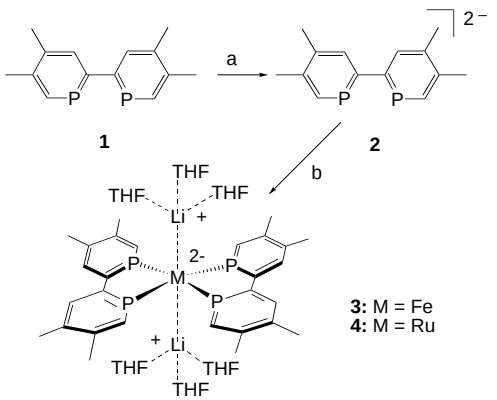
# Dianionic Iron and Ruthenium(2 − ) Biphosphinine Complexes: A Formal $d^{10}$ Ruthenium Complex with a Square Planar Geometry**

Patrick Rosa, Nicolas Mézailles, Louis Ricard, François Mathey, Pascal Le Floch,* and Yves Jean

Though the Collman's reagent $[Fe(CO)_4]^{2-}$ is probably one of the most popular and useful reagents in organic synthesis,[1] our knowledge of dianionic Group 8 metal complexes still remains limited. In addition to the carbonyl ruthenium analogue $[Ru(CO)_4]^{2-}$, only a few other complexes are known: the complete series of $PF_3$ derivatives $[M(PF_3)_4]^{2-}$ (M = Fe, Ru, Os),[2] the isocyanide complexes $[Ru(CNR)_4]^{2-}$ synthesized by Cooper and co-workers,[3] and the amazing Jonas' iron complexes $[Fe(C_2H_4)_4]^{2-}$ and $[Fe(cod)_2]^{2-}$ (cod = cycloocta-1,5-diene).[4] We have begun to explore the use of sophisticated phosphinine-based ligands in an effort to design phosphorus equivalents of carbonyl ligands.[5] This we recently illustrated by the successful stabilization of an $Au^0$ center encapsulated in a silacalix-[4]-phosphinine macrocycle[6] and the synthesis of dianionic 2,2′-biphosphinine complexes of Group 4[7] and 9 metals.[8] Herein we report the successful stabilization of dianionic Fe and Ru 2,2′-biphosphinine complexes.

All our syntheses were carried out using dianion **2** which is readily obtained by reduction of 2,2′-biphosphinine **1** (tmbp) using lithium in excess.[9] Reaction of two equivalents of **2** with one equivalent of $[\{FeCl_2(thf)_{1.5}\}_n]$ or $[Ru(cod)(acac)_2]$ (acac = 2,4-pentanedione, acetylacetone) in THF at low temperature, yielded complexes **3** an **4**, respectively, which were isolated as highly moisture and oxygen sensitive powders (Scheme 1).

The formulation of these two complexes was confirmed by NMR spectroscopic data ($^1H$ and $^{13}C$). To gain more structural information, an X-ray crystal structure analysis of complex **4** was carried out (Figure 1).[10] Remarkably, the overall geometry of **4** is not tetrahedral as usually observed for $ML_4$ $d^{10}$ complexes,[8] but square planar;[11] the iron complex **3** is assumed to have the same structure. The two biphosphinines are roughly located in the same plane ($\Theta = 7.29°$, $\Theta$ being the interplane angle) and the two cationic $[Li(thf)_3]^+$ units are located above and below the plane in apical positions. Though the structure roughly resembles an octahedron, the Ru···Li separation (2.740(3) Å) is long and exceeds the sum of the covalent radii (2.60 Å) indicating only a very weak, mainly




Scheme 1. Syntheses of **3** and **4**: a) Li (excess), THF, 25 °C, 2 h. b) $[\{FeCl_2(thf)_{1.5}\}_n]$ or $[Ru(cod)(acac)_2]$, THF −80 °C → RT.

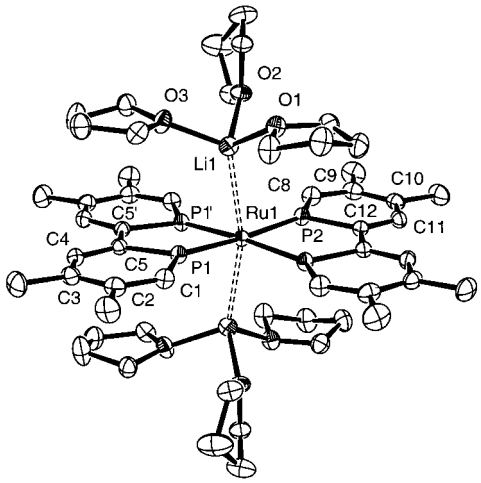



Figure 1. Molecular structure of **4**. Thermal ellipsoids are set at the 50 % probability level. The hydrogen atoms are omitted for clarity. Important distances [Å] and angles [°]: Ru1-P1 2.2131(5), Ru1-P2 2.2168(5), Ru1···Li1 2.740(3), P1-C5 1.777(2), P1-C1 1.740(3), C1-C2 1.381(3), C2-C3 1.418(3), C3-C4 1.393(3), C4-C5 1.395(2), C5-C5′ 1.436(3), Li1-O1 2.015(3), Li1-O2 1.984(4), Li1-O3 2.001(4); P1-Ru1-P2 174.85(2), P1-Ru1-Li1 82.89(7), P1-Ru1-P1′ 79.19(2), P2-Ru1-Li1 91.99(7), C5-P1-C1 102.12(8), P1-C1-C2 125.6(2), C1-C2-C3 122.8(2), C2-C3-C4 121.8(2), C3-C4-C5 127.0(2).

electrostatic, interaction between the Ru and Li centers. This structure markedly differs from that of the iron carbonyl derivative[12] as well as that of the Jonas' complex $[Fe(C_2H_4)_4][\{Li(tmeda)\}_2]$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethyl 1,2-ethanediamine) in which Fe–Li and C–Li bonds are found.[4] Another interesting structural feature is provided by the internal bond distances in the two ligands. Apparently, a significant electronic transfer occurs from the metal into the π* LUMO of the biphosphinine as shown by the shortening of the C–C connection between the two rings (average 1.437 Å in **4** vs. 1.490 Å in **1**) and the lengthening of the internal P=C bonds (1.770 Å in **4** vs. 1.736(4) Å in **1**). All distances in the cycles are similar to those found in the radical anion $\mathbf{1}^{\bullet-}$.[13] A first insight to this particular geometry was given by extended Hückel (EH) calculations[14, 15] on the $[Ru(bp)_2]^{2-}$ ion (bp = $C_{14}H_{16}P_2$ parent compound). The analysis of the electronic structure reveals that only the four low-lying d orbitals of this square-planar complex are actually occupied. The two extra

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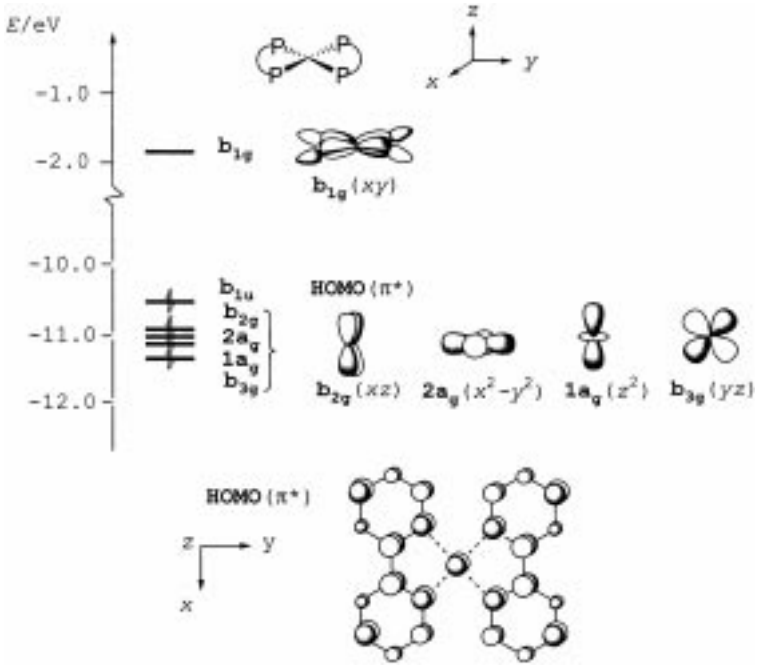
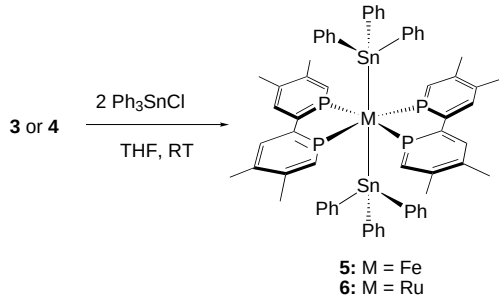



Scheme 2. Electronic structure of the $[Ru(bp)_2]^{2-}$ complex (five highest occupied MOs and the vacant fifth orbital of the d block). Symmetry labels are given assuming an idealized $D_{2h}$ symmetry. For the sake of clarity, only the metal contribution is drawn for the four occupied d orbitals.

electrons are located in the $b_{1u}$ orbital which is depicted in Scheme 2. This orbital results from the in-phase combination of the π* LUMO on each biphosphinine ligand which is further stabilized by a bonding interaction with the parallel p metal orbital. Therefore, the formal $d^{10}$ $[Ru(bp)_2]^{2-}$ complex is in fact a $d^8$ ruthenium species coordinated by two radical anions $\mathbf{1}^{\bullet-}$. This electron counting is consistent with the square-planar geometry observed and rationalizes the bond length changes in the biphosphinine ligands upon coordination to the metal center.

Though a significant part of the electron density resides on the ligands, the metal centers in **3** and **4** remain the reaction center when triphenyltin chloride is used as reagent and complexes $[M(tmbp)_2(Ph_3Sn)_2]$ **5** and **6** were isolated as very stable solids (Scheme 3). The structure of the iron complex **5** was confirmed by an X-ray crystal structure analysis (not shown).

Further studies aimed at investigating the reactivity of these new dianionic Fe and Ru(2 – ) species are currently underway.




Scheme 3. Syntheses of **5** and **6**.

*Experimental Section*

General procedure for the syntheses of complexes **3** and **4**: Biphosphinine **1** (123 mg, 0.50 mmol) was treated with excess lithium at 25 °C in THF (10 mL). After 2 h, the green solution obtained (dianion **2**) was cooled to −80 °C and $[Ru(cod)(acac)_2]$ (92 mg, 0.23 mmol) or $[\{FeCl_2(thf)_{1.5}\}_n]$ (53 mg, 0.23 mmol) were added. After stirring for 5 min, the red solution obtained was slowly warmed to 25 °C. The solvent was evaporated and the resulting red solid was washed with diethyl ether (10 mL). The high sensitivity of **3** and **4** towards oxygen and moisture, and the presence of traces of LiCl salts precluded the determination of yields and satisfactory elemental analyses. Suitable crystals of **4** for X-ray structure analysis were grown from THF solution in a sealed tube at −18 °C. Crystals were separated from the mother liquor at this temperature to avoid dissolution and then protected with paratone oil for handling.

**3**: $^{31}P$ NMR (81 MHz, $C_4D_8O$, 25 °C): $\delta = 196.9$ (s); $^1H$ NMR (200 MHz, $C_4D_8O$, 25 °C): $\delta = 2.29$ (s, 12H; Me), 2.40 (s, 12H; Me), 7.94 (m, 4H, $H_{3,3'}$ or $H_{6,6'}$), 8.12 (m, 4H, $H_{3,3'}$ or $H_{6,6'}$); $^{13}C$ NMR (200 MHz, $C_4D_8O$, 25 °C): $\delta = 22.5$ (s, Me), 24.45 (s, Me), 115.4 (m, $C_{4,4'}$ or $C_{5,5'}$), 126.3 (m, $C_{3,3'}$ or $C_{6,6'}$), 133.9 (m, $C_{3,3'}$ or $C_{6,6'}$), 139.2 (m, $C_{4,4'}$ or $C_{5,5'}$), 144.2 (m, $C_{2,2'}$).

**4**: $^{31}P$ NMR (81 MHz, $C_4D_8O$, 25 °C): $\delta = 188.7$ (s); $^1H$ NMR (200 MHz, $C_4D_8O$, 25 °C): $\delta = 2.37$ (s, 12H; Me), 2.52 (s, 12H; Me), 8.03 (m, 4H, $H_{3,3'}$ or $H_{6,6'}$), 8.12 (m, 4H, $H_{3,3'}$ or $H_{6,6'}$); 8.21 (m, 4H, $H_{3,3'}$ or $H_{6,6'}$); $^{13}C$ NMR (50 MHz, $C_4D_8O$, 25 °C): $\delta =$ 22.7 (s, Me), 24.3 (s, Me), 116.1 (m, $C_{4,4'}$ or $C_{5,5'}$), 126.5 (m, $C_{3,3'}$ or $C_{6,6'}$), 133.2 (m, $C_{6,6'}$ or $C_{3,3'}$), 138.5 (m, $C_{4,4'}$ or $C_{5,5'}$), 146.3 (m, $C_{2,2'}$).

General procedure for the syntheses of complexes **5** and **6**: Dianionic complexes **3** and **4**, prepared as above in THF, were treated with $Ph_3SnCl$ (175 mg, 0.5 mmol) at 25 °C. After stirring for 10 min, the solvent was evaporated and the resulting solid was washed twice with diethyl ether (10 mL) and then dissolved in $CH_2Cl_2$ (10 mL). After filtration on celite, the solvent was evaporated. After standing in THF for several days, **5** and **6** were isolated as orange crystals.

**5**: Yield 231 mg (70%); m.p. >220 °C; elemental analysis (%) calcd for $C_{64}H_{62}FeP_4Sn_2$: C 61.58, H 5.01; found: C 61.65, H 4.90; $^{31}P$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 231.9$ (pseudo t, $^2J(P,Sn) = 326.0$ Hz); $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.45$ (s, 24H, Me), 6.37 – 6.99 (m, 30H, $ShPh_3$), 7.93 – 8.17 (m, 8H, $H_{3,3'}$ and $H_{6,6'}$); $^{13}C$ NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 23.1$ (s, Me), 22.5 (virtual t, AXX′, $\Sigma J(C,P) = 5.0$ Hz, Me), 126.9 (pseudo t, $^4J(C,Sn) = 9.7$ Hz, $C_{para}$ $SnPh_3$), 127.1 (pseudo t, $^3J(C,Sn) =$ 40.4 Hz, $C_{meta}$ $SnPh_3$), 129.7 (m, $C_{3,3'}$), 130.2 (m, $C_{5,5'}$ or $C_{4,4'}$), 137.2 (pseudo t, $^2J(C,Sn) = 33.4$ Hz, $C_{ortho}$ $SnPh_3$), 141.0 (m, $C_{6,6'}$), 145.8 (s, $C_q$ $SnPh_3$), 146.0 (m, $C_{4,4'}$ or $C_{5,5'}$), 151.1 (m, $C_{2,2'}$).

**6**: Yield 144 mg (40%); m.p. >220 °C; elemental analysis (%) calcd for $C_{64}H_{62}RuP_4Sn_2$: C 59.42, H 4.83; found: C 59.31, H 4.90; $^{31}P$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 221.0$ (pseudo t, $^2J(P,Sn) = 193.3$ Hz); $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.45$ (s, 12H, Me), 2.48 (s, 12H, Me), 6.49 – 6.88 (m, 30H, $SnPh_3$), 8.11 – 8.26 (m, 8H, $H_{3,3'}$ and $H_{6,6'}$); $^{13}C$ NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 22.2$ (s, Me), 24.1 (m, Me), 126.5 (pseudo t, $^4J(C,Sn) = 9.7$ Hz, $C_{para}$ $SnPh_3$), 126.9 (pseudo t, $^3J(C,Sn) = 40.0$ Hz, $C_{meta}$ $SnPh_3$), 130.6 (m, $C_{3,3'}$), 131.1 (m, $C_{5,5'}$ or $C_{4,4'}$), 137.2 (pseudo t, $^2J(C,Sn) =$ 34.7 Hz, $C_{ortho}$ $SnPh_3$), 139.9 (m, $C_{6,6'}$), 146.0 (s, $C_q$ $SnPh_3$), 146.0 (m, $C_{4,4'}$ or $C_{5,5'}$), 151.1 (m, $C_{2,2'}$).

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[8] $ML_4$ $d^{10}$ [M(tmbp)$_2$][Na(2.2.2)] (M = Co and Rh, tmbp = 4,4′,5,5′-tetramethyl-2,2′biphosphinine) complexes adopt a pseudo tetrahedral geometry, see: N. Mézailles, P. Rosa, L. Ricard, F. Mathey, P. Le Floch, *Organometallics* **2000**, *19*, 2941.

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[10] X-ray structure data for **4**: crystal dimensions $0.22 \times 0.20 \times 0.18$ mm, monoclinic, space group $C2/c$, $a = 15.9260(9)$, $b = 15.6630(6)$, $c = 21.7990(12)$ Å, $\alpha = 90.000(3)$, $\beta = 91.382(2)$, $\gamma = 90.000(3)^\circ$, $V = 5436.2(5)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.271$ g cm$^{-3}$, $\mu = 0.451$ cm$^{-1}$, $F(000) = 2200$, $\theta_{max} = 30.05^\circ$, $h,k,l$ ranges: 0 to 22, 0 to 22, −30 to 30; 31542 reflections collected of which 7612 were unique ($R_{int} = 0.031$), 6354 reflections with $I > 2\sigma(I)$ and 298 parameters refined, GOF($F^2$) = 1.057, final $R$ indices: $R_1 = 0.0359$, $wR_2 = 0.0912$, max./min. residual electron density 0.867(0.066)/−0.0484(0.066) e A$^{-3}$. Data collection: Nonius Kappa CCD diffractometer, $\phi$ and $\omega$ scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR 97,[16] refinement against $F^2$ (SHELXL97[17]) with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151419. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## Stepwise Building of Polyphosphirene Chains

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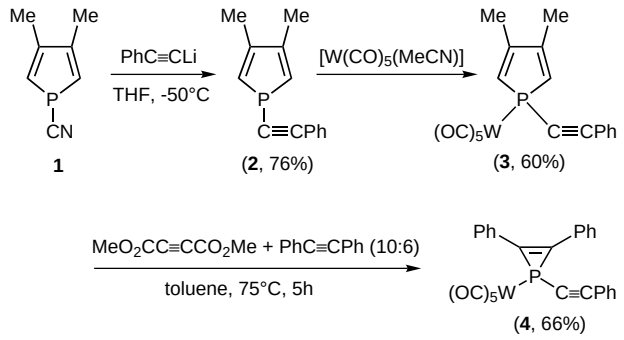
As a result of its very peculiar structural and electronic properties, the phosphirene ring occupies a special niche in carbon–phosphorus heterocyclic chemistry.[1] Whereas the foundations of its chemistry are now well established, almost nothing is known about oligomeric or macrocyclic molecules containing several phosphirene units. Recently, both 2,2′-biphosphirenes[2] and the related 2,2′-bisphosphiranes[3] have been described, but their syntheses cannot by easily extrapolated to yield higher oligomers. Herein, we wish to present an iterative approach which opens a route to a new class of polyphosphirenes.

Our initial idea was to synthesize a 1-alkynylphosphirene derivative and to investigate the reactivity of its C≡C triple bond toward terminal phosphinidene complexes. For this purpose, we needed to prepare an alkynylphosphinidene precursor. Accordingly, we first synthesized the 1-alkynylphosphole **2** and the corresponding P–W(CO)$_5$ complex **3** from the 1-cyanophosphole **1**.[4] Fearing a [P+C≡C] self-condensation of the alkynylphosphinidene intermediate, we then decided to combine the synthesis of the 7-phosphanorbornadiene precursor[5] with its generation and trapping by a reactive alkyne such as diphenylacetylene (tolan).[6] On that basis, **3** was allowed to react with a 10:6 mixture of dimethyl acetylenedicarboxylate and tolan. Tolan proved to compete efficiently with the self-condensation of the phosphinidene intermediate and the desired 1-alkynylphosphirene complex **4** was obtained in satisfactory yield (Scheme 1).




Scheme 1. Synthesis of a 1-alkynylphosphirene complex.

The C≡C triple bond of **4** is highly hindered by the phosphirenyl substituent, nevertheless, a typical terminal phosphinidene complex such as [PhPW(CO)$_5$] readily cycloadds to it to give the 1,2′-biphosphirene **6** (Scheme 2).

The $^{31}$P NMR spectrum of **6** confirms the presence of the two phosphirene rings: $\delta(^{31}P) = -186.5$ (P1), −142.6 (P2),

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