Synthesis and crystal structure of a bis(phosphiren-1-yl)–iron complex[1]

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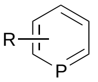
1-Chloro-1*H*-phosphirenes 5 react with disodium tetracarbonylferrate to furnish the novel mono-complexed bis(phosphirenyl)s 7 which, in turn, are converted to the doubly-complexed species 8 by treatment with nonacarbonyldiiron.

Investigations on the synthesis and reactivity of λ^3-phosphinines **1** in the 1960s played a major role in the development of the chemistry of low-coordinated phosphorus.[2,3] Somewhat later, their classical valence isomers such as, for example, λ^3,σ^2-Dewar-benzenes **2**,[4] phosphaprismanes **3**[5] and λ^3,σ^3-benzvalenes **4**[5] were also prepared.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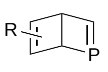
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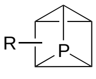
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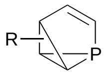
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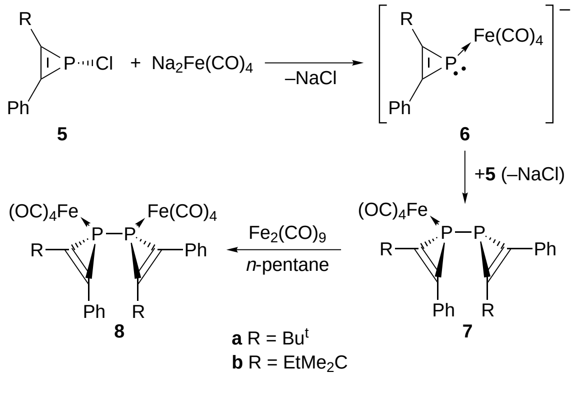
The Dewar-benzene derived from 2,4,6-tri-*tert*-butyl-1,3,5-triphosphinine was recently added to this list.[6] In contrast, very little information about the diphosphinines is available,[7] and the valence isomers derived from them are still unknown. We now report the first synthesis of a complexed bis(phosphirenyl), representing a new type of phosphinine valence isomer.

The starting materials for the syntheses of the bis(phosphirenyl)s **7a**,**b** were the 1-chloro-1*H*-phosphirenes **5a**,**b** (Scheme 1).[8] Reactions of the latter with disodium tetracarbonylferrate (0.5 equiv.) furnished the mono-complexed bis(phosphirenyl)s **7a**,**b** in good yields (60%). The composition and constitution of the products were elucidated with the help of NMR and mass spectroscopy.‡ Because of the presence of centres of chirality at the two phosphorus atoms and their configurational stability, these reactions give rise to two diastereomers which, however, cannot be separated by column chromatography. One of the diastereomers in each case can be enriched up to a ratio of 8:1 (**7a**) or 4 : 1 (**7b**) (as determined from their ^{1}H NMR spectra) by crystallization.

The formation of **7** is reflected in the ^{31}P NMR spectra by a significant $^1J_{P,P}$ coupling constant of 427 Hz. The complexed ring phosphorus atom gives rise to a signal at considerably lower field than that of the uncomplexed ring (δ −88, as compared to −132). Complexation with the tetracarbonyliron fragment is also apparent in the ^{13}C NMR spectra from a drastic reduction in the intracyclic $^1J_{C,P}$ coupling constant of the complexed phosphirene to 22–27 Hz, in comparison to 50–57 Hz for the uncomplexed ring. A similar phenonemon has also been reported for complexation reactions of other 1*H*-phosphirenes.[9c] The signals for the ring carbon atoms of **7a**,**b** occur in the typical region for 1*H*- phosphirenes.[9]



Scheme 1

The initial reductive substitution of the chlorine atom of **5** by the tetracarbonyliron fragment results in the anionic phosphirene complex **6** which participates in an immediate nucleophilic substitution with a second molecule of **5** to afford **7**.

Treatment of the compounds **7a**,**b** with nonacarbonyldiiron results in the formation of the symmetrical, doubly-complexed bis(phosphirenyl)s **8a**,**b** in yields of 63% (**8a**) and 54% (**8b**).§ As a consequence of the high symmetry of compounds **8** their ^{31}P NMR spectra each contain only one singlet signal. Complexation of the additional tetracarbonyliron fragments effects further shifts to lower field [δ −69.3 (**8a**) and −70.5 (**8b**)].

The ^{13}C NMR spectra of **8** do not show any significant changes in chemical shifts due to the additional complex fragments in comparison to those of **7**.

An X-ray crystallographic analysis of the complex **8a** confirmed the proposed structure (Fig. 1).¶ In the crystal the two tetracarbonyliron fragments and, respectively, the two phosphirene rings have *syn* orientations to each other. Because of the extreme steric situation, the two phosphirene rings are somewhat twisted, as reflected in torsional angles of 39.4° [Fe(1)–

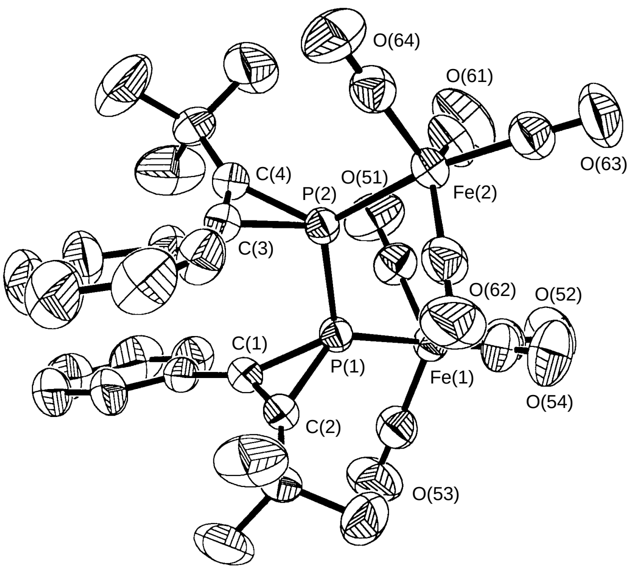


Fig. 1 Crystal structure of **8a**. Selected bond lengths (Å) and angles (°): Fe(1)–P(1) 2.2311(7), Fe(2)–P(2) 2.2185(7), P(1)–P(2) 2.2516(10), P(1)–C(1) 1.793(2), P(1)–C(2) 1.796(2), P(2)–C(3) 1.793(2), P(2)–C(4) 1.797(2), C(1)–C(2) 1.317(3), C(3)–C(4) 1.319(3); C(1)–P(1)–C(2) 43.05(11), C(1)–P(1)–P(2) 108.23(8), C(2)–P(1)–P(2) 108.97(8), C(3)–P(2)–C(4) 43.11(11), C(3)–P(2)–P(1) 108.55(8), C(4)–P(2)–P(1) 109.05(8), C(2)–C(1)–P(1) 68.60(14), C(1)–C(2)–P(1) 68.3(2), C(3)–C(4)–P(2) 68.3(2), C(4)–C(3)–P(2) 68.58(14).

P(1)–P(2)–Fe(2)] and 33.9° [C(1)–P(1)–P(2)–C(4)]. The P(1)–P(2) bond length amounts to 2.2516(10) Å and is thus somewhat lengthened as a result of the spatially demanding substitution pattern. The intracyclic P–C bond lengths of 1.793 to 1.797 Å, as well as the carbon–carbon double bond length of 1.317 Å, are of the expected sizes for a complexed 1*H*-phosphirene.[9c] Similary, the C–P–C bond angles of 43.05(11) and 43.11(11)° are comparable with those of other 1*H*-phosphirenes.[9]

We thank the Landesregierung von Rheinland-Pfalz for a graduate grant (to J. S.) and the Fonds der Chemischen Industrie for generous financial support.

Notes and References

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‡ *Selected data* for **7a** (only values for the major diastereomer are given): mp 97–99 °C; δ_P (81 MHz, $CDCl_3$) −88.1 (d, $^1J_{P,P}$ 427.3, P-1), −134.2 (d, $^1J_{P,P}$ 427.3 P-2); δ_H(200 MHz, $CDCl_3$) 1.44 [br s, 18 H, $C(CH_3)_3$], 7.40–7.51 (m, 6 H, *m/p*-Ph), 7.57–7.65 (m, 4 H, *o*-Ph); δ_C (50 MHz, $CDCl_3$) 29.22 [d, $^3J_{C,P}$ 1.7, $C(\mathit{C}H_3)_3$], 29.53 [s, $C(\mathit{C}H_3)_3$], 33.86 [dd, $^2J_{C,P}$ 6.4, $^3J_{C,P}$ 3.0, $\mathit{C}(CH_3)_3$], 34.24 [d, $^2J_{C,P}$ 6.8, $\mathit{C}(CH_3)_3$], 120.33 (d, $^1J_{C,P}$ 50.8, C-5), 124.80 (dd, $^1J_{C,P}$ 22.0, $^2J_{C,P}$ 4.2, C-3), 127.30 (d, $J_{C,P}$ 7.6, Ph), 128.62 (s, Ph), 128.87 (s, Ph), 129.73 (d, $J_{C,P}$ 5.1, Ph), 130.41 (d, $J_{C,P}$ 4.2, Ph), 131.33 (s, Ph), 138.50 (d, $^1J_{C,P}$ 57.7, C-6), 140.51 (dd, $^1J_{C,P}$ 27.1, $^2J_{C,P}$ 5.1, C-4), 213.94 [d, $^2J_{C,P}$ 19.5, $Fe(CO)_4$]; *m/z* (EI, 70 eV) 546 (8) [M^+], 276 (100) [$M^+ - 4CO - C_{12}H_{14}$] (Calc. for $C_{28}H_{28}FeP_2O_4$: C, 61.56; H, 5.17. Found: C, 60.90; H, 5.07%) (HR-MS: calc. for M^+: 546.0813. Found: 546.0813). For **7b**: δ_P (81 MHz, $CDCl_3$) −90.6 (d, $^1J_{P,P}$ 427.6, P-1), −132.2 (d, $^1J_{P,P}$ 427.6, P-2); δ_H (200 MHz, $CDCl_3$) 0.96 (t, 3 H, $^3J_{H,H}$ 7.6, $CH_2C\mathit{H}_3$), 1.12 (t, 3 H, $^3J_{H,H}$ 7.0, $CH_2C\mathit{H}_3$), 1.42 [s, 3 H, $C(CH_3)_2$], 1.43 [s, 3 H, $C(CH_3)_2$], 1.46 [s, 3 H, $C(CH_3)_2$], 1.47 [s, 3 H, $C(CH_3)_2$], 1.63–1.92 (m, 4 H, $C\mathit{H}_2CH_3$), 7.37–7.53 (m, 6 H, Ph), 7.57–7.77 (m, 4 H, Ph); δ_C (100 MHz, $CDCl_3$) 8.67 (d, $^4J_{C,P}$ 6.3, $CH_2\mathit{C}H_3$), 9.13 (d, $^4J_{C,P}$ 4.5, $CH_2\mathit{C}H_3$), 25.66 [s, $C(\mathit{C}H_3)_2$], 26.28 [d, $^3J_{C,P}$ 5.4, $C(\mathit{C}H_3)_2$], 26.45 [s, $C(C\mathit{H}_3)_2$], 26.88 [s, $C(\mathit{C}H_3)_2$], 34.36 (d, $^3J_{C,P}$ 5.4, $\mathit{C}H_2CH_3$), 34.39 (s, $\mathit{C}H_2CH_3$), 37.01 [s, $\mathit{C}(CH_3)_2Et$], 37.65 [d, $^2J_{C,P}$ 5.4, $\mathit{C}(CH_3)_2Et$], 120.89 (d, $^1J_{C,P}$ 51.2, C-5), 125.12 (d, $^1J_{C,P}$ 22.4, C-3), 127.03 (d, $^3J_{C,P}$ 8.3, *o*-Ph), 127.16 (d, $^3J_{C,P}$ 7.2, *o*-Ph), 128.32 (s, Ph), 128.58 (s, Ph), 129.41 (d, $^2J_{C,P}$ 16.2, *i*-Ph), 129.48 (d, $^2J_{C,P}$ 14.4, *i*-Ph), 130.12 (s, Ph), 131.18 (s, Ph), 138.25 (d, $^1J_{C,P}$ 57.5, C-6), 141.38 (dd, $^1J_{C,P}$ 28.3, $^2J_{C,P}$ 4.0, C-4), 213.73 [d, $^2J_{C,P}$ 18.0, $Fe(CO)_4$]; *m/z* (EI, 70 eV): 574 (1) [M^+], 143 (100) [$C_{11}H_{11}^+$] (HR-MS: calc. for M^+: 574.1135. Found 574.1130).

§ *Selected data* for **8a** (only values for the major diastereomer are given): mp 135 °C (decomp.); δ_P (81 MHz, $CDCl_3$) −69.3 (s); δ_H (200 MHz, $CDCl_3$) 1.52 [s, 18 H, $C(CH_3)_3$], 7.41–7.54 (m, 6 H, *m/p*-Ph), 7.55–7.61 (m, 4 H, *o*-Ph); δ_C (50 MHz, $CDCl_3$) 29.27 [pseudo t, $^3J_{C,P} + {}^4J_{C,P}$ 4.2, $C(\mathit{C}H_3)_3$], 34.82 [pseudo t, $^2J_{C,P} + {}^3J_{C,P}$ 3.4, $\mathit{C}(CH_3)_3$], 126.07 (pseudo t, $^3J_{C,P} + {}^4J_{C,P}$ 3.4, *o*-Ph), 128.52 (pseudo t, $^1J_{C,P} + {}^2J_{C,P}$ 15.2, C-2/C-2′), 128.93 (s, *m*-Ph), 130.38 (pseudo t, $^2J_{C,P} + {}^3J_{C,P}$ 5.9, *i*-Ph), 130.55 (d, $^5J_{C,P}$ 1.7, *p*-Ph), 142.20 (pseudo t, $^1J_{C,P} + {}^2J_{C,P}$ 22.0, C-3/C-3′), 213.11 [pseudo t, $^2J_{C,P} + {}^3J_{C,P}$ 17.0, $Fe(CO)_4$]; *m/z* (EI, 70 eV): 714 (0.02) [M^+], 332 (100) [$M^+ - 8CO - C_{12}H_{14}$] (Calc. for $C_{32}H_{28}Fe_2P_2O_8$: C, 53.82; H, 3.95. Found: C, 53.12; H, 4.20%). For **8b**: δ_P (81 MHz, $CDCl_3$) −70.5 (s); δ_H (400 MHz, $CDCl_3$) 0.90 (t, 6 H, $CH_2C\mathit{H}_3$), 1.42 [s, 6 H, $C(C\mathit{H}_3)_2Et$], 1.45 [s, 6 H, $C(C\mathit{H}_3)_2Et$], 1.80 (q, 4 H, $C\mathit{H}_2CH_3$), 7.34–7.46 (m, 6 H, *m/p*-Ph), 7.67–7.73 (m, 4 H, *o*-Ph); δ_C (100 MHz, $CDCl_3$) 8.79 (d, $^4J_{C,P}$ 8.8, $CH_2\mathit{C}H_3$), 26.00 [s, $C(\mathit{C}H_3)_2Et$], 26.21 [s, $C(\mathit{C}H_3)_2Et$], 34.24 (d, $^3J_{C,P}$ 10.4, $\mathit{C}H_2CH_3$), 38.28 [d, $^2J_{C,P}$ 14.5, $\mathit{C}(CH_3)_2Et$], 126.32 (d, $^1J_{C,P}$ 20.0, C-2/C-2′), 128.93 (s, *m*-Ph), 129.87 (pseudo t, $^2J_{C,P} + {}^3J_{C,P}$ 7.2, *i*-Ph), 130.38 (d, $^3J_{C,P}$ 6.4, *o*-Ph), 130.54 (d, $^5J_{C,P}$ 3.2, *p*-Ph), 141.61 (pseudo t, $^1J_{C,P} + {}^2J_{C,P}$ 12.0, C-3/C-3′), 213.74 [d, $^2J_{C,P}$ 4.8, $Fe(CO)_4$]; *m/z* (EI, 70 eV) 742 (0.04) [M^+], 143 (100) [$C_{11}H_{11}^+$]. (Calc. for $C_{32}H_{28}Fe_2P_2O_8$: C, 55.02; H, 4.35. Found: C, 53.95; H, 4.10%).

¶ *Crystal data* for **8a**: $C_{32}H_{28}Fe_2O_8P_2$, M = 714.18 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 10.102(2), b = 18.273(4), c = 18.775(4) Å, β = 99.86(3)°, V = 3414.7(12) Å^3, Z = 4, D_c = 1.389 Mg m^{-3}, μ = 0.989 mm^{-1}, F(000) = 1464. Crystal dimensions 0.35 × 0.20 × 0.15 mm^3, 26 734 reflections collected, 6321 independent reflections (R_{int} = 0.0382), 4511 reflections with $I > 2\sigma(I)$, goodness-of-fit on F^2 = 1.205, R [$I > 2\sigma(I)$] = 0.0370, wR_2 = 0.0896; R (all data) = 0.0534, wR_2 = 0.0945; maximum residual density 0.420 e Å^{-3}. Data were collected on a STOE Imaging Plate Diffraction System at room temperature with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved with SHELXS-86 [ref. 10(*a*)] and refined with SHELXL-93 [ref. 10(*b*)]. CCDC 182/787.

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Received in Liverpool, UK, 22nd December 1997; 7/09127C