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Two-Coordinate First Row Transition Metal Complexes with Short Unsupported Metal−Metal Bonds

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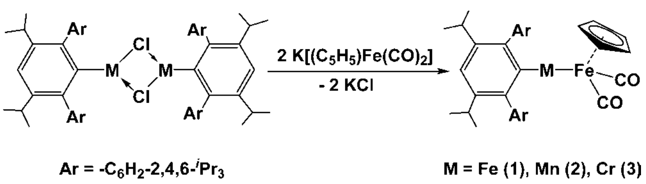
Abstract: A series of first row transition metal complexes with unsupported M−Fe bonds, (3,5-^{i}Pr$_2$-Ar*)MFe(η^5-C_5H_5)(CO)$_2$ (M = Fe (**1**), Mn (**2**), Cr (**3**), 3,5-^{i}Pr$_2$-Ar* = -C_6H-2,6-(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$), was synthesized by salt metathesis. They were characterized by ^{1}H NMR, UV−vis spectroscopy, X-ray crystallography, and SQUID magnetic measurements. Two distinct Fe atoms in **1** were confirmed by Mössbauer spectroscopy. All three compounds feature short metal−metal bond distances (Fe−Fe, 2.3931(8) Å (**1**); Mn−Fe, 2.4512(5) Å (**2**); Cr−Fe, 2.4887(5) Å (**3**)). Their DFT computed structures were in excellent agreement with the experimental data and revealed a dative bonding interaction between the metals.

Understanding the nature of metal−metal bonds is of fundamental chemical importance.[1] Among the numerous complexes containing a direct metal−metal bond, those unsupported by bridging ligands have attracted particular interest because of their inherent simplicity.[2] A number of first row transition metal species with bridged homo- or heteronuclear metal−metal bonds are known, but unbridged complexes are less numerous[3,4] and are almost exclusively stabilized by π-acid ligands at each metal.[5] Recently, Wieghardt and co-workers reported a dimeric compound [{Fe(tim)}$_2$] (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene), which contains an unbridged Fe−Fe bond.[6] In addition, the group of Roesky reported the synthesis of [{HC(CMeNAr)$_2$}Mn]$_2$ (Ar = -C_6H_3-2,6-^{i}Pr$_2$), which has an unsupported Mn−Mn bond.[7] These compounds were prepared by reduction of ligand-substituted metal salts with alkali metals. Our attempts to prepare an Fe−Fe bonded complex stabilized by the large terphenyl ligand Ar′ (Ar′ = -C_6H_3-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$) via reduction of [Ar′Fe(μ-Br)]$_2$ led to a low yield of the dimeric product [Ar′FeFeAr′],[8] in which the Fe−Fe unit was supported by a bridging terphenyl ligand incorporating strong η^6-metal-flanking-ring interactions to each iron. We now show that an unsupported Fe−Fe bond can be constructed by the reaction of [(3,5-^{i}Pr$_2$-Ar*)Fe(μ-Cl)]$_2$ (3,5-^{i}Pr$_2$-Ar* = -C_6H-2,6-(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$)[9] with K[(η^5-C_5H_5)Fe(CO)$_2$].[10] We also show that the corresponding unbridged heterometallic Mn−Fe and Cr−Fe species can be prepared in a similar fashion.

Scheme 1. Synthesis of **1**, **2**, and **3**



Treatment of [(3,5-^{i}Pr$_2$-Ar*)Fe(μ-Cl)]$_2$ with 2 equiv of K[(η^5-C_5H_5)Fe(CO)$_2$] at ca. −78 °C gave, after workup and recrystallization from hexane, dark red crystals of (3,5-^{i}Pr$_2$-Ar*)FeFe(η^5-C_5H_5)(CO)$_2$ (**1**) in 64% yield (Scheme 1). The ^{1}H NMR spectrum of **1** exhibits paramagnetically shifted resonances which span the chemical shift range +66 to −69 ppm. The μ_{eff} of **1** ranged from 4.5 to 5.0 μ_B at 5−300 K (Figure S1), suggesting an $S = 2$ ground state with little first-order orbital angular momentum contribution. Zero-field Mössbauer spectroscopy at 300 and 190 K (Figure S3 and Table S1) revealed the presence of two different Fe atoms. A signal ($\delta = 0.42$ mm/s, $\Delta E_Q = 0.96$ mm/s at 190 K) was consistent with two-coordinate Fe(II).[11] Another signal ($\delta = 0.08$ mm/s, $\Delta E_Q = 1.73$ mm/s at 190 K) was consistent with an Fe atom in an [(η^5-C_5H_5)Fe(CO)$_2$] fragment.[12] In addition, a signal ($\delta = 0.15$ mm/s, $\Delta E_Q = 1.94$ mm/s at 190 K) indicated the presence of some [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ dimer (literature value: $\delta = 0.227(2)$ mm/s, $\Delta E_Q = 1.912(5)$ mm/s at 77 K),[12] whose presence could be due to disproportionation or oxidation of **1**.

X-ray crystallography confirmed the formulation of **1** which includes an unsupported Fe−Fe bond (Figure 1). The Fe(1)−Fe(2) distance (2.3931(8) Å) is much shorter than those in other known species with unsupported Fe−Fe bonds: e.g., [{Fe(tim)}$_2$] (2.6869(6) Å),[6] [(η^3-C_3H_5)Fe(CO)$_3$]$_2$ (3.138(3) Å),[5a] {[(C_5H_5N)$_4$Na]$_2$[Fe_2(CO)$_8$]}$_\infty$ (2.815(1) Å),[5b] [Fe($CO_2{}^t$Bu)(CO)$_4$]$_2$ (2.840(1) Å),[5c] and (*N*-methyllutidinium)$_2$-

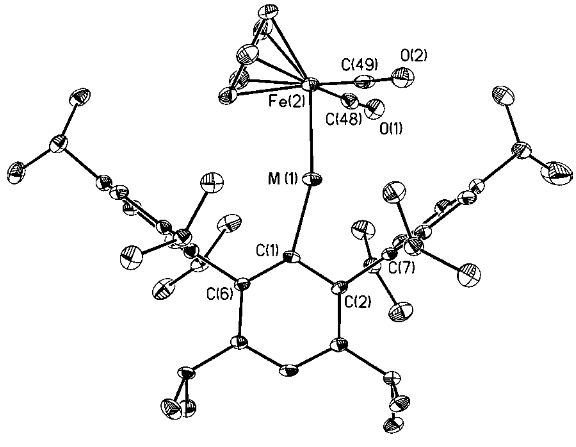


Figure 1. Solid state molecular structure of **1** or **2** (M = Fe (**1**) or Mn (**2**); H atoms and solvent molecules are not shown; thermal ellipsoids are shown at 30% probability). Selected bond distances (Å) and angles (deg) of **1** (corresponding data for **2** are shown in brackets): M(1)−Fe(2) 2.3931(8) [2.4512(5)], M(1)−C(1) 2.022(4) [2.081(2)], C(1)−M(1)−Fe(2) 163.94(12) [166.82(6)], M(1)−C(1)−C(2) 107.9(3) [109.33(15)], M(1)−C(1)−C(6) 133.6(3) [131.99(17)], C(2)−C(1)−C(6) 118.5(4) [118.7(2)].

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[$Fe_2(CO)_8$] (2.780(1) Å).[5d] It is also shorter than the 2.52 Å interatom distance in iron metal.[13] When it is compared to the Fe−Fe lengths in bridged compounds (2.2−3.12 Å),[1,14] the Fe−Fe distance in **1** lies in the shorter end of the range. It is noteworthy that the reported shortest Fe−Fe bonds (2.198(2) Å, $Fe_2(DPhBz)_3$, HDPhBz = *N*,*N*′-diphenylbenzamidine; 2.2318(8) Å, $Fe_2(DPhF)_3$, HDPhF = *N*,*N*′-diphenylformamidine) were calculated to have a bond order of 1.5.[14a] The coordination at Fe(1) deviates from linear geometry to afford a C(1)−Fe(1)−Fe(2) angle of 163.94(12)°. This is similar to those observed in a number of mononuclear, two-coordinate iron species, such as $Fe\{N(SiMePh_2)_2\}_2$ (169.0(1)°),[15] $Fe\{N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)(CH_2{}^tBu)\}_2$ (168.8(2)°),[16] $Fe(NMesBMes_2)_2$ (166.6(1)°, Mes = 2,4,6-$Me_3C_6H_2$),[17] $Fe(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (164.44(12), 171.06(12)°),[18] and $FeAr'_2$ (159.34(6)°).[19] The Fe(1)−C(1) distance (2.022(4) Å) in **1** is similar to the Fe−C σ-bond lengths in [Ar′FeFeAr′] (2.028(4) and 2.048(4) Å),[8] $Fe(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (2.040(3) Å),[18] $FeAr'_2$ (2.059(1) Å),[19] and (η^6-C_6H_6)Fe(Ar*-3,5-$^iPr_2$) (2.029(4) Å).[9] The angles at C(1) are distorted from idealized trigonal values (e.g., Fe(1)−C(1)−C(2) 107.9(3)°, Fe(1)−C(1)−C(6) 133.6(3)°), possibly due to a secondary interaction between Fe(1) and the *ipso*-carbon of a flanking ring (Fe(1)−C(7) 2.686(4) Å).

To test the generality of the salt metathesis route, the reactions between [(3,5-$^iPr_2$-Ar*)M(μ-Cl)]$_2$ (M = Mn,[9] Cr[20]) and K[(η^5-C_5H_5)Fe(CO)$_2$] were investigated. The reaction with [(3,5-$^iPr_2$-Ar*)Mn(μ-Cl)]$_2$ yielded yellow crystals of (3,5-$^iPr_2$-Ar*)MnFe(η^5-C_5H_5)(CO)$_2$ (**2**) in 57% yield upon recrystallization from hexane (Scheme 1). In addition, a small portion of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ cocrystallized during the preparation (identity confirmed by X-ray crystallography), suggesting a lower stability of **2** in comparison to **1**. Magnetic studies of **2** revealed a nearly ideal Curie paramagnetism behavior with μ_{eff} = 5.1 to 5.2 μ_B at 5−300 K (Figure S2). This is consistent with high-spin Mn(II) but may be lower than the idealized spin-only value 5.92 μ_B perhaps because of the inclusion of the above-mentioned diamagnetic impurity [(η^5-C_5H_5)Fe(CO)$_2$]$_2$.

The X-ray crystal structure of **2** showed that it is essentially isomorphous and isostructural to **1** in the solid state (Figure 1). It features an unsupported Mn−Fe bond. The only examples of unsupported Mn−Fe bonds are found in mixed metal carbonyl derivatives[21] or clusters.[22] The Mn(1)−Fe(1) distance in **2** is 2.4512(5) Å, which is shorter than the other known unsupported Mn−Fe bonds (2.601−2.843 Å).[21,22] Similar to **1**, the C(1)−Mn(1)−Fe(1) angle in **2** (166.82(6)°) distorts from linearity and is comparable to the corresponding angles in $Mn(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (166.41(13), 173.00(13)°),[18] $Mn(NMesBMes_2)_2$ (160.4(2)°),[23] and $Mn\{N(SiMePh_2)_2\}_2$ (170.7(1)°).[24] The Mn(1)−C(1) distance (2.081(2) Å) is comparable to those in (μ-η^6:η^6-C_7H_8){Mn(Ar*-3,5-$^iPr_2$)}$_2$ (2.088(3) and 2.089(3) Å)[9] and $Mn(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (2.095(3) Å).[18] The secondary metal−carbon distance is longer (Mn(1)−C(7) 2.788(3) Å) than that in **1**, and there is a lower degree of distortion from the trigonal planar geometry at the C(1) atom (Mn(1)−C(1)−C(2) 109.33(15)°, Mn(1)−C(1)−C(6) 131.99(17)°).

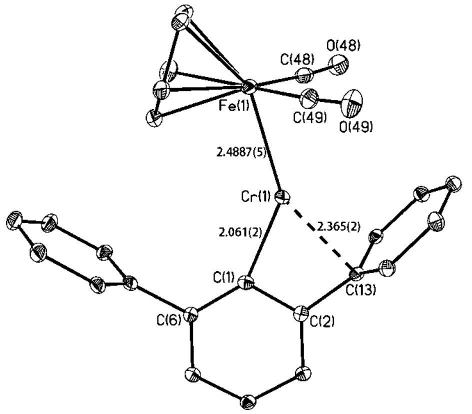

Figure 2. Representation of solid state structure of **3** with selected bond distances (Å) (H atoms and isopropyl groups are not shown for clarity; thermal ellipsoids are shown at 30% probability). Selected bond angles (deg): C(1)−Cr(1)−Fe(1) 141.31(6), Cr(1)−C(1)−C(2) 98.52(14), Cr(1)−C(1)−C(6) 143.22(16), C(2)−C(1)−C(6) 118.25(19).

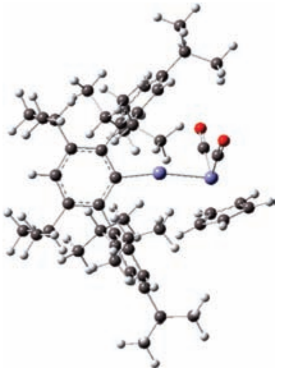

Figure 3. Graphic representation of the optimized structure of **1** (Fe, blue; O, red; C, black; H, white). A comparison of selected calculated and experimental bond distances and angles is given in Table 1.

The corresponding Cr−Fe complex (3,5-$^iPr_2$-Ar*)CrFe(η^5-C_5H_5)(CO)$_2$ (**3**) was isolated in an analogous manner to **1** and **2**. Red crystals of **3** were obtained by the reaction of [(3,5-$^iPr_2$-Ar*)Cr(μ-Cl)]$_2$ with K[(η^5-C_5H_5)Fe(CO)$_2$] followed by recrystallization from hexane (Scheme 1). The solid state structure of **3** (Figure 2), determined by X-ray crystallography, features an unsupported Cr−Fe bond. Binuclear compounds containing Cr−Fe bonds are relatively scarce, and unsupported Cr−Fe bonded species are limited to three carbonyl derivatives.[25] The Cr(1)−Fe(1) distance in **3** (2.4887(5) Å) is much shorter than the observed values in these structures: [PPN]$_2$[FeCr(CO)$_9$] (2.941(2) Å, PPN = bis(triphenylphosphine)iminium),[25a] [PPN][HFeCr(CO)$_9$] (2.956(7) Å),[25a] and (η^5-C_5H_5)$_2$CrFe(CO)$_5$ (2.901(1) Å).[25b] In contrast to the two-coordination of Fe(1) in **1** and of Mn(1) in **2**, the Cr(1) atom in **3** affords a quasi trigonal planar geometry (C(1)−Cr(1)−Fe(1) 141.31(6)°), due to the relatively close interaction between Cr(1) and C(13) (Cr(1)−C(13) 2.365(2) Å). There is a large difference between the two exocyclic bond angles at C(1) (Cr(1)−C(1)−C(2) 98.52(14)°, Cr(1)−C(1)−C(6) 143.22(16)°). The Cr(1)−C(1) distance (2.061(2) Å) is slightly shorter than those in the Cr(I) species [(3,5-$^iPr_2$-Ar*)Cr(L)] (L = THF, 2.087(3) Å; L = PMe_3, 2.116(2) Å)[20] and Ar′CrCrAr′ (2.131(1) Å),[26] but is similar to that in the Cr(II) derivative [Ar′Cr(μ-Cl)]$_2$ (2.041(3) Å).[27] The room temperature μ_{eff} of **3** was determined to be 4.3 μ_B by the Evans′ method, which is consistent with high-spin d^4 Cr(II). The electronic spectrum of **3** features an absorption at 504 nm (470 mol^{-1} L cm^{-1}), which is similar to that of **1** (504 nm, 460 mol^{-1} L cm^{-1}). In contrast, **2** displays a weak shoulder absorption at 446 nm. In addition, all three compounds display a much higher CO stretching frequency (1958, 1902 (**1**); 1962, 1891 (**2**); 1933, 1879 (**3**) cm^{-1}) in comparison to the ionic salt [$^nBu_4N$][(η^5-C_5H_5)Fe(CO)$_2$] (1865, 1788 cm^{-1}),[28] suggesting a significant degree of electron donation from the [(η^5-C_5H_5)Fe(CO)$_2$] to the [(3,5-$^iPr_2$-Ar*)M] fragment.

To gain further insight into the electronic structures of **1** and **2**, DFT calculations were performed at the spin-unrestricted B3LYP level. The optimized structures of **1** (Figure 3) and **2** (Figure S5) are in excellent agreement with their crystallographic data. As illustrated in Table 1, an Fe−Fe distance of 2.403 Å was calculated for **1**. The calculated Mn−Fe distance of 2.458 Å for **2** is also

Table 1. Calculated and Experimental Bond Distances (Å) and Angles (deg) for **1**

	Experimental	Calculated
Fe(1)−Fe(2)	2.3931(8)	2.403
Fe(1)−C(1)	2.022(4)	2.039
C(1)−Fe(1)−Fe(2)	163.94(12)	166.5
Fe(1)−C(1)−C(2)	107.9(3)	110.3
Fe(1)−C(1)−C(6)	133.6(3)	130.0
C(2)−C(1)−C(6)	118.5(4)	119.7

close to the experimental value of 2.4512(5) Å (Table S4). The natural charges for Fe(1) and Fe(2) in **1** are +1.12 and −1.35, respectively, clearly indicating an intramolecular electron transfer from Fe(1) to Fe(2). A similar effect was observed in **2**, where natural charges for Mn(1) and Fe(1) of +1.18 and −1.34, respectively, were calculated. Calculated natural spin densities of Fe(1) in **1** (3.79) and Mn(1) in **2** (4.87) are consistent with the SQUID magnetic characterization and the +2 oxidation states for the two unsaturated metal centers. The low Wiberg bond order for **1** (0.36) and **2** (0.34) indicates limited covalent interactions between the metals. Investigations of the frontier orbitals (Figures S6 and S7) suggested that a dative bond (HOMO) was formed after the formal electron transfer (one electron from Fe(1) to Fe(2) in **1**; Mn(1) to Fe(1) in **2**). In addition, the UV−vis absorption maxima of **1** and **2** were predicted to be at 561 and 451 nm, respectively, and each absorption is contributed from a mixture of several transitions (Figures S8 and S9).

In summary, the synthesis of binuclear complexes containing the shortest unsupported M−Fe (M = Fe, Mn, Cr) bonds was achieved by a salt metathesis route. Extension of this synthetic route to other metal−metal combinations and investigation of the reactivity of these M−Fe bonds toward small molecules are underway.

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Supporting Information Available: Experimental procedures, computational details, Mössbauer spectra and fitting parameters of **1**, graphical representations of the magnetic data, and crystallographic data of **1**−**3** (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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