Synthesis and Reactivity of Rhodium(I) and Iridium(I) Chloride Complexes of a Trisphosphinine[†]

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The $SiMe_2$ linked tris(phosphinine) **1** reacts with $[M(COD)Cl]_2$ (M = Rh, Ir) to give the corresponding [M(**1**)Cl] complexes **2** and **3**. The X-ray crystal structure of **2** reveals a highly twisted geometry of **1** around the rhodium center. Abstraction of the chloride ligand with AgOtf in the presence of CH_3CN yields the corresponding cationic complexes **4** and **5**. The CH_3CN ligand can be quantitatively displaced from **4** by CO to form a cationic carbonyl complex **6** in which the Rh center is highly Lewis acidic. It was also shown that, upon reaction with HCl, **3** equilibrates with the $[Ir(\mathbf{1})HCl_2]$ complex **7**.

Introduction

In view of the unique coordinative properties of sp^2-hybridized phosphorus ligands,[1] the incorporation of molecules such as phosphaalkenes and phosphinines (P analogues of imines and pyridines) into polydentate and macrocyclic structures appears as a new and challenging field of investigation in phosphorus chemistry. Recently, a first significant advance toward this goal was made by Geoffroy et al. who reported the synthesis of a bidentate 1,3-bis[phosphaalkene]benzene ligand which can act via CH orthometalation as a mixed tridentate pincer for Pd−Cl fragments.[2] Studies dealing with phosphinines focused so far on either functional monodentate ligands[3] or 2,2′-biphosphinines[4] which revealed an interesting potential for the stabilization of highly reduced transition metal centers. Encouraged by these promising results we developed in 1996 a new and versatile approach toward highly functionalized monophosphinines and polyphosphinines.[5] One of the most rewarding application was the successful synthesis of a $SiMe_2$-linked trisphosphinine **1** which is the first example of a ligand featuring three P═C bonding sites.[6] We rationalized that this ligand could span three sites of a square planar metal complex and therefore focused our preliminary studies on the synthesis and reactivity of mononuclear rhodium and iridium complexes of **1**, which are described here (Scheme 1).

Results and Discussion

Trisphosphinine **1** (2 equiv) was reacted in CH_2Cl_2 with 1 molar equiv of $[M(COD)Cl]_2$ (M = Rh, Ir) precursors, to yield quantitatively by $^{31}P\{^1H\}$ NMR spectroscopy the corresponding (**1**)MCl complexes (M = Rh, **2**; Ir, **3**) (Scheme 2).

Complex **3** is the first example of η^1-Ir phosphinine complex. Indeed, during their studies on 2-(2-pyridyl)phosphinine (NIPHOS), Venanzi et al. isolated a dinuclear complex in which the phosphinine moiety adopts a bridging mode.[7] Characterization of **2** and **3** was achieved by elemental analysis and ^{31}P, ^1H, and ^{13}C NMR spectroscopies.[8] As expected, **2** displayed a characteristic AB_2 spin system in ^{31}P NMR, which was successfully simulated. The analogous Ir complex **3** gave a much simpler AX_2 type spectrum, consisting of a doublet at 221.9 ppm and a triplet at 192.3 ppm ascribed to the external and central units, respectively. Most noticeably, in the two complexes, both ^1H and $^{13}C\{^1H\}$ showed that the methyl substituents of the Si bridges become chemically inequivalent upon complexation. An explanation of this surprising feature was brought by the X-ray crystal study of **2** (see Table 1), which showed that one methyl group experiences the ring current effect of a neighboring phenyl group.[8] It appears that the geometry observed in the solid is retained in solution. Both complexes readily crystallized after hexane layering of a CH_2Cl_2 solution. An ORTEP drawing of **2** is shown in Figure 1. The geometry around the rhodium center appears to be perfectly square planar with L−Rh−L angles values between 88.80(3) and 90.66(3)°. The most interesting feature of this structure concerns the arrangement of the ligand. Indeed, the three phosphinine rings are highly distorted from the plane defined by the Rh and P atoms. This effect likely results from the need to accommodate the long C−Si bond distances. Another view showing this

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[†] This article is dedicated to Prof. Peter Jutzi on the occasion of his 60th birthday.

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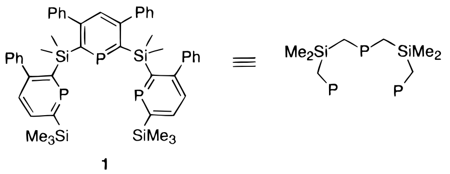
S0020-1669(98)00353-X CCC: $15.00

Scheme 1



Scheme 2

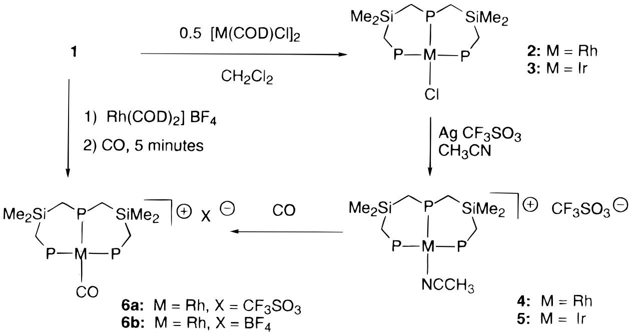


Table 1. Crystallographic Data and Experimental Parameters for the X-ray Structure Analysis

empirical formula	$C_{54}H_{55}Cl_7RhSi_4P_3$	fw	1260.38
a	12.038(1) Å	space group	*P*1 (No. 2)
b	13.098(1) Å	T	−150.0(5) °C
c	1.079(2) Å	λ	0.710 73 Å
α	93.04(2)°	ρ_{calcd}	1.524 g cm^{-3}
β	99.09(2)°	μ	8.6 cm^{-1}
γ	101.66(2)°	$R(F_0)^a$	0.050
V	2746.1(1.3) Å^3	$R(F_0)_w{}^b$	0.091
Z	2		

[a] $R(F_0) = \Sigma(F_0 - F_c)/\Sigma(F_0)$. [b] $R(F_0)_w = [\Sigma(w(F_0 - F_c)^2)/\Sigma(wF_0{}^2)]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Bond Distances (Å)			
Rh−Cl(1)	2.3535(8)	C(9)−C(10)	1.397(4)
P(3)−Rh	2.2890(8)	C(6)−Si(1)	1.905(3)
P(2)−Rh	2.1627(8)	Si(1)−C(5)	1.905(3)
P(1)−Rh	2.2703(8)	P(1)−C(5)	1.734(3)
P(2)−C(6)	1.737(3)	P(1)−C(1)	1.720(3)
P(2)−C(10)	1.723(3)	C(1)−C(2)	1.406(5)
C(6)−C(7)	1.402(4)	C(2)−C(3)	1.350(5)
C(7)−C(8)	1.395(4)	C(3)−C(4)	1.415(5)
C(8)−C(9)	1.391(5)	C(4)−C(5)	1.392(4)
C(1)−Si(3)	1.904(4)		
Bond Angles (deg)			
Cl(1)−Rh−P(3)	88.80(3)	C(11)−Si(2)−C(10)	105.4(1)
P(3)−Rh−P(2)	90.53(3)	Si(2)−C(10)−P(2)	113.7(2)
P(2)−Rh−P(1)	90.66(3)	C(10)−P(2)−C(6)	109.1(1)
P(1)−Rh−Cl(1)	90.03(3)	P(2)−C(6)−C(7)	118.7(2)
P(2)−Rh−Cl(1)	178.34(3)	C(6)−C(7)−C(8)	123.0(3)
P(3)−Rh−P(1)	178.64(3)	C(7)−C(8)−C(9)	126.4(3)
C(15)−P(3)−C(11)	108.0(1)	C(8)−C(9)−C(10)	124.0(3)
P(3)−C(11)−Si(2)	113.7(2)	C(9)−C(10)−P(2)	118.4(2)

distortion is presented in Figure 2. This particular geometry implies that complex **2** exists in the solid state as a racemic mixture of enantiomers, but the centrosymmetrical space group in which the molecule crystallizes precludes their distinction. Apart from this feature all bond distances are normal and compare to those previously reported for classical tris(phosphine)RhCl complexes.[9]

The high steric crowding of the two $SiMe_3$ suggests that the Cl atom would be difficult to substitute. Indeed, unlike what was achieved with tris(phosphine)RhCl complexes,[10] simple addition of NH_4PF_6 salt did not yield the desired cationic complex. More strenuous conditions had to be employed. When either **2** or **3** was reacted with an excess of $AgCF_3SO_3$ and a 5-fold excess of CH_3CN, the $[(\mathbf{1})M(CH_3CN)]^+CF_3SO_3^-$ (M = Rh: **4**, Ir: **5**) complexes were formed quantitatively. The $^{31}P\{^1H\}$ NMR spectrum of **4** is now of AM_2X spin system type and appears as a pseudopentet for P_A and a doublet of doublet for P_M. A simple AX_2 spin system is seen in $^{31}P\{^1H\}$ NMR spectroscopy for the iridium complex **5**.

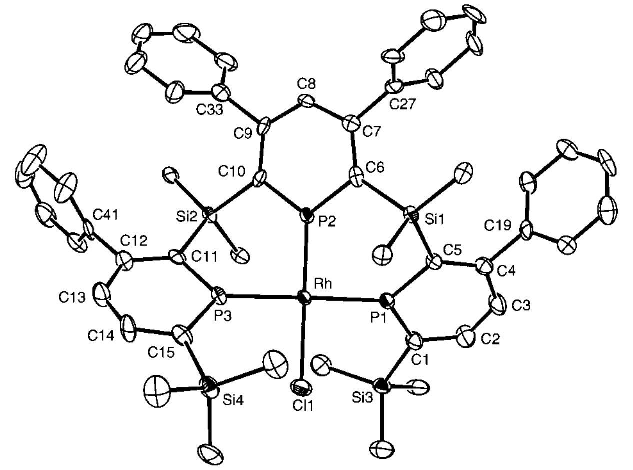


Figure 1. ORTEP drawing of **2**. Ellipsoids are scaled to enclose 50% of the electron density.

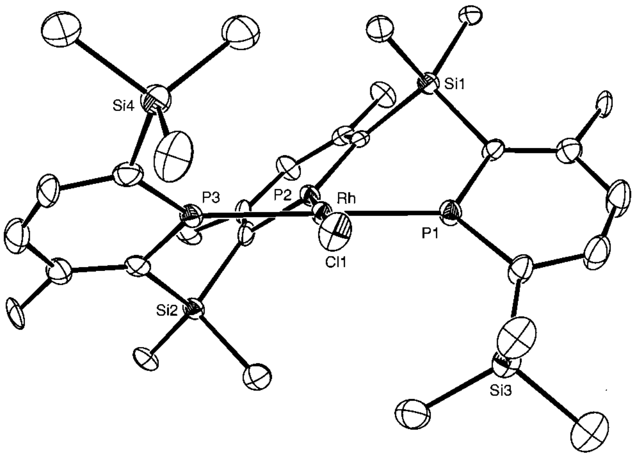


Figure 2. View of **2** along the Rh−Cl axis, showing the distortion of the ligand. Phenyl groups have been omitted for clarity.

The acetonitrile ligand was readily displaced from **4** by a sterically non demanding ligand. Indeed, when CO was bubbled for 5 min in a solution of the cationic complex, the color faded from dark to pale orange and $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of a new complex, **6a**. The signal of the central phosphorus now appeared as a doublet of triplet (J_{P-P} = 83.7 Hz, J_{Rh-P} = 144.7 Hz). As previously mentioned, the ORTEP of **2** reveals the high steric demand of the two $SiMe_3$ substituents located on the terminal phosphinines, and as a consequence, larger two electron donors, such as PR_3 or $CNBu^t$, did not displace CH_3CN. A second method was developed to synthesize cationic complexes in one step from $[Rh(COD)_2]^+$ precursors. Equimolar quantities of $[Rh(COD)_2]BF_4$ and **1** were mixed in CH_2Cl_2 and stirred for 15 min before CO was bubbled

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for 5 min to yield the analogous complex **6b** by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2). The reaction likely involves the formation of a pentavalent $[(\mathbf{1})Rh(COD)]^+$ species from which the second COD ligand is displaced by CO bubbling. A value of 2035 cm^{-1} for the CO stretching mode in IR compared to 2016 cm^{-1} observed in $[(PhP(CH_2CH_2PPh_2)_2Rh(CO)]PF_6$ clearly indicates a weaker π back-donation from Rh to the CO ligand in **6**. This observation is consistent with the stronger π accepting abilities of phosphinines compared to phosphines. Also consistent with this is the fact that we neither observed the formation of pentavalent $[Rh(\mathbf{1})(CO)_2]^+$ nor the formation of an O_2 adduct. All these results clearly indicate that the Lewis acidity of the metal center is greatly enhanced by the coordination of **1**. Another illustrative example is given by the reaction of complex **3** with HCl (eq 1).

$$\mathbf{3} + HCl \xrightleftharpoons{CDCl_3} \underset{\mathbf{7}}{(\mathbf{1})IrHCl_2} \qquad (1)$$

Unlike what is observed for classical tris(phosphine)$IrHCl_2$ complexes which are stable,[10] the hydride complex $(\mathbf{1})IrHCl_2$ (**7**) is in equilibrium with complex **3** at room temperature. This equilibrium is totally displaced toward the reformation of **3** within 1h, which precluded the isolation of pure **7**. In $^{31}P\{^1H\}$ NMR spectroscopy, **7** shows an AMX spin pattern at δ 197.0 (d, $J_{A-X} = 47.9$ Hz, P_A), δ 194.2 (d, $J_{M-X} = 37.0$ Hz, P_M), δ 184.4 (dd, $J_{A-X} = 47.9$ Hz, $J_{M-X} = 37.0$ Hz, P_X) indicating three electronically inequivalent phosphorus centers. Additional evidence supporting the presence of a hydride ligand is provided by the ^1H NMR spectrum which displays a pseudo quartet at -16.6 ppm ($J_{P-H} = 16.6$ Hz). The low magnitude of this coupling constant suggests that the three phosphorus centers are located cis to the hydride. These two pieces of data cannot allow us to unambiguously establish the geometry for complex **7**.

Conclusion

In summary, the synthesis of the first complexes of tris(phosphinine) **1** are reported. Complex **3** is also the first example of a η^1-phosphinine Ir complex. Apart from being a very valuable ligand in itself, **1** can also be seen as a suitable model of polyphosphinine based macrocycles. Studies toward the synthesis of such types of macrocycles and their reactivity with electron-rich metal centers are in progress in our laboratories and will be reported in due course.

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry THF, hexane, were obtained by distillation from Na/benzophenone, dry CH_2Cl_2 and MeCN were obtained by distillation from P_2O_5. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. The following abreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; p, pentet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. $[M(COD)Cl]_2$ (M = Rh,[11] Ir[12]), $[Rh(COD)]_2[BF_4]$[13] were prepared according to published procedures. AgOtf and HCl (1 M in ether) were purchased from Aldrich.

Synthesis of Complexes 2 and 3. Trisphosphinine **1** (0.2 g, 2.36×10^{-4} mol) and $[M(COD)Cl]_2$ (M = Rh, 0.058 g, 1.17×10^{-4} mol; M = Ir, 0.079 g) are weighed in air and placed under N_2. Freshly distilled CH_2Cl_2 (3 mL) is then syringed in the Schlenk flask, and the mixture is allowed to stir at 35 C. ^{31}P NMR spectroscopy indicates that the reaction is over within 15 min both for **2** and for **3**. Reduction of the volume, followed by hexanes precipitation and filtration yields an orange solid (**2**) or a red solid (**3**). Crystallization is achieved by layering hexanes onto a CH_2Cl_2 solution of complex. Yields: **2**, 95%, **3**, 93%.

Data for **2**. ^{31}P NMR ($CDCl_3$), AB_2X: δ 242.36 ($^2J(P-P) = 76.36$, $^1J(P-Rh) = 164.4$, P_A), 241.17 ($^2J(P-P) = 76.36$, $^1J(P-Rh) = 157.1$, P_B). ^{13}C NMR ($CDCl_3$): δ 1.00 (s, $SiMe_2$), 3.05 (s, 2 × $SiMe_3$), 11.32 (s, $SiMe_2$), 127.22−129.96 (m, CH of Ph), 143.03 (bs, 2 × $C_{5'}$), 145.50−146.40 (sets of m, 4 × C_{ipso} of Ph), 152.40 (m, 2 × $C_{3'}$ and C_3, C_5), 156−159.4 (sets of m, 2 × $C_{2'}$, C_2, C_6, 2 × $C_{6'}$). Anal. Calcd for $C_{49}H_{55}ClP_3RhSi_4$: C, 59.59; H, 5.61. Found: C, 59.70.; H, 5.86.

Data for **3**. ^{31}P NMR ($CDCl_3$), AX_2: δ 221.95 (d, $^2J(P-P) = 48.09$, P_X), 192.28 (t, $^2J(P-P) = 48.09$, P_A). ^1H NMR ($CDCl_3$): δ −1.25 (s, 6H, $SiMe_2$), 0.61 (s, 18H, 2x$SiMe_3$), 1.14 (s, 6H, $SiMe_2$), 6.86−7.31 (m, 23H, 4 × Ph, 2 × $H_{4'}$, H_4), 8.16 (ddd, $^3J(H_{5'}-H_{4'}) = {}^3J(H_{5'}-P) = 15.36$, $^5J(H_{5'}-P_{trans}) = 8.68$, 2 × $H_{5'}$). ^{13}C NMR ($CDCl_3$): δ 1.00 (s, $SiMe_2$), 3.05 (s, 2 × $SiMe_3$), 11.32 (s, $SiMe_2$), 127.22−129.96 (m, CH of Ph), 143.03 (bs, 2 × $C_{5'}$), 145.50−146.40 (sets of m, 4 × C_{ipso} of Ph), 152.40 (m, 2 × $C_{3'}$ and C_3, C_5), 156−159.4 (sets of m, 2 × $C_{2'}$, C_2, C_6, 2 × $C_{6'}$). Anal. Calcd for $C_{49}H_{55}ClIrP_3Si_4$: C, 54.65; H, 5.15. Found: C, 54.98.; H, 5.46.

Synthesis of Complexes 4 and 5. Complexes **2** (0.1 g, 1.0×10^{-4} mol) or **3** (0.107 g, 1.0×10^{-4} mol), $AgCF_3SO_3$ (0.035 g, 1.5×10^{-4} mol) are placed in a Schlenk flask under nitrogen. Freshly distilled CH_2Cl_2 is then syringed in, and the mixture is allowed to stir for a few seconds. CH_3CN (2 equiv, 10 μL) is then added using a microsyringe. A fluffy precipitate of AgCl appears instantaneously, and ^{31}P NMR spectroscopy indicates that the reaction is complete. Filtration of the mixture through Celite allows for the removal of the AgCl and excess $AgCF_3SO_3$ precipitates. Evaporation of the solvent leads to **4** or **5** in 96% yields.

Data for **4**. ^{31}P NMR ($CDCl_3$), AM_2X: δ 236.17 ($^2J(P-P) = 83.9$, $^1J(P-Rh) = 164.4$, P_A), 225.57 ($^2J(P-P) = 83.9$, $^1J(P-Rh) = 152.4$, P_B). Anal. Calcd for $C_{52}H_{58}ClF_3NO_3P_3RhSSi_4$: C, 53.03; H, 4.96. Found: C, 53.48; H, 5.26.

Data for **5**. ^{31}P NMR ($CDCl_3$), AX_2: δ 204.36 ($^2J(P-P) = 59.60$, P_X), 189.64 ($^2J(P-P) = 48.09$, P_A). Anal. Calcd for $C_{52}H_{58}ClF_3IrNO_3P_3SSi_4$: C, 49.29; H, 4.61. Found: C, 49.50.; H, 4.85.

Synthesis of Complex 6. Method A. Complex **4** is placed under nitrogen and dissolved in 1 mL of CD_2Cl_2. CO is then bubbled through the dark red solution. The solution become orange within seconds and the bubbling is continued for 5 min. ^{31}P NMR spectroscopy indicates that the reaction is quantitative. The solvent is removed under vacuum, the complex is redissolved in THF and precipitated with hexanes. Filtration of the solid followed by drying yields a yellow solid in 93%.

Method B. $[Rh(COD)_2]BF_4$ (0.05 g, mol) and trisphosphinine **1** (0.105 g, mol) are placed in a Schlenk flask. CH_2Cl_2 is then syringed in. The mixture is allowed first to stir at 35 °C during 5 min then CO is bubbled through the dark orange solution for another 5 min. The solution is stirred at room temperature for 30 min and the solvent is reduced to dryness under vacuum. Purification is achieved as in method A.

Data for **6**. ^{31}P NMR (CD_2Cl_2), AB_2X: δ 223.39 ($^2J(P-P) = 83.6$, $^1J(P-Rh) = 144.5$, P_A), 206.31 ($^2J(P-P) = 83.6$, $^1J(P-Rh) = 144.5$, P_B). IR: $\nu(CO) = 2035$ cm^{-1}. Anal. Calcd for $C_{50}H_{55}BF_4OP_3RhSi_4$: C, 56.29; H, 5.20. Found: C, 55.90.; H, 4.95.

Synthesis of complex 7. Complex **3** is placed under nitrogen and dissolved in 3 mL of $CDCl_3$, and 1 equiv of HCl (1 M solution in Et_2O) is then added using a microsyringe. ^{31}P NMR spectroscopy shows the formation of a new complex within 5 min. However, the oxidative addition is reversible, and complex **3** is quantatively reformed within 1 h 30 min upon standing.

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Data for **7**. ^{31}P NMR (CDCl$_3$), AMX: δ 196.95 (^2J(P−P) = 47.92, P$_A$), 194.17 (^2J(P−P) = 36.97, P$_M$), 184.30 (^2J(P−P) = 47.92, ^2J(P−P) = 36.97, P$_X$). ^{1}H NMR (CDCl$_3$): δ −16.6 (pq, ^2J(H−P) = 16.6).

X-ray Structure Determination for 2. Crystallographic data are summarized in Table 1. Red crystals of **2** suitable for diffraction studies were grown by slow diffusion of hexane into a dichloromethane solution of the compound at room temperature. Data were collected at low temperature on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved by direct methods and refined using the Enraf Nonius MOLEN package. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement. Except for disordered solvent molecules, anisotropic temperature factors were used for all heavy atoms. The asymmetric unit contains an undetermined number of highly disordered dichloromethane molecules. These were modeled by introducing chlorine and carbon atoms that were assigned on the basis of peak heights in the difference Fourier map and given arbitrary occupancies. One of those peaks could not be accounted for, giving rise to a large positive residual in the final Fourier map.

Acknowledgment. Financial support by the CNRS and Ecole Polytechnique is gratefully acknowledged.

Supporting Information Available: An X-ray crystallographic file in CIF format, for complex **2** (tris(phosphinine) rhodium(I) chloride) is available on, the Internet only. Access information is given on any current masthead page.

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