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Neutral and dianionic iron and ruthenium 1,4-diphosphabutadiene complexes†

Audrey Moores, Nicolas Mézailles, Louis Ricard, François Mathey and Pascal Le Floch*
Department of Chemistry, Hétéroéléments et Coordination, UMR CNRS 7653, Ecole Polytechnique, 91128, Palaiseau Cedex, France. E-mail: lefloch@poly.polytechnique.fr; Fax: 33.1.69.33.39.90; Tel: 33.1.69.33.45.70

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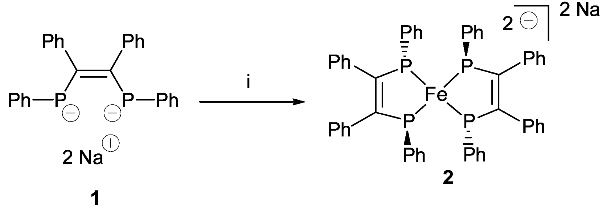
Reaction of a tetraphenyl-1,2-diphosphinyl dianion with [FeCl$_2$(THF)$_{1.5}$] or [Ru(COD)(acac)$_2$] yields dianionic complexes which further react with Ph$_3$SnCl to afford the corresponding bis(1,4-diphosphabutadiene) complexes.

The replacement of nitrogen by phosphorus in low-coordinated species always results in a dramatic change in coordinative properties.[1] This explains why these phosphorus ligands are attracting such an interest in coordination chemistry.[1,2] As attested by a number of recent reports, their use as ligands in homogeneous catalysis is emerging as a new developing area.[3] Among different potential candidates, kinetically protected 1,4-diphosphabutadienes (P equivalents of 1,4-diimines)[4] have already proved to be very promising and studies have emphasized the remarkable catalytic activity of their palladium(II) and nickel(II) complexes.[5] However, only a little is known on the coordination behaviour of these interesting bidentate ligands towards reduced metal-centres and, so far, studies have been essentially focused on group 10 metal complexes.[6] Herein, we report on the synthesis and the reactivity of the first homoleptic dianionic iron and ruthenium complexes.

Two possible pathways can lead to anionic complexes: a classical approach that consists in reducing a preformed complex and a second method relying on the reaction of a reduced ligand with a metallic fragment. The advantage of the latter, which has already proven to be very efficient with 2,2′-biphosphinines, lies in the fact that a sterically protected ligand is not required.[7] In fact, it is well known that the reductive cleavage of the P–P bond of 1,2-dihydrodiphosphetes, the protected forms of non-kinetically stabilised phosphabutadienes, yields such dianions.[8]

All our experiments were thus conducted with dianion **1** which was readily obtained by the two-electron reduction of the tetraphenyl-diphosphete. Reaction of the sodium salt of **1** with [FeCl$_2$(THF)$_{1.5}$][9] and [Ru(COD)(acac)$_2$][10] in THF at low temperature yielded dianionic complexes **2** (Scheme 1) and **3** which proved to be highly oxygen and moisture sensitive.‡§ In the case of **3**, the ^{31}P NMR spectrum of the crude mixture only exhibits one singlet at 105.2 ppm suggesting that the complex adopts a symmetrical structure. Unfortunately complex **3** proved to be thermally instable and decomposed in solution within a few hours. Thus it could neither be characterized at room temperature by ^{13}C NMR spectroscopy, nor be crystallised and its definitive formulation remains uncertain. On the other hand, complex **2** was too poorly soluble to be identified by NMR spectroscopy either but single crystals were obtained by carrying the synthesis in the presence of (2.2.2) cryptand.[11] An ORTEP view of one molecule of **2** is presented in Figure 1. As can be seen, **2** adopts a distorted tetrahedral geometry with an interplan angle of 43.2° between the two metalladiphospholene units. The pyramidality of the phosphorus atoms (average 341°) indicates that **2** cannot be described as a bis(diphosphabutadiene)-dimetallate complex, a non-negligible amount of charge being delocalized over the four phosphorus atoms. This hypothesis is reinforced by the presence of a short C=C connection (1.362 Å).

However, most of the charge probably resides at the metal and reactions of **2** and **3** with triphenyltinchloride cleanly yielded the corresponding bis(diphosphabutadiene) Fe(II) and Ru(II) complexes **4** and **5** which were isolated as pink and green powders, respectively (Scheme 2). Whereas **5**[12] was found to be rather stable, **4**[13] proved to be slightly air-sensitive. In ^{31}P NMR



Scheme 1 *Reagents and conditions*: i, [FeCl$_2$(THF)$_{1.5}$] in THF at −78 °C, 2 hours.

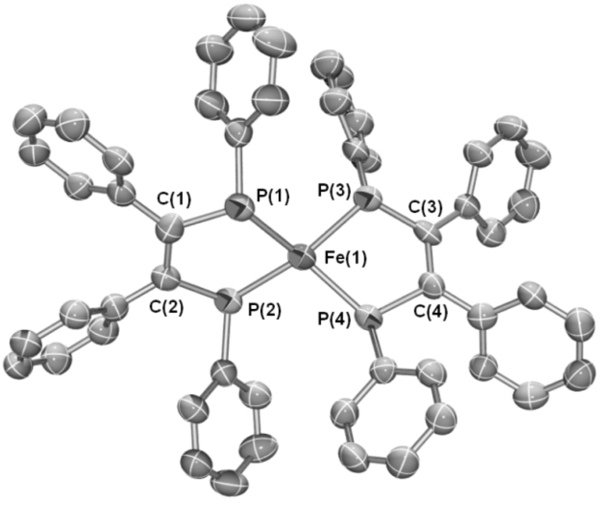
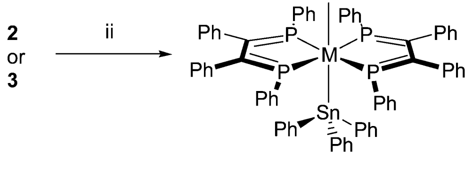


Fig. 1 Molecular structure of complex **2** (cryptand, solvent and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Fe(1)–P(1) 2.2292(2), P(1)–C(1) 1.8097(7), C(1)–C(2) 1.362(1) ; P(2)–Fe(1)–P(1) 81.139(8), C(1)–P(1)–Fe(1) 113.01(2).



4: M = Fe
5: M = Ru

Scheme 2 *Reagents and conditions*: ii, Ph$_3$SnCl in THF at −78 °C, 10 min.

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† Electronic supplementary information (ESI) available: Complete crystallographic data. See http://www.rsc.org/suppdata/cc/b3/b304243j/

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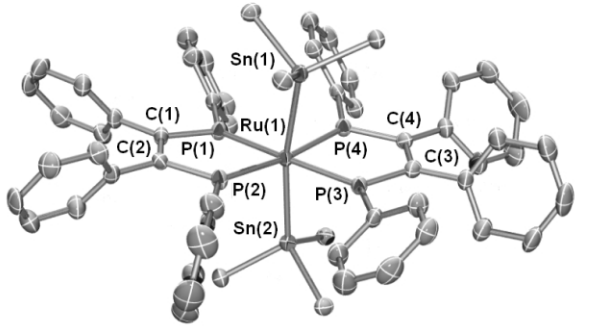

Fig. 2 Molecular structure of complex **5** (phenyl atoms of triphenyltin groups, solvent and hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Ru(1)–Sn(1) 2.6929(3), Ru(1)–P(1) 2.267(1), Ru(1)–P(2) 2.301(1), P(1)–C(1) 1.711(4), C(1)–C(2) 1.441(5) ; P(1)–Ru(1)–P(2) 78.00(3), C(1)–P(1)–Ru(1) 117.3(1), C(2)–C(1)–P(1) 114.3(2).

spectroscopy, both complexes appear as singlets with satellites due to $^2J_{\text{Sn–P}}$ couplings (144.8 Hz for **4** and 57.9 Hz for **5**). They exhibit a strong downfield shift, confirming the presence of two P=C bonds. The formulation of **5** was definitely ascertained by an X-ray crystal study.[14] An ORTEP view of one molecule of **5** is presented in Figure 2. The overall geometry around ruthenium is octahedral as expected for a d^6 complex, the two triphenyltin ligands being located on the main axis. On the other hand, the presence of two P=C bonds is evidenced by the planarity of the P atoms (average Σangles 359.9°) as well as by the two P=C bond distances which fall in the usual range (average 1.721 Å).

In conclusion, we have developed a straightforward access to the first dianionic and neutral iron and ruthenium complexes of 1,4-diphosphabutadienes. Further studies will now focus on other reduced metal complexes and their reactivity as well as on theoretical calculations aimed at understanding the charge distribution in these anionic species.

Notes and references

‡ *Crystal data* for **2**: $C_{212}H_{296}Fe_2N_8Na_4O_{33}P_8$, $M = 3935.99$, monoclinic, space group $C2/c$, $a = 52.679(1)$, $b = 13.722(1)$, $c = 30.639(1)$ Å, $\alpha = 90.00$, $\beta = 113.190(1)$, $\gamma = 90.00°$, $V = 20358.3(1.7)$ Å^3, $Z = 4$, $d = 1.284$ g cm^{-3}, $\mu = 0.286$ cm^{-1} (MoKα, $\lambda = 0.71069$ Å), $T = 150.0(1)$ K, $R_1 = 0.0737$, $^wR_2 = 0.2125$, $GoF = 1.045$, unique data = 10501 (17520 measured, $R_{\text{int}} = 0.0666$, KappaCCD diffractometer), 1203 refined parameters. *Crystal data* for **5**: $C_{89}H_{71}Cl_3P_4RuSn_2$, $M = 1709.18$, monoclinic, Space group $P2_1/c$, $a = 13.3669(1)$, $b = 52.3062(3)$, $c = 12.5912(1)$ Å, $\alpha = 90.00$, $\beta = 115.857(1)$, $\gamma = 90.00°$, $V = 7922.06(10)$ Å^3, $Z = 4$, $d = 1.433$ g.cm^{-3}, $\mu = 1.040$ cm^{-1}(MoKα, $\lambda = 0.71069$ Å), $T = 150.0(1)$ K, $R_1 = 0.0454$, $^wR_2 = 0.1237$, $GoF = 1.015$, unique data = 18771 (32603 measured, $R_{\text{int}} = 0.0302$, KappaCCD diffractometer), 963 refined parameters. CCDC 208890 and 208891. See http://www.rsc.org/suppdata/cc/b3/b304243j/ for crystallographic data in .cif or other electronic format.

§ Experimental procedure for synthesis of **2–3**: A solution of Na naphthalenide in THF (10.28 mL, 0.1 mmol mL^{-1}, 1.028 mmol) was added to tetraphenyl diphosphete (200 mg, 0.514 mmol) in a glovebox. The solution turned instantly from dark green to burgundy-red. It was stirred for 10 minutes at room temperature and then cooled down to −78 °C. [$FeCl_2(THF)_{1.5}$] (resp. [Ru(COD)(acac)$_2$]) (52 mg (resp. 104 mg), 0.254 mmol) was added. The solution was left stirring for a couple of hours before letting it slowly warm up to room temperature. Solvent was removed *in vacuo* and **2** (resp. **3**) was recovered as a brown powder. Yield: 167 mg, 74 % (resp. 185 mg, 78%).

Experimental procedure for synthesis of **4–5**: Crude dianionic complex **2** (resp. **3**) was trapped with triphenyltinchloride (196 mg, 0.514 mmol) at −78 °C. After return to room temperature the solvent was removed *in vacuo* and the brown solid obtained was washed with acetone (3 × 10 mL). **4** (resp. **5**) was recovered as a pink (resp. green) powder. Overall yield: 247 mg, 63% (resp. 262 mg, 65%).

1 K. B. Dillon, F. Mathey and and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998.
2 N. Mézailles, F. Mathey and P. Le Floch, *Prog. Inorg. Chem.*, 2001, **49**, 455.
3 L. Weber, *Angew. Chem., Int. Ed.*, 2002, **41**, 563.
4 (*a*) R. Appel, V. Winkhaus and F. Knoch, *Chem. Ber.*, 1987, **120**, 243; (*b*) G. Märkl, P. Kreitmeier, H. Nöth and K. Polborn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 927; (*c*) M. Yoshifuji, *J. Chem. Soc., Dalton Trans.*, 1998, 3343.
5 (*a*) T. Minami, H. Okamoto, S. Ikeda, R. Tanaka, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2001, **40**, 4501; (*b*) S. Ikeda, F. Ohhata, M. Miyoshi, R. Tanaka, T. Minami, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2000, **39**, 4512; (*c*) F. Ozawa, S. Yamamoto, S. Kawagishi, M. Hiraoka, S. Ikeda, T. Minami, S. Ito and M. Yoshifuji, *Chem. Lett.*, 2001, 972; (*d*) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami and M. Yoshifuji, *J. Am. Chem. Soc.*, 2002, **124**, 10969; (*e*) O. Daugulis, M. Brookhart and P. S. White, *Organometallics*, 2002, **21**, 5935; (*f*) A. Ionkin and W. Marshall, *Chem. Commun.*, 2003, 710.
6 (*a*) G. Sillett, L. Ricard, C. Patois and F. Mathey, *J. Am. Chem. Soc.*, 1992, **114**, 9453; (*b*) C. Tirla, N. Mézailles, L. Ricard, F. Mathey and P. Le Floch, *Inorg. Chem.*, 2002, **41**, 6032.
7 See for example: (*a*) P. Rosa, N. Mézailles, L. Ricard, F. Mathey and P. Le Floch, *Angew. Chem., Int. Ed.*, 2000, **39**, 1823; (*b*) P. Rosa, N. Mézailles, L. Ricard, F. Mathey, P. Le Floch and Y. Jean, *Angew. Chem., Int. Ed.*, 2001, **40**, 1251; (*c*) P. Rosa, N. Mézailles, L. Ricard, F. Mathey and P. Le Floch, *Angew. Chem., Int. Ed.*, 2001, **40**, 4476.
8 (*a*) N. Maigrot, L. Ricard, C. Charrier and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 950; (*b*) N. Maigrot, L. Ricard, C. Charrier and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1031.
9 J. E. Barclay, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1988, 2865.
10 P. Powell, *J. Organomet. Chem.*, 1974, **65**, 89.
11 Crystals of **2** grew in a sealed tube in a mixture THF/hexane (9/1) at −18 °C in equimolar presence of crytand (2.2.2).
12 **5**: ^{1}H NMR (CD_2Cl_2, 300 MHz): 6.38–6.50 ; 6.76–6.89 (2 m, C*H* of $P_2C_2Ph_4$ phenyls), 7.07–7.37 (2 m, C*H* of $SnPh_3$ phenyls).^{13}C NMR (CD_2Cl_2, 75.5 MHz) : 125.62 (s, *C*H of phenyls on $P_2C_2Ph_4$ carbon), 126.73 (s, *C*H of phenyls on $P_2C_2Ph_4$ carbon), 126.93 (m, $\Sigma J_{\text{P–C}} = 2.3$ Hz, *C*H of phenyls on phosphorus), 127.50 (s with sat., $J_{\text{Sn–C}} = 10.4$ Hz, *C*H of $SnPh_3$ phenyls), 127.76 (s with sat., $J_{\text{Sn–C}} = 44.5$ Hz, *C*H of $SnPh_3$ phenyls), 128.93 (large s, *C*H of phenyls on phosphorus), 133.11 (m, $\Sigma J_{\text{P–C}} = 9.7$ Hz, C_{ipso} of phenyls on $P_2C_2Ph_4$ carbon), 135.24 (large s, *C*H of phenyls on phosphorus), 137.04 (s with sat., $J_{\text{Sn–C}} = 37.7$ Hz, *C*H of $SnPh_3$ phenyls), 139.83 (m, $\Sigma J_{\text{P–C}} = 4.1$ Hz, C_{ipso} of phenyls on phosphorus), 147.65 (m, $\Sigma J_{\text{P–C}} = 3.0$ Hz, C_{ipso} of $SnPh_3$ phenyls), 165.82 (m, $\Sigma J_{\text{P–C}} = 3.0$ Hz, $P_2C_2Ph_4$ carbon atome).^{31}P NMR (THF, 121.5 MHz) : 229.01 (s with sat., $^2J_{\text{Sn–P}} = 57.9$ Hz). Anal. Found: C, 66.61; H, 4.56%. Calc. for $C_{88}H_{70}P_4RuSn_2$: C, 66.48; H, 4.44%.
13 **4**: ^{1}H NMR (THF-d_8, 300 MHz): 6.34–7.51 (m, C*H* of phenyls). ^{31}P NMR (THF, 121.5 MHz) : 223.64 (s with sat., $^2J_{\text{Sn–P}} = 144.8$ Hz). Complex **4** decomposes in CD_2Cl_2 or $CDCl_3$ and is too poorly soluble in THF-d_8 for a ^{13}C spectrum to be recorded. Anal. Found: C, 68.57; H, 4.43%. Calc. for $C_{88}H_{70}P_4FeSn_2$: C, 68.43; H, 4.57%.
14 Complex **5** recrystallised in toluene at −18 °C.