Meridional bicyclometalation with iron: a novel way of forming dianionic [C,N,C]-ligands†

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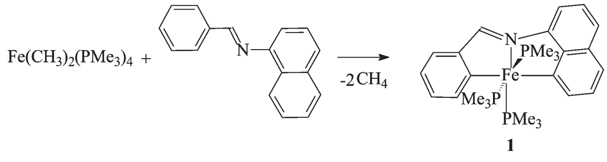
Bicyclometalation of aromatic substrates containing imine anchoring groups is achieved with a dimethyliron complex at −70 °C; azadiene systems undergo a regiospecific activation of 1,4-CH/N interchanged C–H bonds which may be aromatic or vinylic.

The intramolecular C–H activation initiating a cyclometalation reaction is an important and intensely studied elementary step in homogeneous catalysis. One of the primary aims of chemical syntheses is to achieve a selective functionalisation of hydrocarbons through metalation. Using 2-substituted triphenylphosphines as anchoring groups we had been able to obtain stable cobaltacycles and demonstrate a steric control of the regiospecific cyclometalation.[1] Syntheses with catalytic amounts of ruthenium or rhodium, preferentially using an N donor as anchoring group in a substrate molecule, when followed by coordination of a suitable co-substrate and elimination of the metal, have become an indispensable method of C,C coupling in organic chemistry.[2] Surprisingly, exploring the coordination chemistry of the postulated [N,C]-cyclometalated intermediates has remained a great challenge to date.[3] Among the catalytically active compounds those of first row transition elements are lacking so far. Using complexes of low-valent iron we have conducted cyclometalation reactions that mimic the first steps in the proposed catalytic cycle.[2,4]

Upon combining a dimethyliron compound with certain diarylated Schiff bases we have recently observed a reaction sequence consisting of a double metalation at the same complex center and, for the first time, leading to a metallabicycle.[5] Thus *N*-benzylidene-1-naphthylamine when reacted with mole equivalent amounts of dimethyltetrakis(trimethylphosphine)iron at −70 °C afforded the diaryliron compound **1** [eqn. (1)] which was isolated from pentane in 72% yield.



1

(1)

Compound **1** was characterized by elemental analysis, IR ($\nu_{C=N}$ = 1509) and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. The *H*CN proton resonance appears at δ 9.36 (s), and two anisochronic trimethylphosphine signals are present both in the ^1H and ^{31}P NMR spectra.

The green crystals of **1** are stable under argon up to 120 °C, and in air their surface remains unaltered for about 10 min. In the spectra of THF solutions as well as in the crystal, mononuclear complex molecules are detected, showing an octahedrally surrounded iron(II) center in meridional configuration (Fig. 1). The data indicate the absence of isomers or polynuclear compounds as by-products.

The molecular structure of **1**‡ shows a slightly distorted octahedron centered by an iron atom that bears three meridional P donor groups. The three remaining ligand positions are occupied by C and N atoms of the metallacycle. The Fe atom deviates from the P_3 and from the C(1)N(1)C(17) planes by 0.135(1) and 0.005(1) Å, respectively. The normals of these planes point at an angle 89.6(1)°. In particular, the sums of internal angles for both five-membered metallacycles (540.0(5) and 540.0(5)°) approach the ideal value for a planar five-membered ring. This optimum fit consisting of typical bite angles (N1–Fe1–C1 81.21(6) and N1–Fe1–C17 80.47(6)) leads one to conclude, that in the formation of **1** the subsequent metalation steps are initiated by two equally suitable proximity conformations, where at the target point of metalation electron density is transferred from the metal into antibonding σ*(C–H) molecular orbitals.

However, as the reaction sequence is controlled by two consecutive chelating steps rather than by the balance of C,H/metal bond energies, the order of donors [C,N,C] in the frame of atoms of the substrate molecule should equally suit as [N,C,C]

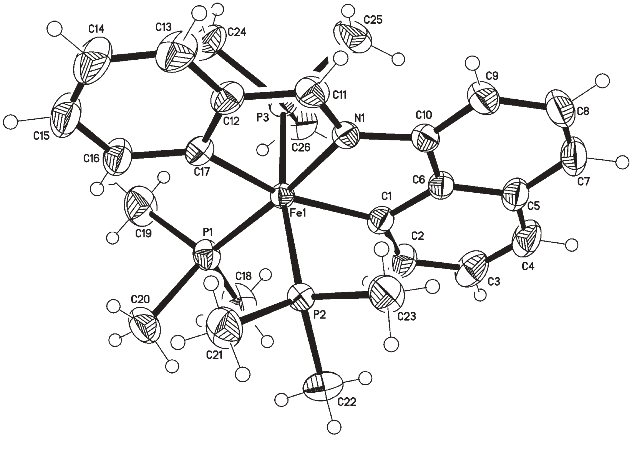


Fig. 1 Molecular structure of **1**: selected bond lengths (Å) and angles (°): Fe1–C1 2.0290(14), Fe1–C17 2.0045(14), Fe1–N1 1.9634(12), Fe1–P1 2.2247(4), Fe1–P2 2.2373(4), Fe1–P3 2.2393(4), N1–C10 1.4098(18), N1–C11 1.303(2); N1–Fe1–C1 81.21(6), N1–Fe1–C17 80.47(6), C1–Fe1–C17 161.68(6), C10–N1–C11 124.19(13), N1–Fe1–P1 174.31(4), P2–Fe1–P3 171.245(16).

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† Electronic supplementary information (ESI) available: Synthesis of **1** and **2** and ^1H, ^{13}C and ^{31}P NMR data. See http://www.rsc.org/suppdata/cc/b4/b413409e/

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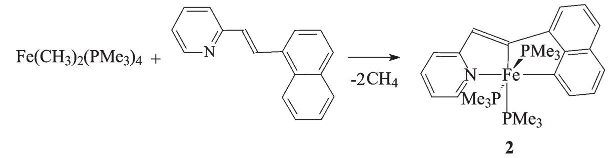
without loss of reactivity according to the principle of 1,4-CH/N-exchanged azadienes.[4]

Indeed, (1-naphthyl)(2-pyridyl)ethene, as a structural isomer of *N*-benzylidene-1-naphthylamine, was smoothly bicyclometalated with iron [eqn. (2)].



(2)

The arylvinyliron compound **2** was obtained in 84% yield and isolated as wine-red sticks (from ether), which are stable under argon up to 122 °C. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows a well resolved doublet of triplets for the metalated carbon coupled to a singular and two equivalent phosphorus nuclei (δ 190.9, $^2J_{P,C}$ = 33.4, 4.5 Hz). The metalated vinylic carbon resonates at δ 242.8 (t, $^2J_{P,C}$ = 28.4 Hz).

An X-ray diffraction analysis‡ was performed on single crystals obtained by cooling ether solutions of **2** to −27 °C. Fig. 2 shows the molecular structure of **2**. In solution **2**, like **1**, shows a meridional octahedral configuration, and in the crystal in spite of different packing, attains a molecular structure which closely corresponds with that of **1** (Fig. 1). In the metallacarbocycle of **2** the internal angle at iron is by 3° larger than in the neighbouring [N,C]-chelate ring. However, the sums of both bite-angles in **1** and **2** are equal (161.8(1)°). Solely the singular trimethylphosphine ligand is subject to the larger *trans* influence of the bridgehead-C anion in **2** as expected showing an increased bond length Fe–P1 by 0.093 Å with respect to **1**.

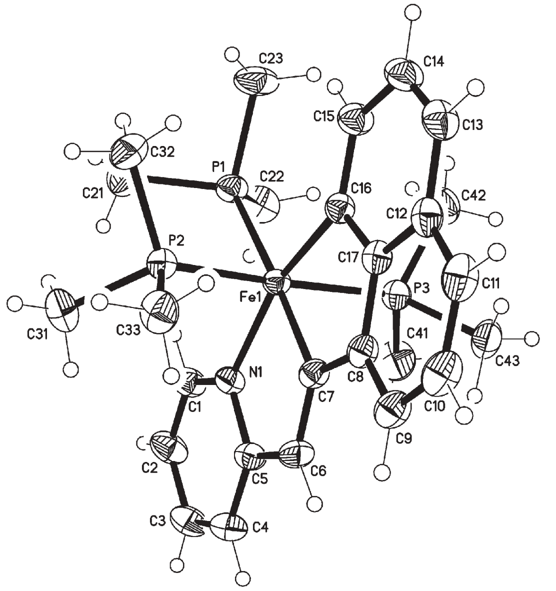


Fig. 2 Molecular structure of **2**: selected bond lengths (Å) and angles (°): Fe1–C16 2.0113(16), Fe1–N1 2.0482(14), Fe1–C7 1.9249(16), Fe1–P1 2.3182(5), Fe1–P2 2.2293(6), Fe1–P3 2.2280(6), C7–C8 1.465(2), C6–C7 1.354(2); C7–Fe1–C16 82.48(7), C7–Fe1–N1 79.44(6), C16–Fe1–N1 161.91(6), C6–C7–C8 124.85(15), C7–Fe1–P1 174.88(5), P2–Fe1–P3 170.14(2).

The crystal structures of **1** and **2** are consistent with the spectroscopic and analytical characterization. The $^{31}P\{^1H\}$ NMR spectra of both bicyclometalated complexes show doublets (**1**; δ 16.8 $^2J_{P,P}$ = 61.2 Hz), (**2**; δ 16.4 $^2J_{P,P}$ = 34.8 Hz) for the two *trans* phosphines and triplets (**1**; δ 22.9 $^2J_{P,P}$ = 61.2 Hz), (**2**; δ − 2.4 $^2J_{P,P}$ = 34.8 Hz) for the singular phosphine. Obviously there is a substantial shift of the latter phosphine ($\Delta\delta$ = 25.3 ppm) when compared with **1** which results from the stronger *trans* influence of carbon. The ^1H, ^{31}P and ^{13}C NMR data are consistent with a meridional arrangement of the aromatic backbone in a σ(C,N,C) or σ(N,C,C) bonding mode. Elemental analyses of **1** and **2** were consistent with crystal structures.

Instead of an orthometalation of the phenyl substituent [eqn. (1)] the reaction cascade for the first time implies a vinyl-metalation at iron [eqn. (2)], which for 2-vinylpyridine has been observed with palladium and platinum[6] and was recently reported by us with cobalt.[4] The second metallacycle in **2** is formed spontaneously with carbon as planar (sp^2)-bridgehead atom just as with nitrogen. This result clearly points to a steric control of the bicyclometalation reaction.

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Notes and references

‡ *Crystal data*: for **1**: $C_{26}H_{38}FeNP_3$, M = 513.3; a = 9.6040(4), b = 10.3792(5), c = 14.1341(6) Å, α = 76.523(1), β = 81.368(1), γ = 75.938(1)°, V = 1322.52(10) Å^3, triclinic, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 0.766 mm^{-1}, T = 298 K, 13779 reflections measured, 6537 unique (R_{int} = 0. 017), final $R1$ ($I > 2\sigma$) = 0.0317, $wR2$ ($I > 2\sigma$) = 0.0839, GOF (on F^2) = 1.034. For **2**: $C_{26}H_{38}FeNP_3$: M = 513.3, a = 15.1229(17), b = 17.561(2), c = 19.738(2) Å, V = 5241.8(10) Å^3, orthorhombic, space group *Pbca*, Z = 8, μ(Mo-Kα) = 0.773 mm^{-1}, T = 298 K, 53823 reflections measured, 6488 unique (R_{int} = 0.0494), final $R1$ ($I > 2\sigma$) = 0.0334, $wR2$ ($I > 2\sigma$) = 0.0852. GOF (on F^2) = 1.011. CCDC 243313 and 243315. See http://www.rsc.org/suppdata/cc/b4/b413409e/ for crystallographic data in .cif or other electronic format.

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