Inorg. Chem. **2008**, *47*, 10205−10207

Inorganic Chemistry
Communication

An Arene-Stabilized Cobalt(I) Aryl: Reactions with CO and NO

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Received August 25, 2008

The half-sandwich cobalt(I) complex (η^6-C_7H_8)CoAr*-3,5-^{i}Pr$_2$ (Ar*-3,5-^{i}Pr$_2$ = $-C_6H$-2,6-(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$) was synthesized by reduction of [3,5-^{i}Pr$_2$Ar*Co(μ-Cl)]$_2$ in toluene. It reacts with CO or NO to afford the unusual complexes [3,5-^{i}Pr$_2$Ar*C(O)Co(CO)] or [3,5-^{i}Pr$_2$Ar*N(NO)OCo(NO)$_2$].

Investigations of the sterically crowded first-row transition-metal moiety MAr*-3,5-^{i}Pr$_2$ (Ar*-3,5-^{i}Pr$_2$ = $-C_6H$-2,6-(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$; M = Cr[1], Mn[2], Fe[2]) have shown that stable η^6 complexes with aromatic rings such as benzene or toluene are not formed in the case of chromium.[1,3] In contrast, for manganese and iron, the stable inverted sandwich [(μ-η^6:η^6-C_7H_8){MnAr*-3,5-^{i}Pr$_2$}$_2$] and half-sandwich species [(η^6-C_6H_6)FeAr*-3,5-^{i}Pr$_2$] can be readily isolated.[2] The instability of the chromium(I) arene complex[4] is noteworthy because the related β-diketiminate/arene complex [(μ-η^6:η^6-C_7H_8)Cr{(C_6H_3-2,6-^{i}Pr$_2$)NC(Me)}$_2$CH] is isolable under ambient conditions.[5] Calculations for (η^6-C_6H_6)MMe model species (M = Cr, Fe, Co) supported a preference for weak η^2 rather than η^6 chromium(I)−ring interactions, whereas strong η^6-C_6H_6−Co interactions were predicted for (η^6-C_6H_6)CoMe.[6] A change in the spin state from a triplet to a singlet was also predicted when the centroid−Co−Me geometry changes from a linear (180°) to a bent (135°) configuration. Indeed, a low-spin state is observed for the Ar′CoCoAr′ [Ar′ = $-C_6H_3$-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$] dimer, which has a bent Co configuration.[1c] However, the high-spin triplet configuration has not been experimentally verified for an essentially linear (η^6-arene)Co(η^1-aryl) system. We now

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(7) 3,5-^{i}Pr$_2$Ar*Co(η^6-C_7H_8) (**2**): A brown solution of [3,5-^{i}Pr$_2$Ar*Co(μ-Cl)]$_2$ (**1**) (4.69 g, 7.11 mmol), prepared analogously to [Li(OEt$_2$)-Ar′CoI$_2$]$_2$[24] from 3,5-^{i}Pr$_2$Ar*Li[3] and $CoCl_2$, in ca. 20 mL of toluene, was added to a suspension of KC_8 (1.02 g, 7.54 mmol) at 0 °C in ca. 20 mL of toluene. After stirring for ca. 24 h, the solvent was removed under reduced pressure and the dark residue was extracted with ca. 100 mL of hexane. The solution was filtered, and the green filtrate was concentrated to ca. 20 mL, which afforded X-ray-quality bright-green crystals of **2**·*n*-hexane after storage at −18 °C for 1 day. Yield: 4.10 g (80%). Mp: 175 °C (black oil). Elem anal. Calcd for $C_{49}H_{69}Co$: C, 82.08; H, 9.70. Found: C, 82.56; H, 10.1. ^{1}H NMR (300.08 MHz, C_6D_6, 27 °C): δ 16.18 (s), 15.67 (s), 14.45 (br d), 8.70 (s), 3.22 (d), 2.53 (d), 2.12 (s), 1.26 (m), 0.91 (s), 0.30 (s), −0.83 (t), −59.16 (s), −62.31 (s). UV/vis [hexanes; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 242 (13 700), 260 (8600), 274 (9700), 316 (5700), 404 (1800). 3,5-^{i}Pr$_2$Ar*C(O)Co(CO) (**3**): A green solution of **2** (0.52 g, 0.73 mmol) in ca. 50 mL of diethyl ether was treated with dry CO gas (1 atm) at room temperature for 2 h. The solution became red within ca. 10 min. After further stirring for ca. 24 h, the solvent was removed under reduced pressure, and the residue was extracted with ca. 15 mL of hexane. Storage at −18 °C for several days gave X-ray-quality red crystals of **3**. Yield: 0.16 g (32%). Mp: 221 °C. Calcd for $C_{44}H_{61}CoO_2$: C, 77.61; H, 9.03. Found: C, 78.15; H, 8.80. ^{1}H NMR (300.08 MHz, C_6D_6, 23 °C): δ 7.34 (s, 1H), 7.07 (m, 4H), 2.96 (sept, 1H), 2.83 (sept, 1H), 2.73 (sept, 1H), 2.56 (sept, 2H), 2.44 (sept, 2H), 1.86 (sept, 1H), 1.34 (d, 6H), 1.29 (d, 6H), 1.24 (d, 6H), 1.20 (d, 6H), 1.14 (d, 6H), 1.03 (d, 6H), 0.98 (d, 6H), 0.86 (d, 6H). IR (Nujol, cm^{-1}) ν 1965 (s). UV/vis [hexanes; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 222 (73 600), 294 (22 500). 3,5-^{i}Pr$_2$Ar*N(NO)OCo(NO)$_2$ (**4**): A green solution of **2** (0.50 g, 0.70 mmol) in ca. 50 mL of diethyl ether was treated with dry NO gas (1 atm) at room temperature for 2 h. The solution turned brown immediately. After stirring for ca. 24 h, the solvent was removed under reduced pressure, and the residue was extracted with ca. 50 mL of hexane. The solution was filtered. and the dark-red filtrate was concentrated to ca. 10 mL, which afforded X-ray-quality reddish-brown crystals of **4** after storage at −18 °C for several days. Yield: 0.10 g (19%). Mp: 163 °C. Calcd for $C_{42}H_{61}CoN_4O_4$: C, 67.78; H, 8.26; N, 7.52. Found: C, 68.31; H, 8.24; N, 7.12. ^{1}H NMR (300.08 MHz, C_6D_6, 23 °C): δ 7.67 (s, 1H), 7.13−7.24 (m, 4H), 2.83 (m, 8H), 1.50 (d, 12H), 1.17−1.38 (m, 36H). IR (Nujol, cm^{-1}) ν 1690 (s). UV/vis [hexanes; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 224 (82 600), 272 (34 800), 364 (85 100).

10.1021/ic8015782 CCC: $40.75
Published on Web 10/15/2008

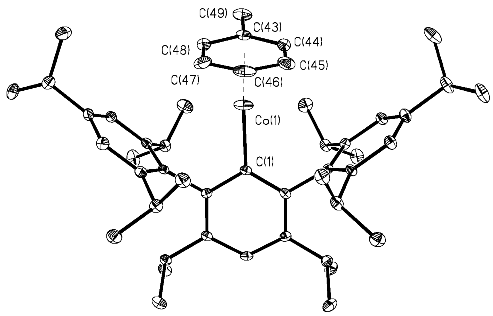

Figure 1. Solid-state molecular structure of **2** (H atoms and solvent molecules are not shown; thermal ellipsoids are shown at 30% probability). Selected bond distances (Å) and angles (deg): Co(1)−C(1) 2.021(2), Co(1)−centroid 1.659(1); C(1)−Co(1)−centroid 167.6(2).

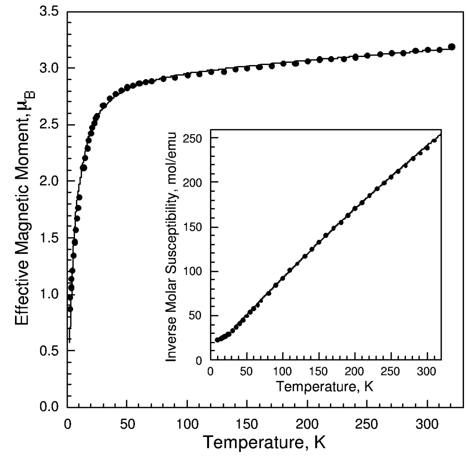

Figure 2. Plot of the effective magnetic moment and inverse molar magnetic susceptibility of **2** (inset) versus temperature. Both solid lines correspond to the best fit obtained by using the method given in ref 12. The magnetic properties have been fit with $S_1 = S_2 = 1$, $g = 2.08(1)$, $J = -1.8(1)$ cm^{-1}, $D = 35(3)$ cm^{-1}, and $N\alpha = 0.00059(5)$ emu·mol^{-1}.

report the synthesis and characterization of 3,5-^{i}Pr$_2$Ar*Co(η^6-C_7H_8). We also describe its reactions with CO and NO to give the new complexes 3,5-^{i}Pr$_2$Ar*C(O)Co(CO) and 3,5-^{i}Pr$_2$Ar*N(NO)OCo(NO)$_2$.

Reduction of [3,5-^{i}Pr$_2$Ar*Co(μ-Cl)]$_2$ (**1**) with KC_8 in toluene afforded bright-green crystals of 3,5-^{i}Pr$_2$Ar*Co(η^6-C_7H_8) (**2**) in 80% yield.[7] The X-ray structure of **2** (Figure 1) confirmed the η^1 and η^6 bonding patterns for the 3,5-^{i}Pr$_2$Ar* and toluene ligands, respectively, as well as a +1 oxidation state at cobalt.[8] Monovalent cobalt complexes have received increased attention because of their ability to activate small molecules and their effectiveness at binding oxo or nitrene functionalities in group transfer reactions.[9] The structure of **2** is related to that of [(HC{C(Me)NC$_6$H$_3$-2,6-Me$_2$}$_2$)Co(η^6-C_7H_8)], which has a Co−centroid distance of 1.747(2) Å.[9a] The Co(1)−centroid distance in **2** is 1.659(1) Å, which is almost 0.1 Å shorter, possibly as a result of the lower coordination number at the cobalt center. However, it is longer than the corresponding distance (1.602 Å) in the cobalt(I) complex Co(PMe$_3$)$_2$(BPh$_4$),[10] where cobalt interacts with a phenyl ring in an η^6 fashion. The C(1)−Co(1)−centroid angle in **2** is 167.6°, and the Co(1)−C(1) σ-bond length is 2.021(2) Å, which is close to 1.984(2) Å observed in the square-planar bis(imido)pyridindylcobalt(I) complex [C$_5$H$_3$-N{2,6-C(Me)N(C$_6$H$_3$-2,6-^{i}Pr$_2$)}$_2$CoCH$_2$SiMe$_3$][11] and is essentially the same as the 2.008(3)−2.019(3) Å range found in Ar′CoCoAr′.[1c] The ^{1}H NMR spectrum of **2** exhibits paramagnetically shifted resonances between 20 and −70 ppm, suggesting a high-spin d^8 ($S = 1$) electronic configuration for the cobalt(I) center, which was further confirmed by the study of its magnetic properties. The variation of the inverse molar magnetic susceptibility with respect to temperature is shown in Figure 2.[12] The plot is linear above ca. 150 K, yielding a Curie constant of 1.42 emu·K·mol^{-1}, a Weiss temperature of −42 K, and μ_{eff} of 3.37 μ_B. Below 150 K, the inverse molar susceptibility deviates only slightly from linearity possibly as a result of zero-field splitting and very weak long-range coupling. The data are thus consistent with the presence of two unpaired electrons and a high-spin configuration at the metal center.

The reactivity of complex **2** toward CO and NO was also studied. The reaction of **2** with CO proceeded smoothly and within minutes produced the new acyl/carbonyl complex [3,5-^{i}Pr$_2$Ar*C(O)Co(CO)] (**3**) as red crystals in 32% yield.[7] An X-ray crystal structure of **3** (Figure 3) revealed that the cobalt center is coordinated to a terminal carbonyl group as well as an acyl group formed by insertion of a CO molecule into the Co−C σ bond.[8] The facile insertion of CO into the metal−ligand bond may be contrasted with the behavior of related cobalt(I) and iron(I) β-diketiminate complexes, where insertion is not observed for the bond to the stabilizing bulky ligand.[9,13] There is also a strong interaction between cobalt and the flanking aryl ring. The Co−centroid distance

(8) Crystallographic data for **2**·n-hexane, **3**, and **4** at 90 K with Mo Kα (λ = 0.710 73 Å) radiation. **2**·n-hexane: a = 30.400(2) Å, b = 10.9345(8) Å, c = 14.7054(11) Å, V = 4888.3(6) Å^3, M = 803.14, orthorhombic, space group $Pna2_1$, Z = 4, R1 = 0.0438 [$I > 2\sigma(I)$ data], wR2 = 0.1242 for all data. **3**: a = 13.867(2) Å, b = 14.236(2) Å, c = 21.655(4) Å, α = 75.604(3)°, β = 85.861(3)°, γ = 84.494(3)°, V = 4116.6(12) Å^3, M = 680.86, triclinic, space group $P\bar{1}$, Z = 4, R1 = 0.0632 [$I > 2\sigma(I)$ data], wR2 = 0.1773 for all data. **4**: a = 9.533(3) Å, b = 25.390(8) Å, c = 20.019(7) Å, β = 97.844(5)°, V = 4800(3) Å^3, M = 744.88, monoclinic, space group $P2_1/n$, Z = 4, R1 = 0.1841 [$I > 2\sigma(I)$ data], wR2 = 0.5236 for all data.

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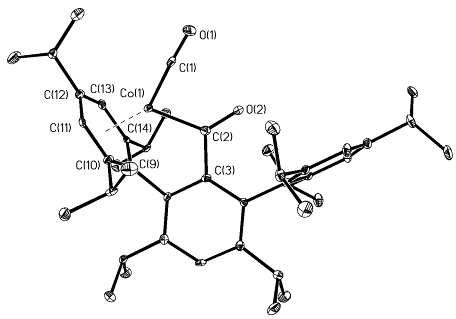

Figure 3. Solid-state molecular structure of **3** (one of two independent molecules shown; H atoms and solvent molecules are not shown; thermal ellipsoids are shown at 30% probability). Selected bond distances (Å) and angles (deg): Co(1)−C(1) 1.739(5), Co(1)−C(2) 1.926(5), Co(1)−centroid 1.599(2), C(1)−O(1) 1.162(5), C(2)−O(2) 1.227(5); Co(1)−C(1)−O(1) 176.6(4), Co(1)−C(2)−O(2) 126.8(4).

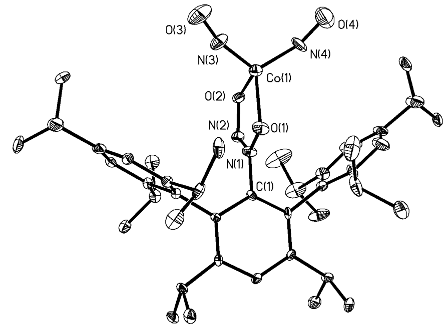

Figure 4. Solid-state molecular structure of **4** (H atoms and solvent molecules are not shown; thermal ellipsoids are shown at 30% probability). Selected bond distances (Å) and angles (deg): Co(1)−N(3) 1.643(9), Co(1)−N(4) 1.618(11), Co(1)−O(1) 1.920(8), Co(1)−O(2) 1.944(8), N(1)−O(1) 1.334(10), N(1)−N(2) 1.274(12), N(2)−O(2) 1.299(11), N(3)−O(3) 1.168(12), N(4)−O(4) 1.189(14); O(1)−Co(1)−O(2) 79.9(3), N(3)−Co(1)−N(4) 111.0(5), Co(1)−N(3)−O(3) 164.7(11), Co(1)−N(4)−O(4) 159.8(11).

[1.599(2) Å] is much shorter than that in **2** [1.659(1) Å] and is close to that in $Co(PMe_3)_2(BPh_4)$ (1.602 Å) mentioned above.[10] The average Co(1)−C(1) and C(1)−O(1) distances are 1.739(5) and 1.162(5) Å, respectively. These are comparable to those in other cobalt(I) carbonyl compounds, such as $[\{PhB(CH_2PPh_2)_3\}Co(CO)_2]$[9c] [Co−C = 1.729(5) and 1.744(5) Å; C−O = 1.170(5) and 1.140(5) Å] and $[(TIMEN^{xyl})Co(CO)]Cl$[9d] [TIMEN = tris[2-(3-arylimidazol-2-ylidene)ethyl]amine; Co−C = 1.8463(19) Å, C−O = 1.101(3) Å]. The relatively short metal−carbon and long C−O bond lengths in **3** imply a strong back-bonding between the cobalt center and the terminal carbonyl.[14] The IR spectrum of **3** featured a CO stretching band at 1965 cm^{-1}, indicating considerable Co−CO back-bonding. No resonance broadening or shifting was observed in the ^1H NMR spectrum of **3**, as predicted for an 18-valence electron diamagnetic species. The possible mechanism of formation of **3** may involve the initial carbonylation of **2** with the elimination of toluene. A migratory insertion of one of the carbonyls into the Co−C(aryl) σ bond, facilitated by a strong Co−η^6 flanking ring interaction, may then occur.

Exposure of **2** to a large excess of NO (1 atm) resulted in reddish-brown crystals of $[3,5\text{-}^iPr_2Ar^*N(NO)OCo(NO)_2]$ (**4**) in 19% yield.[7] Unfortunately, despite numerous attempts, high-quality crystals could not be grown. Nonetheless, an X-ray data set of sufficient quality to establish its structure was obtained,[8] and this is shown in Figure 4. The complex features a four-coordinate cobalt center with distorted tetrahedral geometry. The $[3,5\text{-}^iPr_2Ar^*N(NO)O]^-$ anion, formed by insertion of NO into the Co−C σ bond[15] with concomitant NO coupling and N−N bond formation, binds cobalt as a bidentate ligand in a η^2-O,O fashion. Such double NO insertion behavior is known for early-transition-metal−alkyl or −aryl complexes[16] such as $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Ph)_2$, $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$, and WMe_6, which react with NO to form $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Ph)(\eta^2\text{-}O_2N_2CH_2Ph)$,[17] $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2CH_2SiMe_3)$,[18] and $WMe_4(\eta^2\text{-}O_2N_2Me)_2$,[19] respectively. In contrast, similar double insertion into late-transition-metal−carbon σ bonds is rare.[20] Both terminal NO ligands in **4** feature wide Co−N−O angles [Co(1)−N(3)−O(3) 164.7(11)°, Co(1)−N(4)−O(4) 159.8(11)°] such that an 18-electron configuration is attained. The IR spectrum of **4** shows N−O bands at 1660 and 1720 cm^{-1} consistent with its behavior as a three-electron ligand.[21] No cobalt-arene interaction was apparent. The structure of the $3,5\text{-}^iPr_2Ar^*N(NO)O$ ligand in **4** resembles that of Cupferron $[PhN(NO)O]NH_4$, a common analytical reagent,[22] and the related derivatives of NONOates, $[R_2NN(NO)O]^-$, which are smooth nonenzymatic releasers of nitric oxide in physiological media.[23]

In conclusion, the unusual arene-stabilized cobalt(I) aryl complex **2** has been prepared and characterized. It readily undergoes addition/migratory insertion reactions with CO or NO. Further exploration on the reactivity of **2** with other small molecules and atom-transfer reagents is underway.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-0641020) for financial support. B.D.E. thanks the NSERC of Canada for a postdoctoral fellowship.

Supporting Information Available: ^1H NMR spectra for **2**−**4** and X-ray crystallographic data (in CIF format) for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8015782

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