Synthesis and Characterisation of *tetrahedro*-Tetraphosphorus Complexes of Rhenium – Evidence for the First Bridging Complex of White Phosphorus

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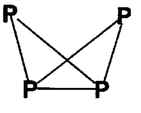
Reaction of white phosphorus with [(triphos)Re(CO)$_2$(OTf)] (**1**) in dichloromethane affords the new tetraphosphorus complex [(triphos)Re(CO)$_2$(η^1-P$_4$)](OTf) (**2**) [triphos = MeC(CH$_2$PPh$_2$)$_3$; OTf = OSO$_2$CF$_3$]. Compound **2** reacts with a second equivalent of **1** to give the binuclear complex [{(triphos)Re(CO)$_2$}$_2$(μ,η^1,η^1-P$_4$)](OTf)$_2$ (**3**) in which a *tetrahedro*-P$_4$ ligand behaves as tethering unit between two [(triphos)Re(CO)$_2$]$^+$ moieties. Complexes **2** and **3** represent the first soluble metal complexes of the tetraphosphorus molecule where the P$_4$ ligand has not undergone any major modification.

The reaction of transition-metal complexes with white phosphorus has been extensively studied and has resulted in a large variety of P$_x$ ligands ($x < 15$) which are often unpredictable.[1] In most instance, the integrity of the P$_4$ molecule is not retained in the final complex and extensive fragmentation and aggregation processes take place.[1][2] In some cases the four atoms of the P$_4$ ligand are incorporated into the coordination polyhedron of the resulting metal complex affording derivatives containing the tetraphosphabicyclobutane[2d,3] (**I**) or the tetraphosphabutadiene[3f,4] (**II**) units. Complexes containing the *cyclo*-P$_4$ (**III**) moiety are also known.[3f,5] In contrast, there are still very few compounds featuring an intact P$_4$ molecule in the form of a simple mono-*hapto*-P$_4$ (**IV**) ligand although this coordination mode would mimic the initial interaction of white phosphorus with the metal species.



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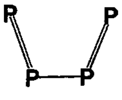

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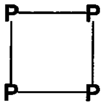

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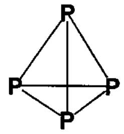
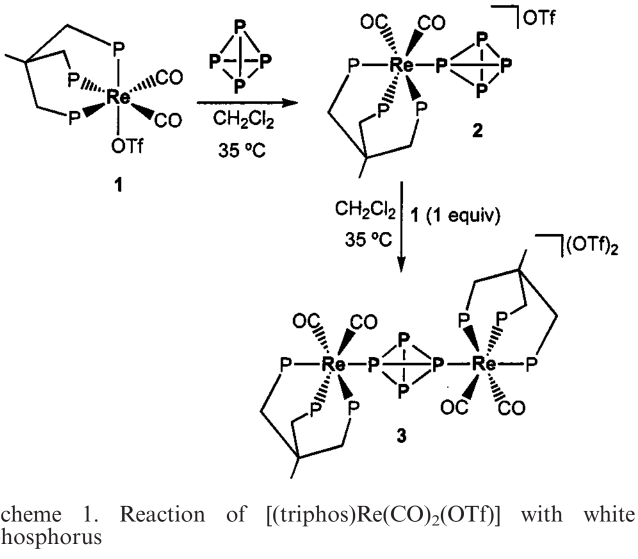


IV

To the best of our knowledge, η^1-tetrahedral P$_4$ complexes remain limited to the [(NP$_3$)M(η^1-P$_4$)] derivatives [M = Ni, Pd; NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$] described in the late 1970s by Sacconi et al.[6,9] The nickel complex was authenticated by X-ray crystallography which confirmed the presence of a tetrahedral Ni^0 complex with one coordination position taken by one of the four P atoms of an intact P$_4$ molecule.[6a] Unfortunately, these complexes are quite insoluble in common organic solvents thus *preventing any characterisation of the tetraphosphorus ligand in solution and any investigation of the reactivity of the coordinated P*$_4$ molecule. Despite synthetic efforts, related complexes have not yet been described in the literature.[1] Now, in this report, we detail the synthesis and the spectroscopic characterisation of the first examples of soluble mono- and dinuclear tetraphosphorus metal complexes for which the η^1-coordination mode of the P$_4$ molecule has been confirmed by ^{31}P-NMR spectroscopy.[7]



Scheme 1. Reaction of [(triphos)Re(CO)$_2$(OTf)] with white phosphorus

Reaction of a dichloromethane solution of the weakly coordinated triflate complex [(triphos)Re(CO)$_2$(OTf)][8] (**1**) [triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane)] with a small excess of white phosphorus at ca. 35°C under nitrogen (Scheme 1), affords, after addition of ethanol/*n*-

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hexane and fast concentration under nitrogen, mustard-coloured microcrystals of [(triphos)Re(CO)$_2$(η^1-P$_4$)](OTf) (**2**) in good yield. Once thus obtained, **2** is slightly air-sensitive and can be manipulated in the air and maintained at room temperature without noticeable decomposition for a few hours. When dissolved in various solvents (dichloromethane, thf, chloroform), **2** is air- and moisture-sensitive and quickly decomposes to an orange uncharacterised solid. **2** exhibits a particularly informative ^{31}P{^{1}H}-NMR spectrum consisting of a temperature-invariant AB$_2$MX$_3$ spin system featuring strong couplings between the nuclei P$_M$ and P$_X$ ($^1J_{PMPX}$ = 235.7 Hz) and P$_A$ and P$_M$ ($^2J_{PAPM}$ = 204.7 Hz). The magnitude of the latter coupling diagnoses the *trans* disposition between one of the triphos P atoms and the unique Re-bonded P atom of the *tetrahedro*-tetraphosphorus ligand. The invariance of the ^{31}P-NMR spectrum indicates that no dynamic process is exchanging the four atoms of the P$_4$ ligand and points to the existence of a P$_4$ moiety freely rotating around the P$_A$−Re−P$_M$ axis. This causes the magnetic equivalence of the basal P atoms of the P$_4$ tetrahedron whose signal appears as a doublet at $\delta = -488.9$ in the high-field region of the spectrum [see trace (a) in Figure 1]. Noticeably, the two sets of resonances of the P$_4$ ligand are slightly deshielded upon coordination by ca. 38.0 ppm (P$_X$) and ca. 136.4 ppm (P$_M$, $\delta = -390.52$) when compared with the free molecule of white phosphorus ($\delta = -526.9$). These relatively small coordination chemical shifts [$\Delta = \delta(\mathrm{P_{M/Xcoord}}) - \delta(\mathrm{P_{4free}})$] suggest that, upon coordination to the (triphos)rhenium moiety, only a minor perturbation of the electron density of the P$_4$ tetrahedron has occurred.

In keeping with these observations, the "distal" P$_3$-face unit of the *tetrahedro*-P$_4$ ligand is still endowed with reactivity towards unsaturated transition metal complexes and electrophiles and we envisage the generation of several new polynuclear compounds and P$_4$-functionalisation products from **2**. We are currently exploring this interesting area and preliminary tests confirm our hypothesis.

As an example, when a dichloromethane solution of **2** is treated with a small excess of **1**, coordination of a second [(triphos)Re(CO)$_2$]$^+$ moiety to the P$_4$ ligand takes place and the dinuclear complex [{(triphos)Re(CO)$_2$}$_2$(μ,η^1,η^1-P$_4$)](OTf)$_2$ (**3**) may be isolated as air-stable pale yellow microcrystals after workup (yield 90%). On the basis of the spectroscopic data, **3** is assigned a bimetallic structure where two [(triphos)Re(CO)$_2$]$^+$ fragments are held together by a tethering P$_4$ unit which behaves as a bridging μ,η^1,η^1 ligand. The formation of a dimeric compound is witnessed by the drastic modification of the high-field part of the ^{31}P{^{1}H}-NMR spectrum which, on moving from **2** to **3**, transforms into an AA′B$_2$B′$_2$MM′X$_2$ spin system [see trace (b) in Figure 1]. Interestingly, upon coordination of the second [(triphos)Re(CO)$_2$]$^+$ unit, a more relevant downfield shift of the signals of the metallated P atoms takes place while the resonance ascribable to the uncoordinated P$_2$ atoms moves slightly downfield. To the best of our knowledge, this kind of coordination mode for a *tetrahedro*-P$_4$ molecule is unprecedented in the rich chemistry of main-group−transition-metal compounds.[1]

Investigations are continuing in our laboratories with the focus on the reactivity of the soluble P$_4$ ligand in **2** and **3**

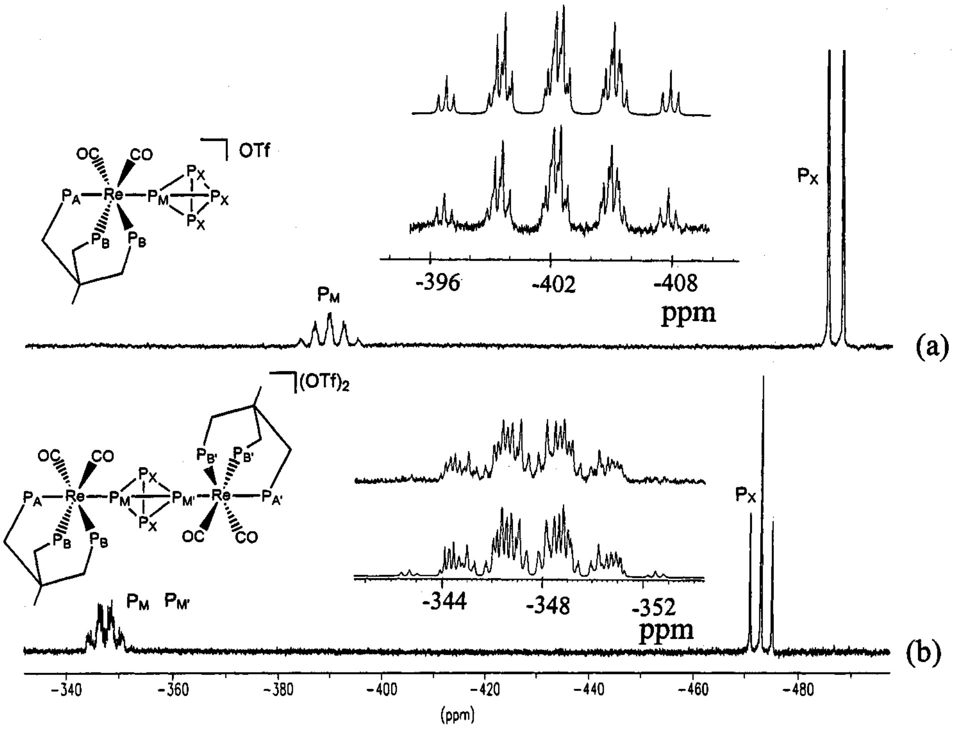

Figure 1. ^{31}P{^{1}H}-NMR spectra of **2** (trace a) and **3** (trace b) in the high-field region (81.01 MHz, CD$_2$Cl$_2$, 298 K, 85% H$_3$PO$_4$ reference); the insets show the computed and experimental multiplets of the metallated P atom of the P$_4$ ligand in the two complexes.

as well as on the possible transferability of naked P atoms to inorganic and organic molecules.

Experimental Section

General Information: Dichloromethane was purified by distillation under nitrogen from P_2O_5. Complex **1** was prepared as described in the literature.[8] − ^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded with a Bruker AC200 or Bruker AVANCE DRX 500 spectrometers operating at 200.13 or 500.13 MHz (^{1}H) and 81.01 or 202.45 MHz (^{31}P), respectively. Peak positions are relative to tetramethylsilane (^{1}H) or 85% H_3PO_4 with downfield values taken as positive (^{31}P). The ^{31}P,^{31}P-2D COSY NMR experiments were conducted with an AVANCE DRX 500 Bruker spectrometer in the absolute magnitude mode using a 90° pulse after the incremental delay. − Elemental analyses (C, H) were performed using a Carlo Erba model 1106 elemental analyzer.

Complex 2: A dichloromethane solution (20 mL) of **1** (0.50 g, 0.49 mmol) was treated at ca. 35°C with a small excess of white phosphorus (0.08 g, 0.64 mmol) under nitrogen. Addition of ethanol/*n*-hexane (10 mL, 1:2 v/v) and concentration of the resulting solution under a brisk current of nitrogen, gave mustard-coloured microcrystals of **2** which were filtered under nitrogen and washed with ethanol (2 × 3 mL) and light petroleum ether (2 × 5 mL). Yield 76%. − IR (nujol mull): $\tilde{\nu}_{CO}$ = 1967 vs, 1912 vs; $\tilde{\nu}_{OTf}$ = 1265 s cm^{-1}. − ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ = 7.80−6.95 (30 H, m, phenyl protons), 2.70−2.40 (6 H, m, PCH_2), 1.58 (3 H, q, $^4J_{HP}$ = 2.8 Hz, CH_3). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 81.01 MHz): AB_2MX_3 spin system; δ = −7.31 (1 P, dtq, $^2J_{PAPM}$ = 204.7 Hz, $^2J_{PAPB}$ = 23.7 Hz, $^3J_{PAPX}$ = 5.2 Hz, P_A), −14.59, (2 P, dd, $^2J_{PBPM}$ = 31.4 Hz, P_B), −390.52 (1 P, qdt, $^2J_{PMPX}$ = 235.7 Hz, P_M), −488.90 (3 P, dd, P_X); the assignments were confirmed by ^{31}P,^{31}P-COSY 2D-NMR spectroscopy and by computer simulation of the spectra. − FABMS; *m/z*: 867 [M$^+$ − P_4]; 839, 811 [M$^+$ − P_4 − *n*CO; *n* = 1−2]. − $C_{44}H_{39}F_3O_5P_7ReS$ (1139.87): calcd. C 46.36, H 3.45; found C 46.1, H 3.4.

Complex 3: Into a Schlenk flask, containing a dichloromethane solution (20 mL) of **2** (0.25 g, 0.22 mmol), a small excess of **1** (0.25 g, 0.25 mmol) was added under nitrogen as a solid in small portions. The solution was slowly heated at 35°C for 15 min and then 10 mL of an ethanol/*n*-hexane mixture (1:2 v/v) was added. Workup as described above for **2** afforded pale yellow microcrystals of **3** which were collected in the air and washed with ethanol (2 × 3 mL) and light petroleum ether (2 × 5 mL). Yield 90%. − IR (nujol mull): $\tilde{\nu}_{CO}$ = 1958 vs, 1919 vs; $\tilde{\nu}_{OTf}$ = 1267 s cm^{-1}. − ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ = 7.75−6.80 (60 H, m, phenyl protons), 2.90−2.50 (6 H, m, PCH_2), 1.72 (3 H, q, $^4J_{HP}$ = 2.9 Hz, CH_3). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 81.01 MHz): δ = $AA'B_2B'_2MM'X_2$ spin system; −9.18 (2 P, m, $^2J_{PAPB}$ and $^2J_{PA'PB'}$ = 23.5 Hz, $^2J_{PAPM}$ and $^2J_{PA'PM'}$ = 201.0 Hz, $^3J_{PAPX}$ and $^3J_{PA'PX'}$ = 5.0 Hz, P_A and $P_{A'}$), −15.03 (4 P, m, $^2J_{PBPM}$ and $^2J_{PB'PM'}$ = 28.2 Hz, P_B and $P_{B'}$), −347.61 (2 P, m, $^1J_{PMPX}$ and $^1J_{PM'PX'}$ = 168.8 Hz, $^1J_{PMPM'}$ = 182.4 Hz, P_M and $P_{M'}$), −473.37 (2 P, td, P_X). − $C_{88}H_{78}F_6O_{10}P_{10}Re_2S_2$ (2155.84): calcd. C 49.03, H 3.65; found C 48.8, H 3.5.

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