Insertion Reactions of Isocyanides and Nitriles into Unsupported Iron–Aryl Bonds: The Synthesis of a Dimeric Iron(II) Homoleptic Iminoacyl Complex

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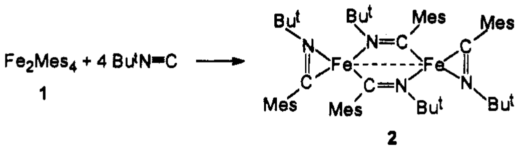
Summary: The reaction of the dimer Fe_2Mes_4 [Mes = 2,4,6-$Me_3C_6H_2$] (1) with Bu^tNC led to $[Fe_2\{(\eta^2\text{-}C(Mes)\text{-}NBu^t)\}_2(\mu\text{-}C(Mes){=}NBu^t)_2]$ (2), a thermally stable homoleptic dimeric iminoacyl derivative containing both a terminal and a bridging iminoacyl functionality. 2 has a very short Fe—Fe distance [2.366(2) Å] and a low magnetic moment [3.40 μ_B per iron at 250 K]. A 2-fold insertion was observed in the reaction of 1 with PhCN to give dimer 3, $[\{(PhCN)(Mes)Fe\}_2\{\mu\text{-}N{=}CPhMes\}_2]$, in which the iron atoms are bridged at a distance of 2.860(2) Å from each other by two imino anions. Complex 3 has a magnetic moment of 2.82 μ_B at 250 K, suggesting a strong magnetic coupling between the two iron atoms.

The iron–carbon σ bond is among the most widely used organometallic functionalities in both stoichiometric and catalytic processes.[1] The variety of Fe–C bond containing derivatives employed derives both from the variety of ancillary ligands used and from the different functionalities on the alkyl or aryl group (we note, for example, the important role played by the iron–acyl fragment and its derivatives[2]). Homoleptic alkyl and aryl derivatives of iron, functionalized or not, are rare, normally poorly characterized, and thermally unstable.[3] Additionally, their chemistry is practically unknown; in this context, iron–mesityl represents a rare example of a usable homoleptic iron(II).

Iron–mesityl was synthesized several years ago[4a] and its structure, $[(Mes)Fe(\mu\text{-}Mes)_2Fe(Mes)]$ [Mes = 2,4,6-$Me_3C_6H_2$], 1, has been very recently elucidated.[4b] Complex 1 offers the unique opportunity to study the organometallic chemistry of the Fe–C bond in the absence of an ancillary ligand. We report here a preliminary account of an extended investigation we are doing on the insertion reactions into the iron–carbon bond. This is one of the major reactions of iron organometallic derivatives in stoichiometric or catalytic transformations.[1,3c] Special care should be taken for the synthesis and storage of 1, which is very air and heat sensitive. We report here a revised, large scale synthesis of 1.[5]

The reaction of 1 with Bu^tNC led to the first homoleptic iminoacyl of iron(II). The reaction is carried out at 0 °C in THF and then at room temperature.[6] Complex 2 was isolated as a black crystalline solid. Its thermal stability both in solution and in the solid state is much higher than that of 1. A large and strong band centered at 1601 cm^{-1} can be assigned to the iminoacyl groups.



(1)

Compound 2 contains η^2-C,N and μ_2-C,N iminoacyls, according to the structure reported in Figure 1A.[7] The structure consists of dimers having a C_2 crystallographic symmetry. The six-membered dimetallic ring has a boat

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[5] Procedure for 1: Freshly prepared crystalline $FeCl_2{\cdot}1.5THF$ (20.70 g, 88.2 mmol) was suspended in a mixture of THF (500 mL) and dioxane (100 mL). The suspension was cooled to −30 °C and then reacted with MesMgBr (1.206 M, 147 mL, 177 mmol) with stirring and occasional shaking. The temperature was raised to room temperature and the suspension stirred for 2 h. The magnesium salts were filtered out and the filtrate evaporated to dryness. The solid was dried under vacuum before dissolving in Et_2O (500 mL). A second filtration was performed to eliminate the last traces of magnesium salts. Evaporating Et_2O to 100 mL yielded a deep orange-red crystalline solid, Fe_2Mes_4 (52%). The yield has not been optimized. Anal. Calcd for $C_{36}H_{44}Fe_2$: C, 73.48; H, 7.54. Found: C, 73.20; H, 7.62. The magnetic moment independent of the temperature is 1.71 μ_B *per* iron in the range 80–250 K. It can be affected by thermal decomposition of 1 and is significantly different from that reported in refs 4a and 4b.

[6] Procedure for 2: A THF (100 mL) solution of Bu^tNC (3.30 mL, 39.4 mmol) was dropwise added to a THF (200 mL) solution of 1 (5.80 g, 19.70 mmol) at 0 °C. The solution was then stirred at room temperature overnight and turned black. It was evaporated to dryness and the residue dissolved in *n*-hexane (200 mL). Partial evaporation of the solvent gave 2 (48.5%) as black crystals. Anal. Calcd for $C_{56}H_{80}N_4Fe_2$: C, 73.03; H, 8.76; N, 6.08. Found: C, 72.40; H, 8.80; N, 6.45. IR: ν(C═N) (Nujol) ws band at 1601 cm^{-1}. μ = 3.27 μ_B at 80 K and 3.40 μ_B at 250 K.

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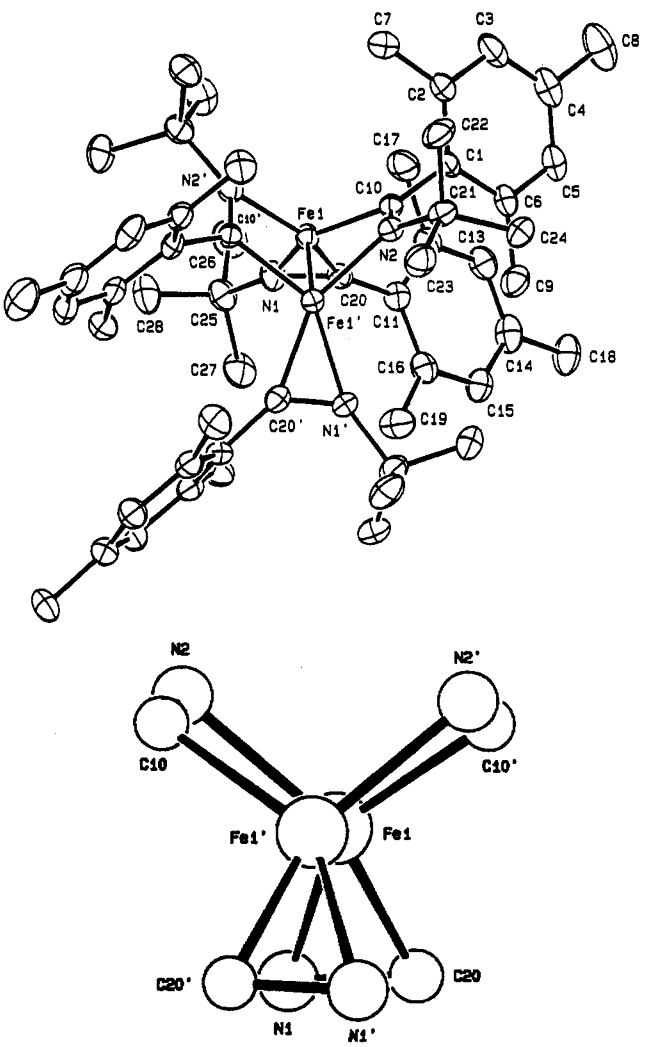
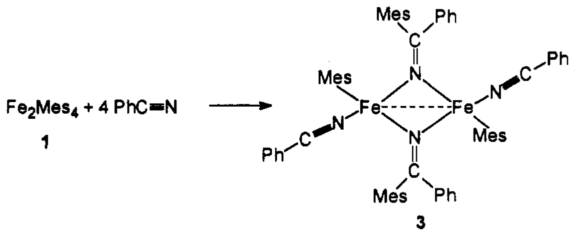


Figure 1. (A, top) ORTEP view of complex 2 (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) are as follows: Fe1–Fe1′ = 2.366(2), Fe1–N1 = 2.001(6), Fe1–N2′ = 1.980(4), Fe1–C10 = 1.958(6), Fe1–C20 = 1.917(7), N1–C20 = 1.262(7), N2–C10 = 1.295(10), C1–C10 = 1.504(9), C11–C20 = 1.478(9); C10–Fe1–C20 = 107.9(3), N1–Fe1–N2′ = 113.6(2), N2′–Fe1–C10 = 99.4(2), N1–Fe1–C20 = 37.5(3), Fe1′–N2–C21 = 133.0(4), Fe1′–N2–C10 = 97.6(4), C10–N2–C21 = 128.7(5), Fe1–C10–N2 = 113.0(5), Fe1–C10–C1 = 119.1(4), C1–C10–N2, 127.9(6). Primes denote a transformation of $0.5-x, y, 1.5-z$. (B, bottom) Coordination sphere of the dimetallic unit in complex 2.

conformation (Figure 1B), and the dihedral angle between the Fe1,C10,N2,Fe1′ and Fe1,C10′,N2′,Fe1′ mean planes is 102.9(1)°. The structural parameters are only slightly different for the η^2- and the μ_2-iminoacyl moieties. The distortion from the regular sp^2 geometry around C10 and N2, and in particular the narrowing of the Fe1–C10–N2 [113.0(5)°] and Fe1′–N2–C10 [97.6(4)°] bond angles, are consistent with a possible metal–metal interaction.[8]

The formation of iron iminoacyl either from migratory insertion of an alkyl into an isocyanide[9] or from other reactions[10] is well-known. The resulting iminoacyl is commonly η^2-bonded to a single metal center,[9,10] while some rare examples are known in which the iminoacyl acts as a μ_2-C,N bridging ligand.[10d] The homoleptic iminoacyl 2 maintains a reactive metal–carbon bond, which we are currently exploring. Homoleptic organometallic derivatives containing α-functional groups are rare for the middle and late transition metals. By contrast, this is not the case for early transition metals.[11,12]

The reaction of 1 with benzonitrile not only sheds light on the possible mechanism of insertion reactions with 1 but also suggests how a mixed ligand insertion derived complex can be obtained when the appropriate sequence of inserting substrates is used.



(2)

The nature of complex 3 suggests that (i) the migratory insertion of the mesityl to the substrate is preceded by the precoordination of the substrate with the iron changing from three- to four-coordinate; (ii) the bridging mesityl group migrates first, while the less reactive terminal mesityl then migrates to the isonitrile in reaction 1, but does not migrate to the less reactive coordinated benzonitrile in reaction 2.

Reaction 2[13] was carried out in toluene at −30 °C, and then the temperature was raised to room temperature. The violet solid was recrystallized from benzene. Regardless of the reaction conditions and the stoichiometry, a single insertion of two benzonitriles was observed, leading to two briding diaryl imino groups ($\nu_{C=N}$, 1602–1613 cm^{-1}), while two other benzonitriles ($\nu_{C\equiv N}$, 2229 cm^{-1}) are coordinated, one to each iron. The ORTEP diagram of

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(7) Structure of 2: $C_{56}H_{80}Fe_2N_4 \cdot C_6H_{14}$, M_r = 1007.2, monoclinic, space group $P2/n$, a = 15.821(6) Å, b = 10.832(8) Å, c = 18.069(5) Å, β = 108.56(3)°, V = 2.936(3) Å^3, Z = 2, ρ_{calcd} = 1.139 g cm^{-3}; λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) 5.31 cm^{-1}; crystal dimensions 0.26 × 0.31 × 0.44 mm. The structure was solved by the heavy atom method and anisotropically refined by full-matrix least squares for all non-H atoms except for the hexane solvent carbon atoms. The C30 carbon atom of hexane was found to be statistically distributed over two positions (A, B) and isotropically refined with site occupancy factors of 0.6 and 0.4, respectively. All but those associated with the hexane solvent hydrogen atoms were found in a difference map and introduced into the final refinement as fixed contributors (U_{iso} = 0.08 Å^2). For 2339 unique observed reflections [$I > 2\sigma(I)$] collected at room temperature ($5 < 2\theta < 50°$) and corrected for absorption, the final R value was 0.056 (R_w = 0.062).

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(13) Procedure for 3: A toluene (100 mL) solution of benzonitrile (2.70 g, 26.70 mmol) was dropwise added to a toluene (150 mL) solution of 1 (3.90 g, 13.30 mmol) at −30 °C. The solution was stirred at room temperature overnight and turned violet and was then concentrated to 100 mL. A violet crystalline solid was obtained (54.6%), which was recrystallized from benzene. Anal. Calcd for $C_{64}H_{64}N_4Fe_2$: C, 76.80; H, 6.44; N, 5.60. Found: C, 76.83; H, 6.81; N, 5.82. IR: ν(C=N) (Nujol) 1602–1613 cm^{-1}; ν(C≡N) (Nujol) 2229 cm^{-1}. μ = 1.42 μ_B at 80 K and 2.82 μ_B at 250 K.

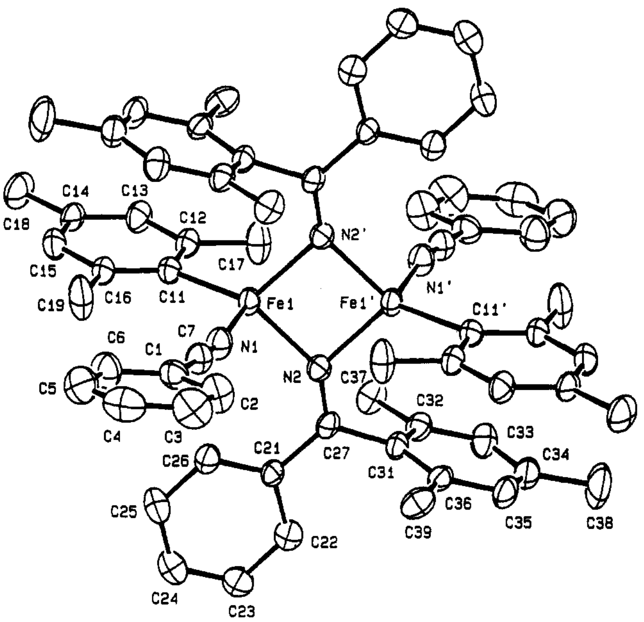

Figure 2. ORTEP view of complex 3 (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) are as follows: Fe1–Fe1′ = 2.860(2), Fe1–N1 = 2.090(5), Fe1–N2 = 2.014(5), Fe1–N2′ = 2.043(5), Fe1–C11 = 2.119(5), N1–C7 = 1.142(9), N2–C27 = 1.288(7), C27–C31 = 1.524(8), C27–C21 = 1.493(7); N1–Fe1–N2 = 101.8(2), N1–Fe1–N2′ = 101.5(2), N1–Fe1–C11 = 114.1(2), N2–Fe1–N2′ = 90.4(2), N2–Fe1–C11 = 122.4(2), N2′–Fe1–C11 = 122.1(2), Fe1–N1–C7 = 171.0(6), Fe1–N2–Fe1′ = 89.6(2), Fe1′–N2–C27 = 126.6(5), Fe1–N2–C27 = 143.6(5), N2–C27–C21 = 123.8(5), N2–C27–C31 = 120.1(5), C21–C27–C31 = 116.1(5). Primes denote a transformation of $-x$, $-y$, $-z$.

3 is shown in Figure 2, with a selection of structural parameters.[14] The dimer has a center of gravity on a crystallographic center of symmetry at (0,0,0). The two irons are bonded to the terminal ligands Mes and PhCN in a normal fashion and they are bridged by a diaryl imino group. The Fe_2N_2 skeleton has a perfectly planar geometry, in a kind of aza—iron—cyclobutadiene structure. The dihedral angle between this plane and the plane containing the other two donor atoms around iron [Fe1,N2,Fe1′,N2′∠Fe1,C11,N1] is 90.1(2)°. The Fe1—C11 bond distance [2.119(5) Å] is significantly longer than that in 1 [2.023(5) Å][4b] and very close to that which we observed in the tricoordinate iron metalate $[Fe(Mes)_3]^-$ [2.117(6) Å].[15] The Fe⋯Fe distance [2.860(2) Å] in 3 is much longer than that in complex 2, even though the two iron(II) atoms are bridged by a single donor atom. The iron—iron distances in complexes 2 and 3 fall respectively in the upper and lower range of a large variety of dinuclear iron complexes.[8]

The magnetic properties of 2 and 3 deserve special comment. In both cases the Fe⋯Fe distance and the nature of the bridging ligand facilitate a significant magnetic coupling between the two iron(II) atoms: complex 2 has a μ of 3.27 μ_B at 80 K and 3.40 μ_B at 250 K, while complex 3 has a μ of 1.42 μ_B at 80 K and 2.82 μ_B at 250 K. We should emphasize that the degree of magnetic coupling is inversely related to the Fe⋯Fe distance. This supports the idea that the bridging ligand is probably a major factor in the coupling between the two d^5 centers.

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Supplementary Material Available: Tables of crystal data (SI), atomic coordinates (SII-SV), thermal parameters (SVI, SVII), and bond distances and angles (SVIII, SIX) for complexes 2 and 3 (11 pages). Ordering information is given on any current masthead page.

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(14) Structure of 3: $C_{64}H_{64}Fe_2N_4{\cdot}2C_6H_6$, M_r = 1157.2, triclinic, space group $P\bar{1}$, a = 12.680(3) Å, b = 13.510(3) Å, c = 10.870(5) Å, α = 107.63(2)°, β = 104.30(3)°, γ = 67.00(2)°, V = 1615.9(10) Å^3, Z = 1, ρ_{calcd} = 1.189 g cm^{-3}; λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 4.91 cm^{-1}; crystal dimensions 0.18 × 0.22 × 0.35 mm. The structure was solved as for 1. The refinement was carried out anisotropically for all non-H atoms. The hydrogen atoms were located by difference methods and introduced into the final refinement as fixed contributors (U_{iso} = 0.08 Å^2). For 2805 unique observed reflections [$I > 2\sigma(I)$] collected at room temperature ($5 < 2\theta < 50°$) and corrected for absorption, the final R value was 0.059 (R_w = 0.063). During the refinement, all the aromatic rings were constrained to be regular hexagons (C–C, 1.395 Å). All calculations were carried out with the use of SHELX-76.

(15) Unpublished results.