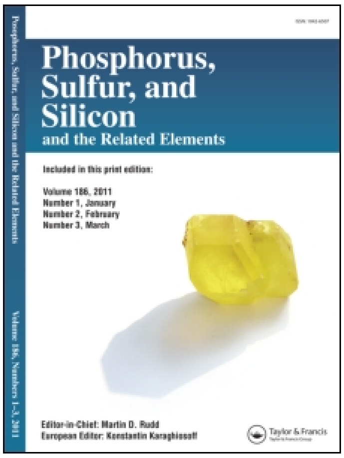

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Bimetallic Activation of White Phosphorus

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The formation of novel complexes [M(dppm)($Ph_2PCH_2PPh_2PPPP$)]OTf (M = Rh, Ir, dppm = bisdiphenylphoshinomethane, OTf = OSO_2CF_3) bearing in their coordination sphere a new type of oligophosphorus ligands results from bimetallic activation and consequent transformation of white phosphorus. These complexes display electrophilic properties and can be activated either electrochemically or by interaction with nucleophilic reagents.

Keywords Bimetallic cooperativity; white phosphorus; rhodium and iridium complexes; polyphosphorus ligands

INTRODUCTION

The development of selective procedures for the preparation of organophosphorus compounds directly from P_4 is an important goal in modern phosphorus chemistry.[1a] In this respect, particular attention has been devoted to the rationalization of the reactivity patterns governing the formation of organometallic complexes bearing in their

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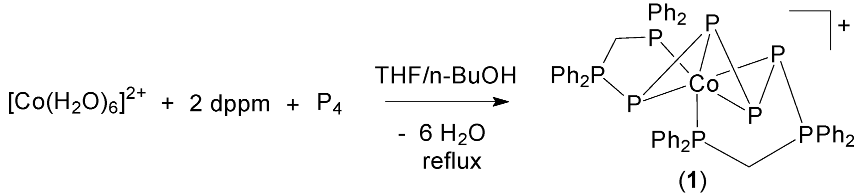
coordination sphere oligophosphorus moieties and to find out possible protocols to accomplish their functionalization and activation.[1]

RESULTS AND DISCUSSION

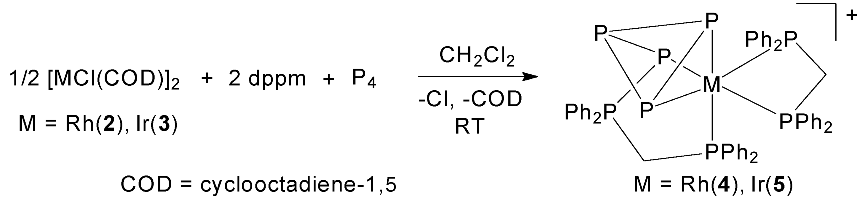
The reactivity of white phosphorus with transition metals is characterized by a vast diversity of bonding conditions and structural motifs resulting in a variety of P_x ($1 < x < 7$) units ranging from single phosphido atoms, either in capping position or embedded in a cluster moiety, to high nuclearity polyphosphorus ligands.[1] Indeed, when the tetraphosphorus array is preserved, different topologies are observed containing either intact or activated P_4 molecule. In the former cases, both monohapto[2] or dihapto coordination modes are observed,[3] whereas the latter topology may feature more diversified coordination types following the opening of one or more edges which generally result in the formation of acyclic tetraphosphorus chains.[1] These units find their thermodynamic sink by either bridging two metal moieties[4] or undergoing electrophilic or nucleophilic attacks from ancillary ligands to form new P—H, P—C and P—P bonds.[5] This bonding situation was observed in the unique cobalt complex [Co($Ph_2PCH_2PPh_2$*PPPP*$Ph_2PCH_2PPh_2$)]BF_4 (**1**) synthesized in Florence more than two decades ago from simple cobalt(II) hydrated salts, dppm (dppm = $Ph_2PCH_2PPh_2$) and white phosphorus in boiling THF/butanol mixture (Scheme 1).[6]



SCHEME 1

The mechanism of formation of the cobalt coordinated tetraphosphabutadiene *zig-zag* P_6 chain in **1** was never clearly understood. Our recent studies of this intriguing activation process have allowed us to collect a variety of experimental results clearly showing the existence of an unexpected bimetallic P_4 activation pathway which may well account for the formation of **1**. In order to get additional information about this process involving Co(II) to Co(I) reduction, we decide to investigate the reactivity of the related M(I) complexes [M(dppm)$_2$]OTf [M = Rh (**2**), Ir (**3**); OTf = OSO_2CF_3] towards white phosphorus.[7]

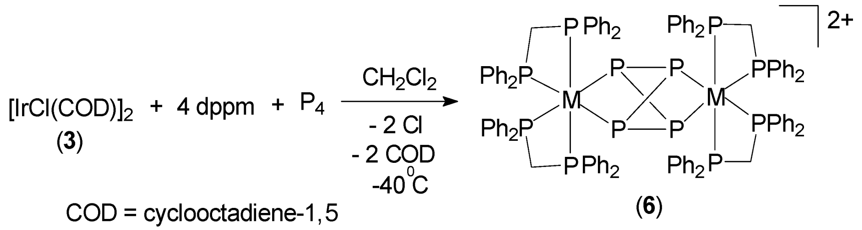
The reaction of [M(dppm)$_2$]OTf with white phosphorus in CH_2Cl_2 at room temperature under nitrogen and subsequent workup gave the novel complexes [M(dppm)($Ph_2PCH_2PPh_2$*PPPP*)]OTf as either orange [M = Rh, (4)] or light yellow microcrystals [M = Ir, (5)] (Scheme 2).



SCHEME 2

Complexes 4 and 5 were characterized by ^1H and ^{31}P NMR spectroscopy, ESI-MS, elemental analysis and single crystal X-ray crystallography.[7]

In order to understand the mechanism ruling the formation of the organometallic complexes **4** and **5** better, we decided to monitor the reactions of **2** and **3** with P_4 by in situ ^{31}P NMR spectroscopy. The iridium complex **3**, which shows the same reactivity of the rhodium analogue, but with a higher kinetic inertness, has been used to develop this part of the present research. The reduced reactivity of the complex **3**, in comparison with its analog **2**, practically slows down the process and has allowed us, firstly, to better follow the reaction by NMR methods and, second, to intercept some of the intermediates that traverse the formation of the final adduct **5**. It was observed that in CD_2Cl_2 white phosphorus immediately reacts with the iridium complex **3** already at −40°C to afford a highly fluxional intermediate species (**6**) featuring three broad resonances at −55.9, −62.2 and −82.6 ppm with identical intensity corresponding to 4P each (Figure 1, Scheme 3).



SCHEME 3

Lowering the temperature to −90°C does not resolve the signals into any fine structure suggesting that a very low energy process is responsible for the fluxionality of the formed intermediate. Slow transformation

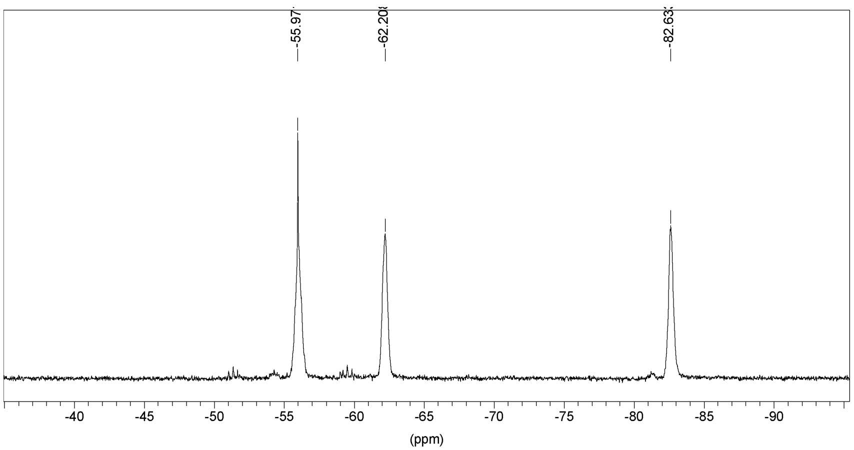
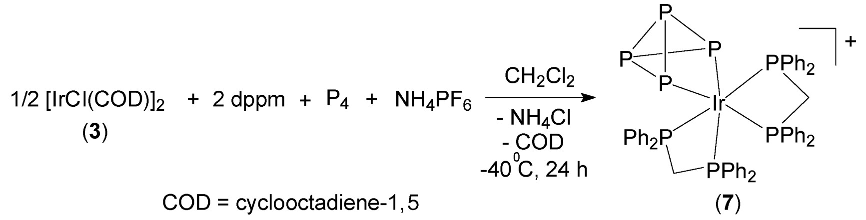


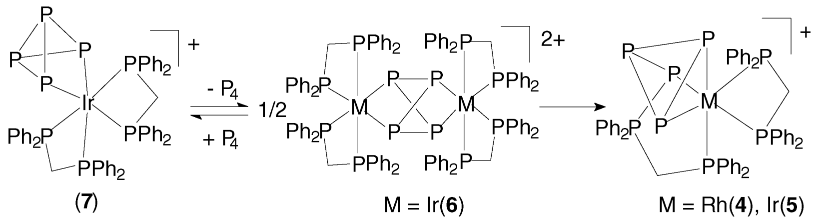
FIGURE 1 $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between 3 and white phosphorus (Ir:P_4 = 2:1) recorded at −40°C in CD_2Cl_2.

of this intermediate species to the final product **5** takes place on increasing the temperature to 25°C. At this temperature, the conversion completes after 2 days. On keeping the iridium/P_4 solution in the refrigerator at −40°C slowly affords a new iridium complex $[Ir(dppm)_2(\eta^2\text{-}P_4)]OTf$ (**7**), which likely was formed via straightforward oxidative addition to P_4(Scheme 4).



SCHEME 4

Pale yellow crystals of **7** could be separated out from the reaction solution after standing overnight at this temperature and were characterized by standard spectroscopic methods and single crystal X-ray crystallography.[7] Remarkably, dissolving a solid sample of **7** in CH_2Cl_2 does not afford directly **5**, but suggests the occurrence of a slow transformation of **7** back to **6** while free P_4 (singlet at $\delta = -527$) is slowly accumulated in the solution. When we increase the temperature, **6** is converted into **5** (Scheme 5).



SCHEME 5

An in-depth study of this system using low-temperature ^{31}P NMR spectroscopy was performed in order to clarify the nature of the elusive intermediate **6**. For this purpose, stock solutions of **3** and P_4 in CD_2Cl_2 were carefully mixed at low temperature (−40°C) in screw-cap 5 mm NMR tubes to prepare four different solutions with **3**/P_4 ratios of 1/0.25, 1/0.50, 1/1, and 1/2. The results of these analyses were intriguing and may be summarized as follows: at the lower P_4 concentration about 50% of unreacted **3** is observed, while the rest of the iridium complex forms **6**. A clean transformation consuming all the white phosphorus added is noticed when the amount of P_4 is doubled (1/0.50, Figure 1). In this event, the intermediate **6** is the only NMR detectable iridium specie. Doubling of white phosphorus ($\geq$1/1) does afford neither the composition of the reaction mixture nor the product distribution showing only free P_4 and **6** in the reaction mixture. An important observation concerns the total absence of any resonance attributable to the Ir(III) monometallic species **7**, which is formed after prolonged standing at low temperature. Thus, the mononuclear species **7** is not directly related to the activation process which likely goes ahead through the formation of a bimetallic complex $[\mathrm{Ir(dppm)}_{22}(\mu,\eta^2{:}\eta^2\text{-}\mathrm{P}_4)]^{2+}$(**6**) where a doubly activated phosphorus tetrahedron is bridging two equivalent $\mathrm{Ir(dppm)}_2$ moieties. Double edge activation of P_4 is not common, but has a few well-documented precedents in the scientific literature. Important examples are $[\{\mathrm{Cp^*Co(CO)}\}_2(\mu,\eta^2{:}\eta^2\text{-}\mathrm{P}_4)]$[8] and $[\{\mathrm{HC(CMeNAr)_2}\}_2\mathrm{Al}_2(\mu,\ \eta^2{:}\eta^2\text{-}\mathrm{P}_4)]$ (Ar = 2,6-$^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$).[4] Although we think that our putative formulation of **6** stands on very robust experimental basis, we cannot a priori exclude a different solution structure for **6**. This is because species featuring $\mu,\eta^1{:}\eta^2\text{-}\mathrm{P}_4$ or $\mu,\eta^1{:}\eta^1\text{-}\mathrm{P}_4$ ligands could also well account for the fluxional behaviour of **6** and to be invoked as putative precursors to mediate the formation of **5** by nucleophilic attack of one dppm end to the activated P_4.

The bimetallic activation of white phosphorus has been already recognized of importance by Cummins et al. in some Mo(III) complexes,[9] and it has been demonstrated experimentally relevant in contrasting

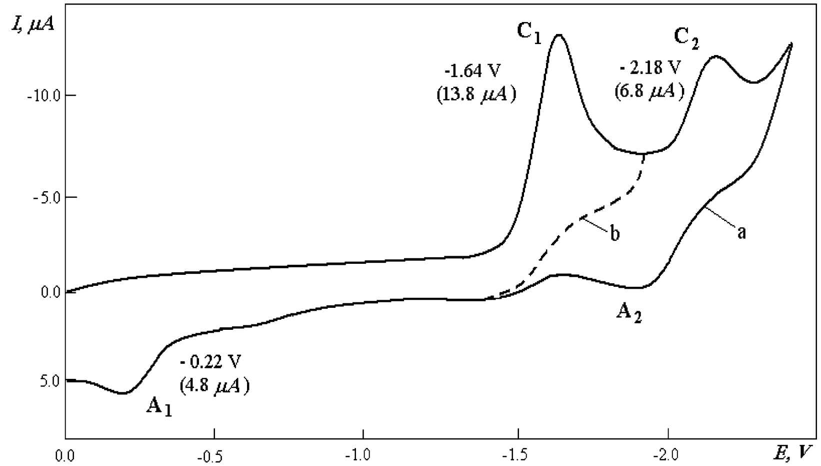


FIGURE 2 Cyclic voltammogram (cathodic part) in DMF of complex 4 (1.0×10^{-2} M) on glassy carbon (GC) electrode in the presence of 0.1 M $(NBu_4)BF_4$ (CV curve was recorded at the first scan: (a) from 0.00 V to −2.50 V and back to 0.00 V; (b) from 0.00 V to −1.90 V and back to 0.00 V; *vs* $Ag/AgNO_3$ 1.0×10^{-2} M inCH_3CN; 50 mV s^{-1}).

the P_4 degradation in the dinuclear complex $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^1:\eta^1\text{-}P_4)](PF_6)_2$[10] with respect to the mononuclear adduct $[CpRu(PPh_3)_2(\eta^1\text{-}P_4)]PF_6$.[2]

As a final note, we report also that electrochemical behaviour of the novel complexes **4** and **5** has been preliminarily investigated using the method of cyclic voltammetry. Both complexes **4** and **5** are electrochemically active at cathodic potentials as reflected in the cyclic voltammogram (Figure 2) and undergo a two-electron reduction at the cathodic peak $\mathbf{C_1}$ (two-electron process).

Thus, complexes **4** and **5** can be activated electrochemically by irreversible transfer of two electrons or by interaction with nucleophiles as confirmed in our recent work.[11] Theoretical studies are in progress to clarify the nature of **6** and the general mechanism accounting for the intriguing single and double P-P coupling between dppm and activated P_4.[12]

In summary, we have shown that bimetallic cooperativity is relevant to promote P_4 activation and to govern the activation products as for the recent reports in N_2[13] and P_4[10] chemistry. Complexes **4** and **5** represent a new bonding mode for a metal-activated P_4 ligand featuring an unprecedented *pentaphosphorus* moiety resulting from the intramolecular coupling of the metal-activated P_4-*tetrahedron* with a neighbouring nucleophilic dppm ligand. The presence of a strong nucleophile seems therefore of great importance in promoting the activation and the functionalization of white phosphorus[14] on the way to phosphorus containing compounds.

A detailed study of the reactivity of these complexes is currently under investigations and will be published in due time.

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