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Two-Coordinate Transition-Metal Centers With Metal–Metal Bonds**

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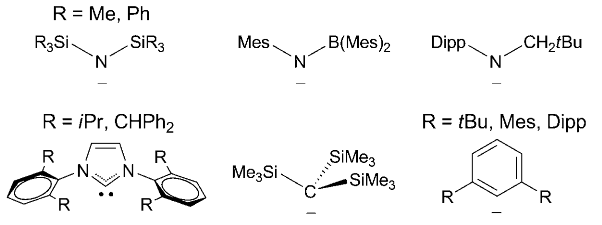
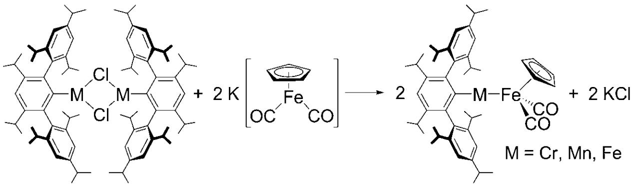
The most common coordination numbers for complexes of transition metals are four, five, and six. However, the use of very bulky supporting ligands can enable the isolation of complexes with low coordination numbers of three and even two.[1,2] Scheme 1 shows some examples of supporting ligands that enforce two-coordination.[2,3] Because of the great steric protection of these supporting ligands, additional ligands and solvent can be prevented from bonding to the metal center. Two-coordinate complexes have been isolated primarily with the 3d transition metals, because of the small size of the metal and consequent ability to more easily block coordination of added donors.[2]



Scheme 1. Bulky supporting ligands that have been used to stabilize two-coordinate complexes of the 3d transition metals. Mes = 2,4,6-$Me_3C_6H_2$, Dipp = 2,6-$iPr_2C_6H_3$.

A recent contribution from Power et al.[4] stands out by demonstrating novel two-coordinate complexes in which part of the steric protection comes not from an organic supporting ligand like those in Scheme 1 but instead from a second metal fragment that forms a metal–metal bond. Complexes of this type that have metal–metal bonds between metals of different character have been termed "xenophilic".[5] Such "stranger-loving" complexes combine the properties of two different metal types, thus providing opportunities for new understanding of bonding and interesting combinations of reactivity modes.

The new xenophilic complexes of the Power group come from the addition of K[CpFe(CO)$_2$] (where Cp = C_5H_5) to three-coordinate dimers [{(aryl)M(μ-Cl)}$_2$] (where aryl = 2,6-(2,4,6-$iPr_3C_6H_2$)$_2$-3,5-$iPr_2C_6H_3$ and M = Cr, Mn, or Fe), as shown in Scheme 2. Elimination of KCl gives the metal–metal-bonded complexes [(aryl)MFe(CO)$_2$Cp]. A representation of the structure of the complex with M = Fe is shown in Figure 1. The illustration shows that the *ortho* substituents of the aryl rings surround the two-coordinate metal center, thus blocking the formation of any third bond to Fe(1). The bulky substituents also hold the metals in near-linear geometries, with angles of 163.9(1)° and 166.82(6)° at Fe and Mn, respectively.



Scheme 2. Synthesis of metal complexes with two-coordinate metals stabilized by metal–metal dative bonds.

The metal–metal distances in the complexes are very short: 2.3931(8) Å for Fe–Fe, 2.4512(5) Å for Fe–Mn, and 2.4887(5) Å for Fe–Cr. The shortness of the bonds may be a

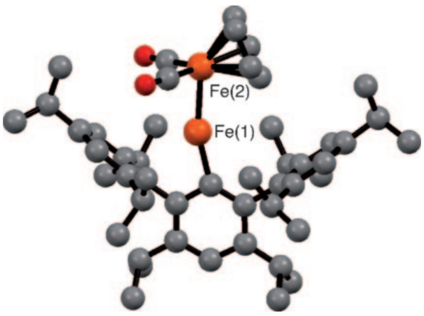


Figure 1. Ball-and-stick view of the crystal structure of [(aryl)Fe-Fe(CO)$_2$Cp]. Fe orange, O red, C gray.

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result of the low coordination number at M, which is two in the Fe–Fe and Fe–Mn complexes. These complexes are the first crystallographically characterized examples that present a two-coordinate transition-metal center with a metal–metal bond. (Here, I define "transition metal" as a metal with a partially filled valence d shell; there are many examples of two-coordinate metals with a d^{10} configuration that engage in metal–metal bonding.) In the new Fe–Cr complex, the chromium atom is three-coordinate instead, by virtue of a short Cr–C(arene) distance of 2.365(2) Å; such weak secondary interactions have been detected previously in low-coordinate complexes of related aryl ligands.[2]

One interesting feature of the bimetallic core in the new compounds is that the two metal centers have different spin states. Magnetic measurements show that in each compound, the low-coordinate metal is paramagnetic and high-spin, while the $\{CpFe(CO)_2\}$ fragment is always diamagnetic with a low-spin electronic configuration at iron. The difference is presumably tied to the coordination of the metal atoms. The small number of bonds to the low-coordinate metal ions gives relatively unperturbed ligand fields that lead to the high-spin configuration, whereas the strong π-backbonding ability of the CO ligands gives larger ligand-field splitting and a low-spin configuration at the higher-coordinate iron atoms. Similar juxtaposition of different spin states has been observed in other xenophilic complexes that contain metal carbonyl fragments.[5]

For the new complexes, the difference in properties between the high-spin and low-spin metal centers was evaluated using both spectroscopy and computations. Mössbauer spectroscopy of the iron–iron complex shows that the environment of the carbonyl-bound iron atom is similar to that in free $[CpFe(CO)_2]^-$. The stretching frequencies of the CO bonds in all three complexes are higher in the bimetallic complexes than in free $[CpFe(CO)_2]^-$, suggesting that some of the electron density is donated from $[CpFe(CO)_2]^-$ into the other metal center. Further, density functional computations show significant differences in charge between the two iron atoms in $[(aryl)FeFe(CO)_2Cp]$, with $+1.12\,e^-$ on Fe(1) and $-1.35\,e^-$ on Fe(2). These combined experimental and computational results indicate that the best description of the metal–metal bond is a dative interaction in which the $\{CpFe(CO)_2\}^-$ fragment shares an iron-based lone pair with the $\{(aryl)Fe\}^+$ fragment. Thus, this diiron species is clearly demonstrated to be a mixed-valence iron(0)–iron(II) complex.

Thus, an approach combining spectroscopy, magnetism, crystallography, and theory has been used to define the characteristics of a new kind of xenophilic complex, in which one of the component metal centers is two-coordinate. The low coordination number at one of the metal centers suggests that this metal may engage in further reactivity; indeed two- and three-coordinate complexes have special facility for activation and transformation of small molecules.[1,6] Metal–metal bonds are also reactive, and this combination of features is distinctive and promising with respect to small-molecule reactions.

The presence of a metal–metal bond also opens the possibility of using communication between the metal centers as a way of controlling reactivity at a two-coordinate metal center. For example, $\{CpFe(CO)_2\}$ fragments are known to bind Lewis acids at the oxygen atoms, with evidence of this interaction coming from both reactivity and structural studies.[7] Thus, it might be possible to influence the electrophilicity of the two-coordinate metal center through Lewis acid binding to the diamagnetic metal center, through a relay effect transmitted by the metal–metal bond. Because of the extensive knowledge about dative metal–metal bonds,[8] other creative ideas are limited only by the imagination of the chemistry community.

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