

Ligand properties of 1*H*-diphosphirenes and diphosphirenylium salts towards iron carbonyl fragments

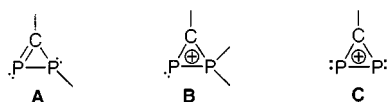
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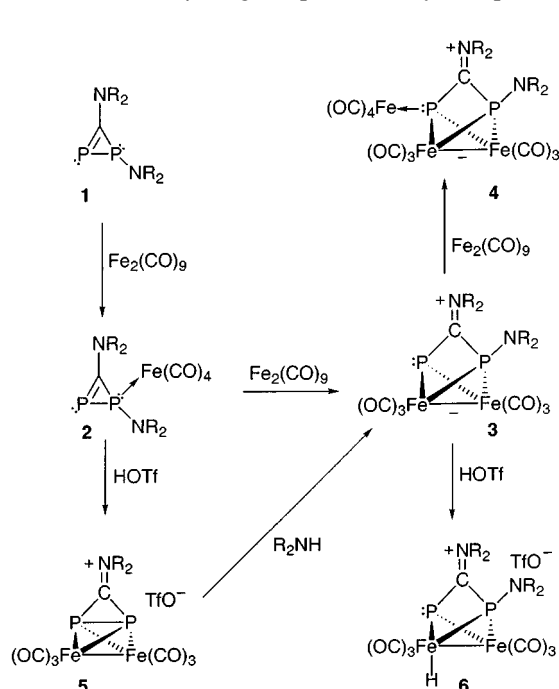
Treatment of η^1 -[1,3-bis(diisopropylamino)-1*H*-diphosphirene]tetracarbonyl iron **2** with trifluoromethanesulfonic acid affords the binuclear [3-diisopropylaminodiphosphirenylium salt] iron complex **5**, which reacts with diisopropylamine giving the opened binuclear iron complex **3**.

The chemistry of phosphorus-containing three-membered rings has attracted considerable attention over the last 15 years.¹ In the diphosphorus-containing series,² the 1*H*-diphosphirenes **A**³ and diphosphirenylium salts **B**⁴ were discovered in the early 1990s. More recently, we have described the synthesis and reactivity of P-functionalized 1*H*-diphosphirenes **A** and diphosphirenylium salts **C** (Scheme 1) as tungsten carbonyl complexes.⁵ Here, we report the ligand behavior of heterocycles **A** and **C** towards iron carbonyl fragments, including the unprecedented cleavage of the P–P bond of the ring framework.



Scheme 1 1*H*-diphosphirene **A**, diphosphirenylium cation **B** and diphosphirenylium cation **C**.

The η^1 -iron tetracarbonyl complex **2** was readily obtained in 85% yield by treatment of **1** with 1 equiv. of $\text{Fe}_2(\text{CO})_9$ (Scheme 2). The end-on coordination of the σ^3 -P was unequivocally established by comparing the spectroscopic data for **2**[†] with those of the related η^1 -tungsten pentacarbonyl complexes.^{5,6}



Scheme 2 R = Prⁱ, Tf = CF₃SO₂.

Addition of 1 equiv. of $\text{Fe}_2(\text{CO})_9$ to **2** afforded the binuclear complex **3**, which was isolated in 42% yield as red crystals. The low-field AB system (δ 125.5 and 122.4, J_{PP} 85 Hz) observed in the ³¹P NMR spectrum for **3** strongly suggests that the three-membered ring has been opened, although the value of the J_{PP} coupling constant remains large. The cleavage of the P–P bond was confirmed by an X-ray diffraction study[‡] (Fig. 1), the P...P distance (P1–P2 2.62 Å) being much longer than that of a classical P–P single bond (2.20–2.35 Å).⁷ The structure of **3** consists of a 1,3-diphosphorus chain bridging a metal–metal bonded $\text{Fe}_2(\text{CO})_6$ unit (Fe1–Fe2 2.61 Å), both phosphorus atoms being bonded to both iron atoms (P1–Fe1 2.21 Å, P1–Fe2 2.22 Å, P2–Fe1 2.29 Å, P2–Fe2 2.33 Å).⁸ The N2P1C1N1P2 skeleton is perfectly planar (maximum deviation from the best plane: 0.036 Å), and the C1–N1 bond length [1.298(9) Å] is in the range expected for a CN double bond, implying that the positive charge has shifted to the nitrogen atom. P1 can be regarded as a typical phosphido phosphorus atom, while P2 is a three-coordinate phosphorus atom with a strongly pyramidal geometry (sum of the angles: 243.3°) suggesting its potential for coordination of an additional transition-metal fragment. Indeed, when **3** was treated with an excess of $\text{Fe}_2(\text{CO})_9$ in THF solution, after two days at room temperature, the trinuclear complex **4** was isolated as red crystals in 70% yield (Scheme 2). The spectroscopic data observed for **4** are very similar to those of **3**,[†] and the structure of **4** has been confirmed by an X-ray diffraction study.[‡] The introduction of the $\text{Fe}(\text{CO})_4$ fragment on P2 does not result in dramatic geometric modifications. In

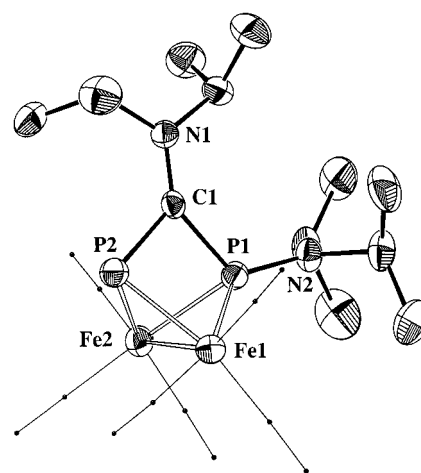


Fig. 1 Thermal ellipsoid diagram (30% probability) of **3** showing the atom numbering scheme. All the carbonyl groups have been omitted, and the isopropyl groups have been simplified. Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.298(9), C(1)–P(1) 1.811(7), C(1)–P(2) 1.841(7), P(1)–N(2) 1.671(7), P(1)–Fe(1) 2.206(2), P(1)–Fe(2) 2.222(2), P(2)–Fe(1) 2.294(3), P(2)–Fe(2) 2.329(3), Fe(1)–Fe(2) 2.613(2); N(1)–C(1)–P(1) 137.9(6), N(1)–C(1)–P(2) 130.4(5), P(1)–C(1)–P(2) 91.4(3), C(1)–P(1)–N(2) 121.1(3), C(1)–P(1)–Fe(1) 94.1(3), C(1)–P(1)–Fe(2) 87.9(2), N(2)–P(1)–Fe(1) 134.3(2), N(2)–P(1)–Fe(2) 131.3(3), Fe(1)–P(1)–Fe(2) 72.31(8), C(1)–P(2)–Fe(1) 90.5(2), C(1)–P(2)–Fe(2) 84.0(2), Fe(1)–P(2)–Fe(2) 68.81(1).

particular, the P...P distance is still long (2.58 Å), and the N2P1C1N1P2 fragment remains planar with the supplementary iron centre Fe3 in the same plane (maximum deviation from the best plane: 0.044 Å). Therefore, in contrast to that observed in the coordination sphere of tungsten (end-on coordination *via* both phosphorus lone pairs of **1**),⁵ the binuclear iron complex **3** formally results from the insertion of a Fe₂(CO)₆ fragment into the P–P bond of **1**, which leaves a phosphorus lone pair available for coordination to a third metal fragment.

Surprisingly, treatment of the 1*H*-diphosphirene mono-nuclear complex **2** with 2 equiv. of trifluoromethanesulfonic acid at –78 °C led to the diphosphirenylium binuclear complex **5**§ (Scheme 2). The presence of a Fe₂(CO)₆ fragment in **5** was unambiguously established from the mass spectrum [*m/z* 454 (M⁺) and 426 (M – CO)⁺], while the cationic three-membered ring structure was apparent from the high-field ³¹P NMR (s, δ –139.8) and low-field ¹³C NMR (t, δ 218.2 *J*_{PC} 93.1 Hz) signals. Interestingly, **5** was not formed when the binuclear iron complex **3** was reacted with trifluoromethanesulfonic acid. Instead, protonation of an iron centre occurred leading to the iron carbonyl hydride **6**.†

Although the mechanism of the reaction of **2** with triflic acid remains obscure, it is quite clear that the formation of the binuclear complex **5** involves a metallic disproportionation process. To achieve an 18-electron configuration for each iron atom in **5**, the three-membered ring must act as a six-electron ligand (*via* the P=P bond and the lone pair of both phosphorus atoms). This coordination mode is similar to that observed in [*cis*-P₂Bu²]₂[Fe₂(CO)₆],⁹ but it necessarily implies that in **5** both phosphorus centres have an unusual inverted tetrahedral geometry.¹⁰

Finally, we investigated the reactivity of this new diphosphirenylium salt complex. Using diisopropylamine, the neutral binuclear complex **3** was obtained in quantitative yield. Therefore, nucleophilic attack occurs at the highly electrophilic phosphorus atom as observed for the tungsten complexes,⁵ but simultaneous cleavage of the P–P bond is observed for the iron complex.

Notes and references

† *Selected spectroscopic data for 2–6*: **2**, δ_P(C₆D₆, 32 MHz) –53.0 (d, *J*_{PP} 195 Hz, PNPri₂), 52.6 (d, *J*_{PP} 195 Hz, σ²-P); δ_C(C₆D₆, 100 MHz) 195.4 (dd, *J*_{PC} 83.6, 34.0 Hz, PCP), 214.7 (d, ²*J*_{PC} 23.1 Hz, CO). **3**, mp 160–162 °C; δ_P(C₆D₆, 32 MHz) 122.4 (d, *J*_{PP} 85 Hz, PNPri₂), 125.5 (d, *J*_{PP} 85 Hz, σ³-P); δ_C(C₆D₆, 100 MHz) 214.0 (s, CO), PCP was not observed; CIMS (NH₃) 555 (MH⁺). **4**, mp 176–178 °C; δ_P(C₆D₆, 32 MHz) AB system 145.7 and 151.0 (*J*_{PP} = 29 Hz); δ_C(C₆D₆, 100 MHz) 213.0 (s, CO), 217.1 (d, *J*_{PC} 13.3 Hz, CO), PCP was not observed; CIMS (NH₃) 723 (MH⁺). **5**, δ_P(C₆D₆, 32 MHz) –139.8; δ_H(CDCl₃, 200 MHz) 4.44 (spt, ³*J*_{HH} 6.1 Hz, 2H, CHN); δ_C(CDCl₃, 100 MHz) 61.5 (s, CHN), 119.9 (q, ¹*J*_{CF} 310 Hz, CF₃), 200.1 (m, CO), 218.2 (t, *J*_{PC} 93.1 Hz, PCP). **6**, δ_P(CDCl₃, 32 MHz) 111.5 (m, *J*_{PP} 92, *J*_{PH} = 46.6, 14.3 Hz, PNPri₂), 140.0 (dd, *J*_{PP} 92, *J*_{PH} 8.3 Hz, σ³-P); δ_H(CDCl₃, 200 MHz) –19.0 (dd, *J*_{PH} 46.6, 8.3 Hz, 1H, FeH). Satisfactory elemental analyses have been obtained for compounds **2**, **3** and **4**.

‡ *Crystallography*: data for **3** and **4** were collected at low temperatures using an oil-coated shock-cooled crystal¹¹ on a Stoe-IPDS with Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods using SHELXS-97¹² and refined with all data on *F*² using SHELXL-97.¹³ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of

the molecules were geometrically idealized and refined using a riding model. A numerical absorption correction was employed, min./max. transmissions for **3** are 0.4325/0.5682 and for **4** 0.7035/0.8889. Refinement of an inversion twin parameter¹⁴ [*x* = 0.49(2), where *x* = 0 for the correct absolute structure and +1 for the inverted structure] confirmed a racemic twinning of **3**.

Crystal data: **3**: C₁₉H₂₈Fe₂N₂O₆P₂, *M* = 554.07, monoclinic, space group *P*2₁/*n*, *a* = 9.885(2), *b* = 18.173(3), *c* = 20.3360(5) Å, β = 99.85(2)°, *V* = 2606.9(9) Å³, *Z* = 4, *F*(000) = 1144, *D*_c = 1.412 g cm^{–3}, μ(Mo-Kα) = 1.269 mm^{–1}, 4 < 2θ < 46°, 3493 reflections, 287 parameters, *R*₁ = 0.0693, *wR*₂ = 0.1942.

4: C₂₃H₂₈Fe₃N₂O₁₀P₂, *M* = 721.96, orthorhombic, space group *Pbca*, *a* = 15.7039(4), *b* = 19.5502(4), *c* = 20.3360(5) Å, β = 90°, *V* = 6243.4(3) Å³, *Z* = 8, *F*(000) = 2944, *D*_c = 1.536 g cm^{–3}, μ(Mo-Kα) = 1.529 mm^{–1}, 4 < 2θ < 46°, 4287 reflections, 370 parameters, *R*₁ = 0.0513, *wR*₂ = 0.1233. CCDC 182/1321. See <http://www.rsc.org/suppdata/cc/1999/1535/> for crystallographic files in .cif format.

§ The ³¹P NMR spectrum showed only one singlet corresponding to complex **5**, while the ¹H and ¹³C NMR spectra revealed the presence of diisopropylammonium trifluoromethane sulfonate.

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