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Synthesis and Characterization of the Metal(I) Dimers [Ar′MMAr′]: Comparisons with Quintuple-Bonded [Ar′CrCrAr′]**

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Metal–metal bonding in the dimeric chromium complex [Ar′CrCrAr′] (Ar′ = C_6H_3-2,6(2,6-*i*$Pr_2C_6H_3)_2$ is derived from the interaction of two d^5 {CrAr′} fragments whose valence electrons are paired to form a quintuple bond.[1–5] The ready synthesis[1] of this complex by the simple reduction of an aryl metal halide precursor[6] suggests the possible formation of similar complexes by other transition metals. Such complexes might exhibit unprecedented types of interactions between metals of various d^n configurations, and their isolation and characterization would permit informative comparisons with the chromium species. Herein, we report the synthesis, structural and spectroscopic characterization of the iron and cobalt derivatives [Ar′MMAr′] (M = Fe (**1**) or Co (**2**)) and clarify that, although they bear a structural resemblance to [Ar′CrCrAr′], their metal–metal bonding has little in common with that of the chromium analogue.

Complexes **1** and **2** were obtained in low yields by the reduction of [{Li(OEt$_2$)$_2$Ar′FeI$_2$}$_2$][6] (or [{Ar′Fe(μ-Br)}$_2$])[7a] and [{Li(OEt$_2$)$_2$Ar′CoI$_2$}$_2$][6] (or [{Ar′Co(μ-Cl)}$_2$])[7b] with the potassium–graphite intercalate KC_8 in tetrahydrofuran. The metal dimers crystallized as very dark red (**1**) or very dark green (**2**) solids. They were initially characterized by X-ray crystallography,[8] which revealed that they had a dimeric structure (Figure 1 and Figure 2, respectively; selected structural data are provided in the Figure legends).

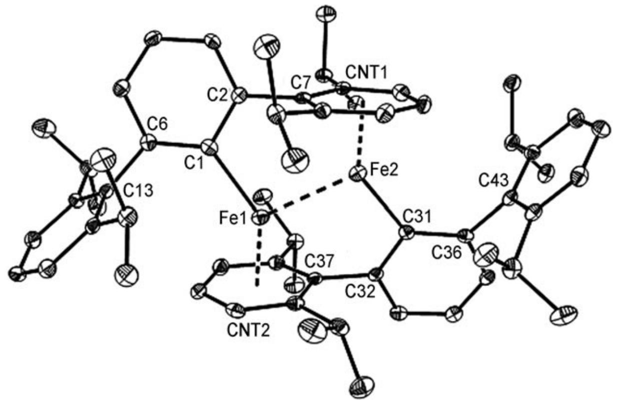

Figure 1. Molecular structure of **1** with thermal ellipsoids presented at a 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Fe1–Fe2 2.5151(9), Fe1–C1 2.028(4), Fe1–C(flanking ring) 2.166(4), 2.192(4), 2.256(4), 2.286(5), 2.309(4), 2.341(5), Fe1–centroid (CNT2) 1.7625(19), Fe2–C31 2.048(4), Fe2–C(flanking ring) 2.173(4), 2.232(4), 2.278(4), 2.276(5), 2.232(5), 2.221(4), Fe2–centroid (CNT1) 1.7333(18), C1-Fe1-Fe2 100.41(13), C1-Fe1-CNT2 139.1(2), Fe1-Fe2-CNT1 119.1(3), C31-Fe2-Fe1 100.39(13), C31-Fe2-CNT1 137.9(2), Fe2-Fe1-CNT2 119.2(2), C1-C2-C7 118.4(4), C31-C32-C37 118.3(4).

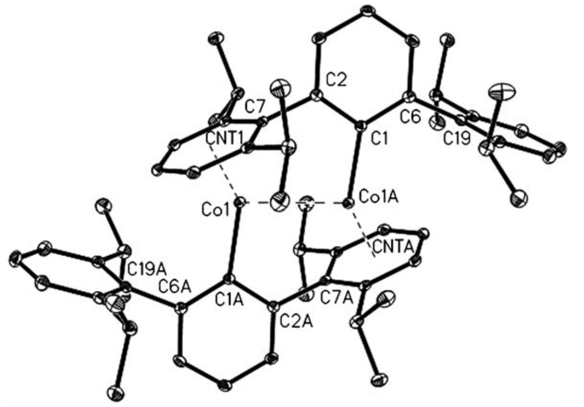

Figure 2. Molecular structure of **1** with thermal ellipsoids presented at a 30% probability level. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [d°]: Co1–Co1A 2.8033(5), Co1–C1A 2.0058(16), Co1–C(flanking ring) 2.1111(16), 2.1482(16), 2.2041(17), 2.2686(16), 2.2246(16), 2.1624(16), Co1-CNT 1.7638(16), C1-Co1-Co1A 94.26(5), C1A-Co1-CNT1 143.7(3), Co1A-Co1-CNT1 122.0(3), C1-C2-C7 120.15(14).

The overall *trans*-bent $C_{ipso}MMC_{ipso}$ core configuration is similar to that in [Ar′CrCrAr′].[1] This resemblance is misleading, however, and masks profound differences both in the metal–metal and the metal–ligand interactions. In a manner which appears to be similar to that in [Ar′CrCrAr′], the iron and cobalt atoms are η^1 bonded to an *ipso*-carbon center from the central aryl ring of the terphenyl ligand and are also η^6 bonded to a flanking ring of a terphenyl ligand attached to the other metal center within the dimer. However, in complexes **1** and **2**, these flanking-ring interactions are much stronger than those in [Ar′CrCrAr′], as indicated by the

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[**] We are grateful to the National Science Foundation (CHE-0641020) for financial support. B.D.E. thanks the NSERC of Canada for a postdoctoral fellowship. Ar′ = C_6H_3-2,6-(2,6-*i*$Pr_2C_6H_3)_2$; M = Fe or Co.

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metal–centroid distances, which are almost 0.5 Å shorter. Thus, in **1** the iron–centroid distances are 1.733(2) and 1.763(2) Å and in **2** the cobalt–centroid distance is similar at 1.764(2) Å. These lengths, which may be compared to 2.203(6) Å in [Ar′CrCrAr′], are similar to the iron– and cobalt–centroid distances in the complexes $[HC\{C(Me)N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)\}_2Fe(\eta^6\text{-}C_6H_6)]$,[9] $[3,5\text{-}i\mathrm{Pr}_2Ar^*Fe(\eta^6\text{-}C_6H_6)]$ ($3,5\text{-}i\mathrm{Pr}_2Ar^* = 2,6(2,4,6\text{-}i\mathrm{Pr}_3C_6H_2)_2\text{-}3,5\text{-}i\mathrm{Pr}_2C_6H$),[10] and $[HC\{C(Me)N(2,6\text{-}Me_2C_6H_3)\}_2Co(\eta^6\text{-}C_7H_8)]$.[11] The variation from the mean metal–ring-carbon distance in **1** and **2** is less than 0.07 Å, whereas, in [Ar′CrCrAr′], the corresponding interactions involve only the *ipso* and *ortho* carbon atoms of the flanking rings. A more detailed examination of the structural data for **1** and **2** reveals that the average C–C bond length within the metal-coordinated flanking arene rings is approximately 0.02 Å longer than that in the uncomplexed ring, thus suggesting significant interactions with the metal center.

The most prominent structural parameters in **1** and **2** are the Fe–Fe and Co–Co distances, which present an even greater contrast to the chromium structure. The Fe–Fe (2.515(9) Å) and Co–Co (2.8033(5) Å) separations greatly exceed the Cr–Cr bond length in [Ar′CrCrAr′] (1.8351(4) Å). The Fe–Fe distance slightly exceeds the sum of the single-bond covalent radii for iron (2.48 Å),[12] whereas the Co–Co distance is more than 0.3 Å longer than that predicted for a cobalt–cobalt single bond (2.46 Å).[12] On the basis of these distances an iron–iron single bond could be expected for **1**, whereas, in **2**, the cobalt centers are either weakly bonded or nonbonded. However, the metal–metal distance, by itself, provides only limited information on possible bonding interactions. We used magnetic and computational data for further insights into the nature of bonding in **1** and **2**.

Magnetic measurements for **1** were impeded by the persistent presence of low levels of impurities with high magnetic moments, in spite of numerous attempts to eliminate these by recrystallization. Magnetic measurements on several samples, obtained by separate syntheses, reveal that they essentially exhibit Curie behavior. However, the proximity of two Fe^I centers strongly suggests an exchange interaction between them. As a result we came to the conclusion that **1** is essentially diamagnetic and that the magnetic component which furnishes the Curie behavior may be a superparamagnetic iron oxide or carbide impurity. Diamagnetism is consistent with an Fe–Fe single bond with the two remaining electrons at each iron center becoming paired. Alternatively, the iron centers may be linked by a triple bond, formed by pairing of the three d electrons from each iron center. However, the Fe–Fe distance is more consistent with a single bond. The pairing of the nonbonding electrons at the iron centers may be a consequence of the bent nature of the geometry at iron, in contrast to the linear geometry of the analogous, more crowded, monomer $[3,5\text{-}i\mathrm{Pr}_2Ar^*Fe(\eta^6\text{-}C_6H_6)]$,[10] which has three unpaired electrons. The magnetic data for **2** suggest that the two Co^I, d^8 centers are either very strongly antiferromagnetically coupled (essentially double-bonded through pairing of two electrons from each cobalt center) or each have a diamagnetic, low-spin d^8 configuration. However, the longer Co–Co separation (2.8033(5) Å) does not support the existence of a double bond. A second crystal structure of **2** (crystals obtained from hexane) afforded a noncentrosymmetric structure which, although it featured an essentially unchanged Co–Co distance of 2.8010(6) Å and $Co\text{-}Co\text{-}C_{ipso}$ angles of 94.1(1) and 94.6(1)°, had a torsion angle of 17.2° between the two C_{ipso}–Co–centroid planes. Furthermore, the two cobalt–centroid distances, 1.672(1) and 1.666(1) Å, were approximately 0.1 Å shorter than that of the structure in Figure 2. The independence of the Co–Co distances in the two structures on the torsion angle supports the view that there is no cobalt–cobalt bond. The low-spin configuration of the cobalt centers in **2**, in which the valence d electrons are paired, is not in agreement with the high spin ($S = 1$) configuration found in the mononuclear arene complex $[3,5\text{-}i\mathrm{Pr}_2Ar^*Co(\eta^6\text{-}C_7H_8)]$,[7b] which has a C_{ipso}-Co-centroid angle (167.60°) that is close to linearity. The magnetic moment in this mononuclear compound, $\mu_{\mathrm{eff}} = 3.37\,\mu_B$, is consistent with the presence of two unpaired electrons. ^1H NMR spectroscopic analysis of **2** in $[D_8]THF$ or C_6D_6 displays signals in the region 0–10 ppm.

The low-spin configuration of the cobalt centers in **2** differs from experimental findings for the mononuclear cobalt(I)-arene complex $[3,5\text{-}i\mathrm{Pr}_2Ar^*Co(\eta^6\text{-}C_7H_8)]$[7] and the theoretical data for $[Co(\eta^6\text{-}C_6H_6)]$ half-sandwich complexes, which indicate that they are high spin.[13,14] Recent calculations[5] for the model species $[MeCo(\eta^6\text{-}C_6H_6)]$ also predict a high spin configuration, that is, $S = 1$ for a linear Me-Co-centroid geometry. However, when the Me-Co-centroid angle is 135° (a bending of 45° from linearity), electron pairing is induced and the configuration becomes low spin. In **2**, the C_{ipso}-Co-centroid angle is 143.7° (a bending of 36.3° from linearity), which may be sufficient to induce the low-spin configuration. The presence of paired electrons at each cobalt center might also account for the increased metal–metal separation of **2**, in comparison to that in **1**, as a result of increased interelectronic repulsion.

Density functional (DFT) calculations, optimized at the B3LYP/DVZp level on the model species $[\{2,6\text{-}(2,6\text{-}Me_2C_6H_3)_2\text{-}C_6H_3\}CoCo\{2,6\text{-}(2,6\text{-}Me_2C_6H_3)_2\text{-}C_6H_3\}]$, indicated that the high-spin state is most stable for the molecule (see the Supporting Information), contrary to experimental data. Such a discrepancy may be connected with the strongly multiconfigurational character of the arene–metal–aryl moieties, which is not accounted for in the DFT approach. Furthermore, DFT methods are known to often favor states with higher multiplicities.[17] Similar calculation on the analogous model diiron species have not afforded definitive results to date. The ^3B state was found to be lowest in energy but the ^5A state was found to only be approximately 3 kcal mol^{-1} less stable. Efforts to synthesize a series of diiron and dicobalt species related to **1** and **2**, by using a variety of terphenyl ligands to fully explain their unusual bonding and electronic properties, are currently underway.

Experimental Section

All manipulations were carried out under strictly anhydrous and anaerobic conditions.

[Ar′FeFeAr′] (**1**): A light tan solution of [{Ar′FeBr}$_2$], (0.906 g, 1.7 mmol, synthesized from LiAr′ and FeBr$_2$) in THF (30 mL) was added dropwise over 30 min to a freshly prepared suspension of KC$_8$ (K 0.067 g, 1.7 mmol; C 0.182 g, 15.2 mmol) in THF (25 mL) at 0 °C. The mixture was stirred for 4 days at 25 °C, after which the solvent was removed under reduced pressure. The black residue was extracted with hexanes (60 mL) and filtered through a cannula. The black filtrate was concentrated to approximately 15 mL and stored for 4 days at −13 °C, affording **1** as small red/black blocks (0.030 g, 3.8 % based on Fe). Alternatively, the residue can be extracted with benzene, concentrated, and stored at 7 °C to yield **1** as red/black crystals in 3.3 % yield. M.p. 155–157 °C, sweats at 125 °C. UV/Vis (hexanes), featureless with increasing absorption at shorter wavelengths.

[Ar′CoCoAr′] (**2**): A royal blue solution of [{Ar′CoCl}$_2$] (1.48 g, 1.50 mmol) in THF (30 mL) was added dropwise to a freshly prepared suspension of KC8 (4.404 g, 3.0 mmol) in THF (20 mL) at 0 °C. The solution turned green immediately. The mixture was stirred for approximately 24 h. The solvent was removed under reduced pressure and the black solid residue was extracted with toluene (40 mL). The dark green organic phase was concentrated to approximately 15 mL, which, after standing for 3 days at −18 °C, afforded **2** as green crystals (0.095 g, 7.0 % based on Co). ^{1}H NMR (300 MHz, [D$_8$]THF, 32 °C): $\delta = 1.18$ (br s, 12 H CH(CH_3)$_2$), 1.38 (br s, 12 H CH(CH_3)$_2$), 2.20 (br s, 12 H CH(CH_3)$_2$), 2.35 (br s, 12 H CH(CH_3)$_2$), 2.66 (br s, 4 H CH-(CH$_3$)$_2$), 3.35 (br s, 4 H CH(CH$_3$)$_2$), 6.11 (br s, 4 H ArH$_m$, (2,6-*i*Pr$_2$C$_6$H$_3$)), 6.88 (br s, 2 H, ArH$_p$, (2,6-*i*Pr$_2$C$_6$H$_3$)), 7.06 (br s, 4 H, ArH$_m$, (C$_6$H$_3$)), 8.10 (br s, 2 H ArH$_p$, (C$_6$H$_3$)), 8.85 (br s, 4 H, ArH$_m$, (2,6-*i*Pr$_2$C$_6$H$_3$)), 10.45 ppm (br s, 2 H, ArH$_p$, (2,6-*i*Pr$_2$C$_6$H$_3$)); UV/Vis (hexanes) $\lambda_{max} = 446$ nm (ε 430 cm^{-1}M^{-1}).

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[7] a) A sample preparation of [{Ar′Fe(μ-Br)}$_2$] is given in the Supporting Information. Full details and characterization will be published in a full account of this work; b) H. Lei, C. Ni, J. C. Fettinger, P. P. Power, unpublished results.

[8] Crystallographic data for **1** and **2** at 90 K with Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation: **1**: $a = 11.942(1)$, $b = 18.586(2)$, $c = 21.926(2)$ Å, $V = 4866.5(7)$ Å^3, $M_r = 906.89$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $R1 = 0.0539$ ($I > 2\sigma(I)$), $wR2 = 0.1267$ for all data. **2**·2C$_7$H$_8$: $a = 9.7688(4)$, $b = 10.9496(4)$, $c = 14.5087(6)$ Å, $\alpha = 88.104(1)°$, $\beta = 84.035(1)$, $\delta = 76.608(1)°$, $V = 1501.5(1)$ Å, $M_r = 1097.32$, triclinic, space group $P\bar{1}$, $Z = 1$, $R1 = 0.0342$ ($I > 2\sigma(I)$), $wR2 = 0.0848$ all data. CCDC 689809, 689810, 689811, 689812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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