives 4-methylstyrene and 4-methoxystyrene in high yields.

(b) From CpCo(C$_2$H$_4$)$_2$ (3) and Allylbenzenes. In the presence of 3 or 4 allylbenzene was isomerized to β-methylstyrene at ambient temperature within minutes. During the reaction with 3, no intermediates could be detected by ¹H NMR spectroscopy. An approximately 85:15 mixture of *E* and *Z* stereoisomers was formed. This value closely corresponds to the thermodynamic equilibrium mixture.

The isomerization reactions are catalytic and need only traces of 3 or 4. With use of a 1:3 ratio of the respective allylbenzenes and 3 isomerization of the alkenes and formation of the μ_3-arene clusters 5b and 11 could be accomplished in one pot by only slowly raising the reaction temperature (Scheme III). Again the product 5b was isomerically pure. 11 was only formed in minor quantities and could not be completely separated from 4-methoxy-β-methylstyrene. 4-Phenyl-1-butene, where the C=C double bond is separated from the phenyl ring by two CH$_2$ groups, was also quantitatively isomerized to β-ethylstyrene in the presence of excess 3. However, from this mixture only a small yield of the corresponding cluster (CpCo)$_3$-(μ_3-(*E*)-β-ethylstyrene) (12) was obtained (Scheme IV).

X-ray Crystallography. Single-crystal X-ray structure determinations were carried out on (CpCo)$_3$(μ_3-η^2:η^2:η^2-(*E*)-β-methylstyrene) (5b)[5] and (CpCo)$_3$(μ_3-η^2:η^2:η^2-1,1-

(17) Wadepohl, H.; Büchner, K. To be submitted for publication.

Scheme IV

12

Figure 1. Molecular structure of **5b**.

Figure 2. Molecular structure of **6a**.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 6a

|					
Co1–Co2	2.506 (1)	Co3–C6	2.008 (3)	C7–C8	1.403 (5)
Co1–Co3	2.489 (1)	C1–C2	1.426 (4)	C7–C12	1.388 (5)
Co2–Co3	2.496 (1)	C1–C6	1.447 (5)	C7–C13	1.492 (5)
Co1–C1	2.057 (3)	C1–C13	1.498 (5)	C8–C9	1.380 (6)
Co1–C2	2.000 (3)	C2–C3	1.453 (5)	C9–C10	1.352 (7)
Co2–C3	2.013 (3)	C3–C4	1.412 (5)	C10–C11	1.399 (7)
Co2–C4	2.001 (3)	C4–C5	1.447 (5)	C11–C12	1.401 (5)
Co3–C5	2.015 (3)	C5–C6	1.415 (5)	C13–C14	1.316 (5)
		Co1–(C15–C19)	2.075–2.130 (5)		
		Co2–(C20–C24)	2.081–2.124 (5)		
		Co3–(C25–C29)	2.074–2.133 (5)		
Co3–Co1–Co2	60.0 (1)	C13–C1–C6	118.6 (2)	C5–C6–C1	121.9 (2)
Co3–Co2–Co1	59.7 (1)	C3–C2–C1	120.9 (3)	C7–C13–C1	118.4 (3)
Co2–Co3–Co1	60.4 (1)	C4–C3–C2	120.6 (2)	C14–C13–C1	122.7 (3)
C6–C1–C2	117.5 (2)	C5–C4–C3	119.0 (3)	C14–C13–C7	118.9 (3)
C13–C1–C2	120.6 (3)	C6–C5–C4	120.1 (3)		
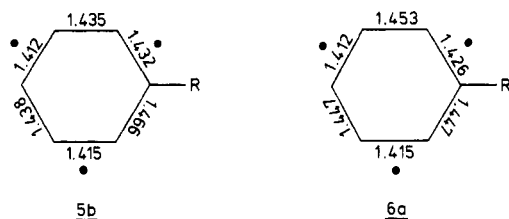
Figure 3. Distribution of carbon–carbon bond lengths (Å) in the μ_3-arene ligands of **5b** (left) and **6a** (right). Small black dots denote the positions of the cobalt atoms.

diphenylethene) (**6a**). The molecular structures are shown in Figures 1 and 2. Significant bond distances and angles are presented in Tables III and IV.

Both compounds have very nearly planar arene rings bound in the μ_3-η^2:η^2:η^2-tricobalt face-capping mode to the (CpCo)$_3$ cluster. In each case the Co$_3$ triangle and the μ_3-arene ring are staggered with respect to each other. The ipso carbon atoms (C1) are slightly displaced from the plane through the five other ring atoms in the direction away from the (CpCo)$_3$ cluster (0.04 Å in **5b**, 0.05 Å in **6a**). The substituents on the bridging C$_6$ rings are also bent away from the metals, resulting in positions of the α-carbon and ring hydrogen atoms of 0.5–0.6 and 0.2–0.3 Å, respectively, outside the μ_3-arene plane. The olefinic planes of the side chains are at dihedral angles of 17° (**5b**) and 28° (**6a**) to the arene rings.

There is only a slight alternation of carbon–carbon bond lengths within the face-capping arene rings (Tables III and IV). Mean values of the longer and shorter bonds are 1.45 and 1.42 Å, with the latter lying on top of the metal atoms. However, the considerable scatter of "equivalent" bond lengths (disregarding the side chain) is obvious (cf. Figure 3). Carbon–carbon bond lengths in the uncoordinated phenyl ring of **6a** range from 1.352 (5) to 1.403 (5) Å.

NMR Spectroscopy. ^{1}H NMR shifts of the face-capping arenes range from δ 4.1 to 4.6 (Table V); ^{13}C chemical shifts are between δ 33 and 62, with the ipso carbons always resonating at a much lower field (δ 50–62) than the CH groups (δ 33–45) (Table VI). At ambient temperature the number of resonances found for the μ_3-arene ring always corresponds to the symmetry of the *free* arene. Three CH signals and one quaternary carbon resonance are observed in derivatives with monosubstituted μ_3-arenes. The 1,4-disubstituted μ_3-arenes give two CH and two quaternary carbon signals (Table VI). In the relevant cases the *E* configuration of the alkenyl side chains can easily be derived from the coupling pattern of the olefinic protons.

The ^{1}H NMR spectrum of the mixture of isomers **7a,b** obtained from 4-methoxystilbene and **3** was assigned by comparing the integrated intensities of the various resonances. The (AB)$_2$ pattern (relative intensity 4 H) of the

Table V. Ambient-Temperature ^{1}H NMR Data (δ) for (CpCo)$_3$(μ_3-arene) Clusters

	μ_3-arene	alkenyl	Cp
5a[a]	4.54,[b] 4.19 (m, 3)	5.05 (d, 1), 4.54	4.54 (br s)[b]
5b[a]	4.4 (m, 2), 4.2 (m, 3)	5.76 (dq, 1), 5.44 (dq, 1)	4.58 (s, 15)
6a[a]	4.58,[c] 4.18 (m, 3)	5.25 (d, 1), 5.03 (d, 1)	4.58 (br s)[c]
6b[d]	4.76 (m, 2), 4.50 (m, 3)	6.68 (d, 1),[f] 6.44 (d, 1)[f]	4.89 (s, 15)
7a[d]	4.76 (m),[e] 4.48	6.52 (d),[f] 6.41 (d)[f]	4.88 (br s)[e]
7b[d]	4.76 (m),[e] 4.48 (m)[e]	6.68 (d),[f] 6.46 (d)[f]	4.88 (br s)[e]
8[a]	4.32 (m, 2),[g] 4.10 (m, 2)[g]	6.00 (dd, 1), 5.01 (dd, 1), 4.74 (dd, 1)	4.55 (s, 15)
9[h]	4.55 (m, 2),[g] 4.18 (m, 2)[g]	6.09 (dd, 1), 5.10 (dd, 1), 4.83 (dd, 1)	4.67 (s, 15)
10[h]	4.6 (m, 2), 4.25 (m, 3)	5.89 (q, 1)	4.69 (s, 15)
11[h]	4.59 (m, 2),[g] 4.23 (m, 2)[g]	5.80 (m, 1), 5.55 (m, 1)	4.72 (br s, 15)
12[h]	4.53 (m, 2), 4.24 (m, 3)	5.87 (d, 1), 5.58 (m, 1)	4.68 (s, 15)
18[h]	4.3 (m, 5)	1.93 (t, 2),[i] 1.70 (m, 2)[i]	4.70 (s, 15)

[a] In toluene-d_8. [b] Overlapping signals, total intensity 18. [c] Overlapping signals, total intensity 17. [d] In CD$_2$Cl$_2$. [e] Overlapping signals. [f] AB system. [g] (AB)$_2$ pattern. [h] In C$_6$D$_6$. [i] Alkyl H.

Table VI. Selected ^{13}C NMR Chemical Shifts (δ) of (CpCo)$_3$(μ_3-arene) Clusters (Ambient Temperature)

	μ_3-arene		C_α	C_β	Cp
	C_{ipso}	CH			
5a[a]	59.3	41.1, 40.1, 39.6	149.7	104.7	82.6
5b[b]	56.1	41.8, 40.9, 39.2	140.1	116.4	82.7
6a[b]	54.7	42.2, 41.3, 39.8	156.7	107.9	82.9
6b[c]	55.5	42.3, 41.5, 39.7	138.4[d]	120.1[d]	82.8
8[a]	e	44.0, 40.2	145.5	104.6	83.1
9[b]	53.7, 49.3	38.4, 33.1	145.7	104.3	83.8
10[b]	58.6	42.9, 41.1, 39.5	148.0[d]	118.3	83.1
12[b]	56.0	41.9, 40.9, 39.2	137.4[d]	123.5[d]	82.7
18[b]	62.0	44.7, 40.4 39.2	45.0	26.3	82.5

[a] In toluene-d_8. [b] In C$_6$D$_6$. [c] In CD$_2$Cl$_2$. [d] Not definitely assigned. [e] Due to the low solubility quaternary carbons could not be detected unambiguously.

noncoordinated 1,4-disubstituted arene ring in **7a** (δ 7.31 and 6.82, Table V) served as a reference to assign the singlets at δ 3.77 and 3.36 to the methoxy groups of **7a** and **7b**, respectively. From the intensity ratio of the nonoverlapping signals the relative concentrations of **7a** and **7b** could be determined.

^{1}H and ^{13}C NMR spectra of the compounds **5a,b** and **6b** were investigated at variable temperature (Tables VII and VIII). Temperature-dependent proton NMR spectra of **5b** are depicted in Figure 4. Cooling the sample results

Table VII. Low-Temperature ^{1}H NMR Data (δ) for (CpCo)$_3$(μ_3-arene) Clusters

	T, K	μ_3-arene	alkenyl	Cp
5a	220^a	4.42 (m, br, 5)	5.03 (s, 1), 4.80^b	4.89 (s, 5), 4.80,^{b} 4.66 (s, 5)
5b	200^c	4.32 (m, 2), 4.17 (m, 3)	5.80 (dq, 1), 5.50 (dq, 1)	4.60 (s, 5), 4.59 (s, 5), 4.49 (s, 5)
6b	190^a	4.46 (m, br, 5)	6.63 (d, 1), 6.32 (d, 1)	4.93 (s, 5), 4.80 (s, 5), 4.78 (s, 5)

^{a} In CD$_2$Cl$_2$. ^{b} Overlapping signals, total intensity 6. ^{c} In toluene-d_8.

Table VIII. Selected Low-Temperature (200 K) ^{13}C NMR Chemical Shifts (δ) of (CpCo)$_3$(μ_3-arene) Clusters

	μ_3-arene		Cp
	C$_{ipso}$	CH	
5a^a	58.3	43.0, 40.5, 40.1, 39.2, 38.2	83.4, 81.82, 81.79
5b^b	56.1	45.3, 41.0, 39.5, 38.7, 38.6	83.5, 83.0

^{a} In CD$_2$Cl$_2$. ^{b} In THF-d_8.

in a splitting of the singlet due to the three CpCo groups into a 1:1:1 pattern of singlets. The two multiplets of the arene ring protons change to a broad feature. Apart from minor changes in line width the rest of the spectrum remains unchanged. In the ^{13}C NMR spectrum at 200 K six resonances are observed for the μ_3-arene ring carbons. Due to accidental overlap only two of the expected three ^{13}C NMR signals for the Cp ligands are resolved. However, in the ^{13}C{^{1}H} DEPT spectrum of **5a** three CH signals at δ 81–84 are clearly separated at 190 K.

Chemical Reactivity. The reactivity of (CpCo)$_3$(μ_3-(E)-β-methylstyrene) (**5b**) was tested with various reagents directed to attack the metal cluster, the cluster-coordinated arene ring, or the olefinic side chain. The μ_3-β-methylstyrene ligand could not be displaced by various other arenes (benzene, toluene, xylenes, mesitylene, hexamethylbenzene, mellitic acid hexamethyl ester, hexafluorobenzene). Addition of the Lewis acids BF$_3$·OEt$_2$, AlCl$_3$, AlCl$_2$Et, AlEt$_3$, and TiCl$_4$ to p-xylene solutions of **5b** resulted in the immediate formation of dark precipitates. No soluble products could be obtained on treatment of these solids with H$_2$O or methanol. Two-electron donors such as PMe$_3$ and P(OMe)$_3$ did not react with **5b** even after several hours at 60 °C. With 1 bar or carbon monoxide only traces of the mononuclear degradation product CpCo(CO)$_2$ were formed. In contrast to the reaction at atmospheric pressure the starting material could not be recovered after stirring of a THF solution of **5b** under 50 bar of CO for 24 h. Apart from traces of CpCo(CO)$_2$ only a brown intractable material was formed.

After treatment of **5b** with methyllithium, followed by quenching of the reaction mixture with D$_2$O or methanol, most of the starting material (60–80%) could be recovered unchanged, by chromatography.

Reaction of **5b** with N-bromosuccinimide, diazomethane, or ethyl diazoacetate did not lead to the expected products resulting from bromination of the allylic position or addition of the respective carbenes to the exocyclic double bond.[18] Again, most of the starting complex was recovered from the reaction mixture. Treatment of **5b** with bromine resulted in complete decomposition.

In contrast, catalytic hydrogenation of the olefinic double bond in **5b** was easily achieved under mild conditions (1 bar of H$_2$, ambient temperature) with Wilkinson's catalyst Rh(PPh$_3$)$_3$Cl or Pd on charcoal. The NMR
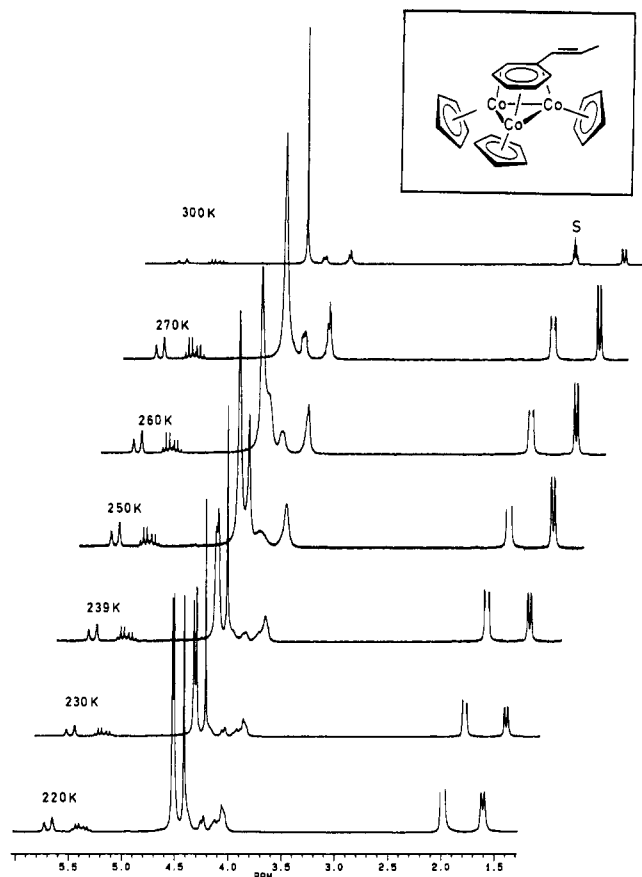

Figure 4. Variable-temperature (200 MHz) ^{1}H NMR spectra of **5b** in toluene-d_8 (S = solvent).

spectra (Tables V and VI) clearly show that the (CpCo)$_3$(μ_3-arene) core remained intact in the hydrogenation reaction. The product, (CpCo)$_3$(μ_3-n-propylbenzene) (**18**), was obtained in 86% yield after chromatographic purification and recrystallization. **18**, along with unreacted **5b**, was also obtained in 10% yield as the only isolable product from the reaction of **5b** with SiHMe$_2$Ph in boiling toluene with AIBN as a radical initiator.[19] No traces of a hydrosilylation product of **5b** were found.

Further complexation of the uncoordinated phenyl ring in the cluster (CpCo)$_3$(μ_3-stilbene) (**6b**) could not be achieved by reaction with Cr(CO)$_3$(NCMe)$_3$. After 10 h at 80 °C only formation of Cr(CO)$_6$ and CpCo(CO)$_2$ was evident (by IR spectroscopy); 35% of the starting material **6b** could be recovered unchanged. Similar results were obtained with Cr(CO)$_3$(pyridine)$_3$/BF$_3$·OEt$_2$ as a transfer reagent for the Cr(CO)$_3$ group. In both cases no traces of the known mononuclear complex (CO)$_3$Cr(η^6-stilbene)[20] were found. Neither **6a** nor **6b** reacted further with excess **3** or **4**.

Discussion

Synthetic Aspects. In the last step of the synthesis of Os$_3$(CO)$_9$(μ_3-η^2:η^2:η^2-C$_6$H$_6$) (**2**) the μ_3-benzene ligand was generated from a cyclohexadienyl ligand coordinated to the preformed triosmium cluster.[4] **2** was not obtained from Os$_3$(CO)$_{12}$ or Os$_3$(CO)$_{10}$(NCMe)$_2$ and benzene. Instead, CH activation took place, leading to Os$_3$(μ-H)$_2$(CO)$_9$(μ_3-

---

(18) The same reaction conditions as are recommended[8] for the free ligands were used.

(19) In a control experiment, which was carried out under identical conditions but without the silane, complex **18** was not formed.

(20) (a) Ercoli, R.; Calderazzo, F.; Alberola, A. *Chim. Ind. (Milan)* **1959**, *41*, 975. (b) Drefahl, G.; Hörland, H.-H.; Kühne, K. *Chem. Ber.* **1965**, *98*, 1826.

$\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)$ with a bridging benzyne molecule.[21]

Our route to tricobalt clusters with face-capping μ_3-arene ligands does not attempt to attach the arene ligand to a preformed metal cluster but, rather, assembles the metal cluster on the backbone of the alkenylbenzene ligand. The preparative results presented above show that this is indeed a method with some generality. However, only the most reactive sources of CpCo fragments, namely CpCo-$(C_2H_4)_2$ (3) and $CpCo(C_6Me_6)$ (4), can be utilized for the reaction. With $CpCo(\eta^4\text{-}C_5H_6)$, CpCo(1,5-cyclooctadiene), and $CpCo(CO)_2$ we were unable to obtain even traces of $(CpCo)_3(\mu_3\text{-arene})$ clusters. This also holds true for photochemical activation of $CpCo(CO)_2$ at both ambient and low temperature.

No definitive statement can be made at this point about the identity of the organocobalt species attacking the styrene derivative in the first step of the reaction. Associative or dissociative pathways could be used. Both have been demonstrated for the thermal substitution of L in the complexes $CpML_2$ (M = Co, Rh).[22,23]

No $(CpCo)_3(\mu_3\text{-arene})$ clusters were obtained from 3 and benzene or alkylbenzenes such as toluene, xylenes, or propylbenzene. Therefore, the olefinic side chain must play a vital role during the formation of the tricobalt cluster. Primary reaction very likely takes place at the exocyclic carbon–carbon double bond. This is illustrated by the rapid isomerization reactions of the organic substrates ((Z)- into (E)-olefins, allylbenzenes into 1-propenyl derivatives). Such reactions of olefins are catalyzed by a large variety of transition-metal compounds.[24] In the present case they are complete within minutes at room temperature in the presence of either 3 or 4. Preliminary kinetic data for this reaction indicate an autocatalytic mechanism.[17]

From our studies on model systems[25] we believe the stepwise assemblage of the tricobalt cluster to take place on the template of the 1-alkenylbenzene ligand. We have proposed a mechanism involving mononuclear $CpCo(\beta,\text{-}\alpha,1,2\text{-}\eta^4\text{-alkenylbenzene})$ and dinuclear $(CpCo)_2(\beta,\alpha,1\text{-}\eta^3{:}2\text{-}4\text{-}\eta^3\text{-alkenylbenzene})$ intermediates.[25] In this mechanism the first attack of the aromatic π-system by [CpCo] is made possible by the 1-alkenyl substituent, which serves as a handle to guide the metal fragment to the arene ring. Once the arene-bridged tricobalt cluster has been formed, the olefinic side chain on the arene is no longer necessary. Consequently, hydrogenation to give the corresponding $(CpCo)_3(\mu_3\text{-alkylbenzene})$ derivatives proceeds readily without destruction of the cluster.

The influence of the degree and type of substitution of the alkenylbenzene ligand on the tendency of formation of the corresponding $(CpCo)_3(\mu_3\text{-arene})$ clusters is not clear as yet. It seems that an increase of the number of substituents on both the arene ring and the exocyclic double bond generally makes the reaction more difficult. Indeed, the dominant product from 3 and 4-methoxystilbene is 7a, with the less substituted phenyl ring capping the $(CpCo)_3$ cluster.

Chart II

10a   OR   10b

Table IX. C–C Bond Lengths in Metal-Bound Arenes[a]

compd	d(C–C) in the μ_3-arene, Å		ref
5b	1.420 (5)	1.446 (5)	this work
	0.020	0.031	
6a	1.418 (5)	1.449 (5)	this work
	0.014	0.006	
$Os_3(CO)_9(C_6H_6)$	1.41 (3)	1.51 (3)	4
	0.08	0.11	
$Os_3(CO)_8(C_2H_4)(C_6H_6)$	1.41 (3)	1.47 (3)	31
	0.06	0.06	
$Ru_6C(CO)_{11}(C_6H_6)_2$	1.39 (2)	1.48 (2)	4
	0.05	0.04	
$Rh(111)/C_6H_6/CO^b$	1.33 (15)	1.81 (15)	32
$Rh(111)/C_6H_6/2\ CO^b$	1.46 (15)	1.58 (15)	33b
$Pd(111)/C_6H_6/2\ CO^b$	1.40 (10)	1.46 (10)	33d
$Pt(111)/2\ C_6H_6/4\ CO^c$	1.65 (15)	1.76 (15)	33b
$(CO)_3Cr(C_6H_6)^d$	1.401 (2)	1.420 (2)	34
	0.001	0.003	

[a] Standard deviations of the individual values are given in parentheses. For compounds with two rows of data, the first line gives the mean values of the alternating long and short bonds and the second line gives the difference between the largest and smallest individual values. [b] $C_{3v}(\sigma_d)$ site. [c] C_2 site. [d] η^6-Benzene.

Styrene itself is a special case, giving mainly products derived from hydrogen transfer to a cyclopentadienyl ring. The hydrogen atoms presumably stem from scission of olefinic CH bonds.[17] So far we cannot offer an explanation for this behavior compared to the different reactivities of 4-methylstyrene and 4-methoxystyrene, which gave $(CpCo)_3(\mu_3\text{-4-methylstyrene})$ (8) and $(CpCo)_3(\mu_3\text{-4-meth-oxystyrene})$ (9) in high yields.

Whereas the degree of substitution on the side chain is important, the substitution site is less so. The yield of the corresponding $(CpCo)_3(\mu_3\text{-arene})$ clusters formed from 3 and α- or β-methylstyrene and 1,1- or 1,2-diphenylethylene respectively were equally high. However, $(CpCo)_3(\mu_3\text{-1,1-diphenylpropene})$ (10) was only obtained from 1,1-diphenylpropene and 4. Only one of the two possible isomers 10a,b was formed (Chart II). Without a crystal structure analysis we cannot tell these apart. For steric reasons structure 10a appears to be more likely. Quite surprisingly, from 1,2-diphenylpropene and 3 or 4 no μ_3-arene cluster could be obtained.

Solid-State Structure. The X-ray crystal structure analyses establish the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ bonding mode of the arenes in the title compounds. Compared to the sizes in the free arenes (d(CC) $\approx$ 1.37–1.40 Å[26]) and in η^6-bound arenes in complexes with metals of the first transition series (d-(CC) $\approx$ 1.40–1.42 Å[27]) the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-bound phenyl rings are substantially expanded (Table IX). Although, due to the influence of the unsaturated substituent, the $\mu_3\text{-}C_6$ rings are distorted from the 3-fold symmetry, the observed

(21) (a) Deeming, A. J.; Underhill, M. *J. Organomet. Chem.* 1972, 42, C60; *J. Chem. Soc., Dalton Trans.* 1974, 1415. (b) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* 1983, 2257.
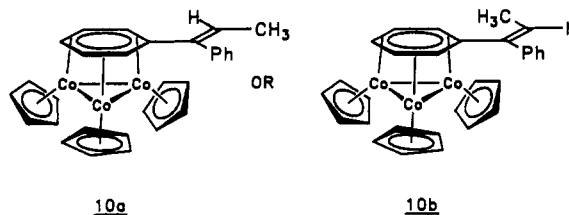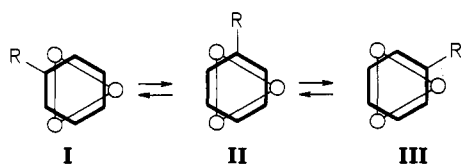
(22) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* 1966, 88, 1657.

(23) Janowicz, A. H.; Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1981, 103, 1516.

(24) Warwel, S. In *Methoden der Organischen Chemie (Houben-Weyl)*; Falbe, J., Ed.; Thieme; Stuttgart, Germany, 1986; Vol. E18₁, Chapter 3, and references cited therein.

(25) Wadepohl, H.; Büchner, K.; Pritzkow, H. *Organometallics* 1989, 8, 2745.

(26) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr.* 1975, B31, 221.

(27) (a) Silverthorn, W. E. *Adv. Organomet. Chem.* 1975, 13, 47. (b) Gastinger, R. E.; Klabunde, K. J. *Transition Met. Chem.* (Weinheim) 1979, 4, 1. (c) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* 1982, 82, 499.

Scheme V[a]

[a] CpCo groups are shown as open circles.

$C_{3v}(\sigma_d)$ $C_{3v}(\sigma_v)$ C_{6v} C_{2v}

Figure 5. Possible adsorption sites for benzene on a close-packed metal surface.

slight alternation of the carbon–carbon bond lengths within the cluster-coordinated arene rings is significant. The effect of substitution of free benzene on the carbon–carbon bond lengths has been studied with use of X-ray crystallography,[26] but no clear conclusion was reached. In principle it should be possible to correct for this effect in **6a** by comparing the bond length patterns within the coordinated and the free phenyl rings. Inspection of the thermal parameters, however, indicates considerable anisotropic motion of the latter ring, which makes the bond lengths between the affected atoms less reliable.[28]

In Table IX we have compiled the available structural data for face-capping μ_3-arene rings in molecular clusters along with data from metal surface adsorbates and the mononuclear $(CO)_3Cr(\eta^6\text{-}C_6H_6)$. Due to the large standard errors associated with the carbon–carbon bond lengths in the ruthenium and osmium clusters, an assessment of the bonding in the μ_3-benzene rings is difficult. Some of the data seem to indicate a bond alternation larger than that present in **5b** and **6a**. Because of the limitations of the surface analysis method (low-energy electron diffraction[35]) the standard deviations of the surface structures are higher by 1 order of magnitude. Therefore, the strong deviations from the 6-fold symmetry reported for chemisorbed benzene (Table IX) have to be regarded with caution.

As expected for geometrical reasons, the arene rings in the $(CpCo)_3(\mu_3\text{-arene})$ clusters are more expanded than the terminal benzene ligand in the mononuclear $(CO)_3Cr(\eta^6\text{-}C_6H_6)$. However, the magnitude of the Kekulé-type distortions is remarkably similar. In both cases the observed bond alternation can be attributed to a mixing of bonding and antibonding arene π orbitals, which is induced by the 3-fold symmetry of the complexes.[36] The same

conclusion was reached in a theoretical study of benzene on the Rh(111) surface.[37]

NMR Spectra and Solution Dynamics. Compared to those of η^6-bound arenes in mono- and polynuclear complexes, the resonances of the μ_3-arene ring hydrogens[27] and carbons[38] are shifted to higher field. The variable-temperature NMR spectra of the $(CpCo)_3(\mu_3\text{-arene})$ clusters can easily be interpreted by assuming a hindered mutual rotation of the $(CpCo)_3$ triangle and μ_3-arene ring. The two conformations that reflect minima of potential energy are shown in Scheme V.

The chemical configurations (or rotamers) I and III in Scheme V are identical. With a monosubstituted arene, configurations I and II (or II and III, respectively) are mirror images. If the dynamic process involves a series of 60° rotations (I → II → III, i.e. [1,2]-shifts of the arene ring relative to the Co_3 triangle), we are dealing with a racemic mixture of enantiomers that can interconvert by a 60° rotation of the rings. In the case of 120° rotations (I → III, i.e. [1,3]-shifts) the enantiomers do not interconvert.[57] In an achiral medium both optical isomers give the same NMR spectra and, therefore, a set of three resonances with a 1:1:1 intensity ratio is observed for the anisochronous Cp rings at low temperature when the arene rotation is slow on the NMR time scale (cf. Figure 4).

With a series of [1,2]-shifts, interchange of the configurations I and II in principle may well require a higher activation energy than the interchange of configurations II and III, since the bulky substituent R has to pass "across" a CpCo group in the further process. At higher temperatures rapid mutual rotation of $(CpCo)_3$ and μ_3-arene rings effectively averages the Cp rings and introduces a mirror plane into the μ_3-arene ligand.[39]

The benzene ligands in the clusters $Os_3(CO)_{9-n}L_n(\mu_3\text{-}C_6H_6)$ ($n = 1, 2$) are also dynamic.[31] The ring whizzing in $Os_3(CO)_8(RCH=CH_2)(\mu_3\text{-}C_6H_6)$ (R = H, Ph) probably involves [1,2]-shifts (i.e. consecutive arene rotations by 60°) of the benzene ring relative to the basal Os_3 triangle.[31]

Relationship to Surface Chemisorption States of Benzene. It has been proposed that molecular organometallic clusters could be used as models for the surface adsorption states of organic molecules.[40] Before we ad-

(28) As suggested by one reviewer, an analysis[29] of the librational motion of the μ_3-arene and phenyl rings as well as the Cp rings in **6a** was carried out. Inspection of the Hirshfeld $\Delta_{A,B}$ values[30] indicated that the rigid-body motion of the uncoordinated phenyl ring is indeed larger than that of the μ_3-phenyl (see also Figures 1 and 2). However, probably due to the limited accuracy of the thermal parameters from our ambient-temperature X-ray data, no satisfactory agreement of observed and calculated vibrational tensors could be obtained by using the "attached rigid group" approximation with various assumptions for the libration axes.

(29) Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem.* **1988**, *100*, 910; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 880 and references cited therein. The program used for the calculations was a recent version of THMA (Trueblood, K. N. *Acta Crystallogr.* **1978**, *A34*, 950).

(30) (a) Hirshfeld, F. L. *Acta Crystallogr.* **1976**, *A32*, 239. (b) Rosenfield, R. E., Jr.; Trueblood, K. N.; Dunitz, J. *Acta Crystallogr.* **1978**, *A34*, 828.

(31) Gallop, M. A.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1809.

(32) Van Hove, M. A.; Lin, R. F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 2532.

(33) (a) Mate, C. M.; Somorjai, G. A. *Surf. Sci.* **1985**, *160*, 542. (b) Lin, R. F.; Blackman, G. S.; Van Hove, M. A.; Somorjai, G. A. *Acta Crystallogr.* **1987**, *B43*, 368. (c) Ohtani, H.; Wilson, R. J.; Chiang, S.; Mate, C. M. *Phys. Rev. Lett.* **1988**, *60*, 2398. (d) Somorjai, G. A. *Pure Appl. Chem.* **1988**, *60*, 1499 and references cited therein.

(34) (a) Rees, B.; Coppens, P. *Acta Crystallogr.* **1973**, *B29*, 2516. (b) Angermund, K. P. Ph.D. Dissertation; Wuppertal, Germany, 1986. Wang, Y.; Angermund, K.; Goddard, R.; Krüger, C. *J. Am. Chem. Soc.* **1987**, *109*, 587.

(35) Somorjai, G. A.; Van Hove, M. A. *Struct. Bonding (Berlin)* **1979**, *38*, 1 and references cited therein.

(36) Wadepohl, H.; Zhu, L. *J. Organomet. Chem.* **1989**, *376*, 115 and references cited therein.
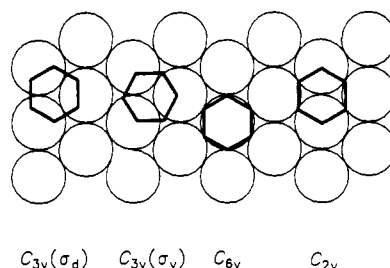
(37) Garfunkel, E. L.; Minot, C.; Gavezzotti, A.; Simonetta, M. *Surf. Sci.* **1986**, *167*, 177.

(38) Mann, B. E.; Taylor, B. F. ^{13}C *NMR-Data for Organometallic Compounds*; Academic Press: London, 1981; p 247 ff.

(39) The quantitative analysis of the observed temperature-dependent NMR line shapes of the Cp resonances is not trivial. In order to distinguish the three possible exchange pathways ([1,2]-shifts, [1,3]-shifts, or random exchange) and to calculate the activation parameters, the resonances observed at low temperature have to be assigned to the individual CpCo sites. A full account of such an analysis will be presented in a separate publication.

(40) (a) Chini, P. *Inorg. Chim. Acta, Rev.* **1968**, *2*, 31; *J. Organomet. Chem.* **1980**, *200*, 37. (b) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959; **1976**, *85*, 451; *Science (Washington, D.C.)* **1977**, *196*, 839. (c) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91 and references cited therein.

dress the validity of this postulate as far as our (CpCo)₃-(μ₃-arene) clusters are concerned, we shall briefly summarize the metal surface chemistry of benzene from the literature.[41] Chemisorbed benzene has been studied with numerous surface analytical methods, mainly on single crystals under ultrahigh-vacuum conditions. On close-packed metal surfaces, adsorption is molecular with the plane of the benzene ring parallel to the metal surface.[42] Various adsorption sites have been discussed (sometimes controversially) in the literature; the most important are the so-called "hollow" ($C_{3v}(\sigma_d)$ or $C_{3v}(\sigma_v)$ site symmetry), "on top" (C_{6v}), "bridge" (C_{2v}) sites (Figure 5).[43]

For example, bridge sites are occupied by benzene molecules on the Pd(111) crystal face.[44] However, in the coadsorbate Pd(111)/C₆H₆/2 CO virtually undistorted benzene is found in hollow ($C_{3v}(\sigma_d)$) sites.[33d] Benzene is in bridge sites[32] or on-top sites[45] on Rh(111), but again coadsorption of carbon monoxide is claimed to force the benzene molecules into hollow adsorption sites.[32,33] Threefold symmetry was also found for the adsorption complexes of benzene on Os(0001)[46] and Ir(111).[47]

Although the experimental evidence is not completely consistent, the symmetry of the adsorbed benzene seems to be largely determined by the adsorption site symmetry; e.g., a hexagonal C₆ ring is found in on-top sites,[45] while a trigonal (Kekulé-type) distortion appears to be present in the adsorption complexes with 3-fold local symmetry.[33,46] The Pd(111)/C₆H₆/2 CO coadsorbate mentioned above seems to be an exception. Since metal surfaces are electron-deficient, there is considerable transfer of charge from the adsorbed benzene to the metal.[37,47,48]

In contrast to the case for benzene, alkyl-substituted arenes such as toluene are chemisorbed irreversibly.[43,49] π-Coordination of the aromatic ring places the methyl hydrogens in close proximity to adjacent reactive surface atoms, thus facilitating C–H bond breaking.[49,50]

The coordination sites of the arene ligands in the molecular clusters are similar to the hollow adsorption sites on the close-packed metal surfaces. The staggered rotational orientation of the M₃ and arene rings found in the solid state corresponds to the $C_{3v}(\sigma_d)$ adsorption geometry. Both coordination to the M₃ clusters and chemisorption on the surface result in a substantial expansion of the arene rings. The small differences observed between the Co₃, Ru₆, and Os₃ clusters are not significant (mean C–C bond lengths within the μ₃-arene rings are 1.43 Å for 5b and 6a, 1.44 Å for Ru₆C(CO)₁₁(C₆H₆)₂,[4] and 1.46 Å for Os₃(CO)₉-(C₆H₆)[4] with standard deviations of the individual bonding distances of 0.005, 0.02, and 0.04 Å, respectively). The high standard deviations (0.15 Å) associated with the corresponding values for the surface adsorbates (Rh(111)/CO/C₆H₆, 1.57 Å;[32] Rh(111)/2 CO/C₆H₆, 1.52 Å[33b]) do not allow a meaningful comparison.

In the clusters and on the surfaces the 3-fold site sym-

metry imposes a Kekulé-type distortion on the coordinated benzene molecules. Again the lack of accuracy of the structures determined by LEED surface crystallography excludes a quantitative comparison. However, there seems to be little doubt that the ring C–C bonds on top of the metal atoms are somewhat shorter than the others. MO calculations also indicate a rather small distortion from regular hexagonal geometry for the surface states of benzene with 3-fold site symmetry.[37,48]

Interestingly, the eclipsed conformation of M₃ and C₆ rings ($C_{3v}(\sigma_v)$ site symmetry), which presumably is a transition state of the arene rotation in the molecular clusters, can be stabilized by coadsorption of sodium on the Rh(111) surface.[51b]

Unfortunately, there is very little information about a possible azimuthal rotation of the adsorbed benzene molecules about the surface normal. In the ordered coadsorbates with CO[32,33b,c] and Na[51b] the benzene molecules seem to be stationary.[52] This may not be the case, however, with low surface coverages and without the presence of adatoms.

MO calculations on (CpCo)₃(μ₃-benzene)[36] and on chemisorbed benzene[37,48] predict a bending of the C–H bonds of the arenes in both systems. For η⁶-benzene in mononuclear complexes, a displacement of the ring hydrogens out of the ring plane toward the metal atom is generally found.[53] Initially a bending of the C–H bonds of the adsorbates toward the metal surface was proposed in order to maximize CHM multicenter interactions.[54] Vibrational spectroscopy does not, however, support this suggestion.[55] Our crystal structures of 5b and 6a show a displacement of the ring hydrogens away from the Co₃ clusters. In the trinuclear clusters, however, there is no possibility to gain stability from CHM bonding involving these hydrogen atoms. In addition, steric repulsions exist with the voluminous Cp rings.

Displacement of chemisorbed benzene by strong donor ligands (e.g. PMe₃) is normally nearly quantitative at low temperatures.[43] When adsorbates on close-packed surfaces are heated, only a small amount of benzene is desorbed molecularly; rather, reaction with the metal surface occurs, leading to a cleavage of the C–H bonds.[43] A similar reaction of Os₃(CO)₉(μ₃-C₆H₆) can be brought about photochemically. Irradiation with light led to an oxidative addition of benzene to the metal cluster with the formation of a cluster-bound benzyne ligand.[56] We did not observe a similar reactivity of the clusters (CpCo)₃(μ₃-arene), which generally showed a higher thermal and chemical stability than their Os₃(CO)₉ analogues.

Conclusions

1. A simple synthetic route to the class of (CpCo)(μ₃-arene) clusters with face-capping arene ligands has been presented. In the one-pot reactions the (CpCo)₃ clusters are assembled from mononuclear building blocks on the

(41) For a compilation of leading references see: Steinrück, H.-P.; Huber, W.; Pache, T.; Menzel, D. *Surf. Sci.* **1989**, *218*, 293.

(42) Johnson, A. L.; Muetterties, E. L.; Stöhr, J. *J. Am. Chem. Soc.* **1983**, *105*, 7183 and references cited therein.

(43) Muetterties, E. L. *Pure Appl. Chem.* **1982**, *54*, 83 and references cited therein.

(44) Waddill, G. D.; Kesmodel, L. L. *Phys. Rev.* **1985**, *B31*, 4940.

(45) (a) Neumann, M.; Mack, J. U.; Bertel, E.; Netzer, F. P. *Surf. Sci.* **1985**, *155*, 629. (b) Netzer, F. P.; Rosina, G.; Bertel, E. *Surf. Sci.* **1987**, *184*, L397.

(46) Netzer, F. P.; Graen, H. H.; Kuhlenbeck, H.; Neumann, M. *Chem. Phys. Lett.* **1987**, *133*, 49.

(47) Mack, J. U.; Bertel, E.; Netzer, F. P. *Surf. Sci.* **1985**, *159*, 265.

(48) Anderson, A. B.; McDevitt, M. R.; Urbach, F. L. *Surf. Sci.* **1984**, *146*, 80.

(49) Tsai, M.-C.; Muetterties, E. L. *J. Phys. Chem.* **1982**, *86*, 5067.

(50) Avery, N. R. *J. Chem. Soc., Chem. Commun.* **1988**, 153.

(51) (a) Gland, J. L.; Somorjai, G. A. *Surf. Sci.* **1973**, *38*, 157. (b) Rosina, G.; Rangelov, G.; Bertel, E.; Saalfeld, H.; Netzer, F. P. *Chem. Phys. Lett.* **1987**, *140*, 200.

(52) Slow lateral diffusion of benzene molecules on the Rh(111) surface was, however, observed by scanning tunneling microscopy.[33c]

(53) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(54) (a) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773. (b) Gavin, R. M., Jr.; Reutt, J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3981.

(55) (a) Thiry, P. A. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *30*, 261. (b) Jakob, P.; Menzel, D. *Surf. Sci.* **1988**, *201*, 503.

(56) Gallop, M. A.; Johnson, B. F. G.; Lewis, J.; McCamley, A.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1988**, 1071.

(57) Note added in proof: [1,2]-shifts have been unambiguously proven for 5b and several other derivatives by ¹H EXSY spectroscopy.

backbones of ring-substituted and/or side-chain-substituted vinylbenzene ligands.

2. Although the unsaturated side chains on the arene rings play a crucial role during the formation of the μ_3-arene clusters, they can easily be hydrogenated once the clusters have been formed.

3. From X-ray crystallographic studies considerable expansion but only small Kekulé-type distortions of the μ_3-η^2:η^2:η^2-coordinated arenes are evident. In solution hindered mutual rotation of the (CpCo)$_3$ triangles and C$_6$ rings takes place, which can be frozen out on the NMR time scale at low temperature.

4. The cluster **5b** exhibits a low chemical reactivity toward a variety of reagents directed to attack the metal cluster, the μ_3-arene ring, or the side chain of the latter. At present it is not yet clear if the deactivation is due to the electronic or steric influence of the (CpCo)$_3$ cluster.

5. The (CpCo)$_3$(μ_3-arene) clusters mimic the hollow adsorption sites with $C_{3v}(\sigma_d)$ local symmetry found for benzene on some close-packed metal surfaces. However, distortion from a regular hexagonal geometry of the μ_3-arene rings appears to be much smaller in the molecular clusters.

Synthesis and Reaction Chemistry of the Readily Available Molybdenum S$_2$O Complex [MoO(S$_2$CNEt$_2$)$_2$(S$_2$O)]

David S. Brown, Catherine F. Owens, Bruce G. Wilson, and Mark E. Welker*

Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

The synthesis (by S$_2$O transfer and S$_2$ complex oxidation) and characterization by X-ray diffraction of MoO(S$_2$CNEt$_2$)$_2$(S$_2$O) (1) is reported (monoclinic, $P2_1/n$, a = 9.4749 (15) Å, b = 21.9780 (32) Å, c = 9.6714 (16) Å, β = 107.225 (13)°, Z = 4, $R(F)$ = 3.46%). S$_2$O is bound to the metal in a side-on manner through both of the sulfurs. The geometry around the metal is a distorted pentagonal bipyramid with both sulfurs of S$_2$O in the equatorial plane. In a preliminary reactivity study, 1 has been shown to effect sulfur and oxygen transfer to triphenylphosphine. Complex 1 can also be used as a template for thiosulfinate ester (RSS(O)R') synthesis and as a reagent for oxidative coupling of carbanions.

Introduction

Recently, we have been exploring the reactions of disulfur monoxide (S$_2$O) with a variety of transition-metal complexes.[1] One goal of this project has been to develop practical syntheses of stable S$_2$O complexes to enable us to explore their reaction chemistry. If a transition-metal S$_2$O complex is to be used as a stoichiometric reagent in an organic transformation, it must be readily synthesized

on a reasonable scale from inexpensive starting materials. The S$_2$O complexes that had been reported previously did not appear to fit all these criteria.[2] We have now succeeded in synthesizing MoO(S$_2$CNEt$_2$)$_2$(S$_2$O) (1) by S$_2$O transfer and S$_2$ complex oxidation, and 1 has been char-

(1) (a) Urove, G. A.; Welker, M. E. *Organometallics* **1988**, *7*, 1013. (b) Raseta, M. E.; Cawood, S. A.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8268. (c) Urove, G. A.; Welker, M. E.; Eaton, B. E. *J. Organomet. Chem.* **1990**, *384*, 105. (d) Powell, K. R.; Elias, W. J.; Welker, M. E. *J. Organomet. Chem.*, in press. (e) Raseta, M. E.; Mishra, R. K.; Cawood, S. A.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.*, submitted for publication.

(2) (a) Faller, J. W.; Ma, Y. *Organometallics* **1989**, *8*, 609. (b) Herberhold, M.; Schmidkonz, B. *J. Organomet. Chem.* **1986**, *308*, 35. (c) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1986**, *309*, C29. (d) Herberhold, M.; Schmidkonz, B.; Ziegler, M. L.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 515. (e) Hoots, J. E.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130. (f) Hoots, J. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1226. (g) Dirand-Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Less-Common Met.* **1977**, *54*, 91. (h) Schmid, G.; Ritter, G. *Chem. Ber.* **1975**, *108*, 3008. (i) Schmid, G.; Ritter, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 645. For a review on sulfur oxide coordination compounds, see: Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98.