P_4 Activation

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Heterobimetallic Cooperation Mediates the Transformation of White Phosphorus into Zwitterionic *catena*-Phosphonium(+)diphosphenide(−) Ligands**

*Maria Caporali, Pierluigi Barbaro, Luca Gonsalvi, Andrea Ienco, Dmitry Yakhvarov, and Maurizio Peruzzini**

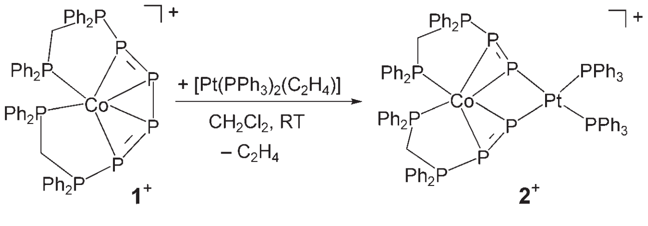
Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

White phosphorus, P_4, the most reactive allotrope of the element, is readily available from rock phosphates and is widely used for the chemical manufacturing of a great variety of organophosphorus derivatives.[1] In a typical industrial procedure, P_4 is treated with Cl_2 at high temperature to yield phosphorus chlorides, which are subsequently treated with organic substrates to afford the organophosphorus derivatives. The growing worldwide market for phosphorus derivatives and increasingly rigorous environmental regulations, which ban dangerous precursors such as chlorine from large-scale industrial processes, are stimulating the quest for methods that avoid chlorine and functionalize white phosphorus under milder conditions.[2] The most efficient approach in this regard would be an as-yet unknown metal-catalyzed functionalization of P_4,[3] although several contributions from our group[4,5] and others[6] have shown the importance of stoichiometric activations mediated by bimetallic transition-metal complexes. Recently, Bertrand et al. have shown that metal-free activation of P_4 can also be achieved by using two equivalents of cyclic alkyl aminocarbenes to synergically activate white phosphorus.[7]

Herein we report our findings that white phosphorus can be activated in a stepwise fashion by two different transition-metal units, which initially activate the P_4 tetrahedron and then break the activated polyphosphorus unit into two zwitterionic diphenyl(alkyl)phosphonium(+)diphosphenide(−) molecules.

The reaction of white phosphorus with $Co(BF_4)_2{\cdot}6H_2O$ and bis(diphenylphosphino)methane (dppm) in refluxing THF/butanol gives $[Co(Ph_2PCH_2PPh_2\textit{PPPP}Ph_2PCH_2PPh_2)]BF_4$ (**1**-BF_4), whose synthesis[8] represents a turning point in the coordination chemistry of white phosphorus.[9] Complex $\mathbf{1}^+$ contains a surprising P_6 ligand which originates from the nucleophilic attack of two PPh_2 ends from two different dppm ligands on the η^4-tetraphosphabutadiene moiety formed by opening of the P_4 molecule. A perusal of the bonding distances—the external P−P distances are shorter then the internal ones (2.172 vs. 2.197 Å)—has allowed Midollini and co-workers to formally attribute the oxidation state −I to Co and to describe the charge distribution of the new hexaphosphorus ligand as a $P^{(+)}{-}P{=}P{-}P{=}P{-}P^{(+)}$ dication where two phosphonium moieties are formally located at each P_6 end.[8] Attempts to react this unique fragment with several electrophiles and nucleophiles were generally unsuccessful, thus indicating the high stability of the η^4-tetraphosphabutadiene ligand.[10]

We have found that the reaction of **1**-BF_4 with $[Pt(C_2H_4)(PPh_3)_2]$ in dichloromethane at room temperature affords the heterobimetallic complex $[Co(\mu,\eta^{1:2:1}\text{-}P{=}P\text{-}PPh_2CH_2PPh_2)_2\{Pt(PPh_3)_2\}]BF_4$ (**2**-BF_4) in almost quantitative yield by elimination of ethene and insertion of the carbene-like PtL_2 moiety into the central P−P bond of the P_6 ligand of $\mathbf{1}^+$(Scheme 1).[11] Work-up as detailed in the Experimental Section gave **2**-BF_4 as a dark brown microcrystalline material in good yield. Complex $\mathbf{2}^+$ was characterized by elemental analysis, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, ESI mass spectrometry, and single-crystal X-ray diffraction (Figure 1).[12] The crystal structure of **2**-BF_4 contains tetrafluoroborate anions, $[Co(\mu,\eta^{1:2:1}\text{-}P{=}P\text{-}PPh_2CH_2PPh_2)_2\{Pt$-



Scheme 1. Synthesis of complex $\mathbf{2}^+$.

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[*] Dr. M. Caporali, Dr. P. Barbaro, Dr. L. Gonsalvi, Dr. A. Ienco, Dr. M. Peruzzini
Istituto di Chimica dei Composti Organometallici
Consiglio Nazionale delle Ricerche (ICCOM CNR)
Via Madonna del Piano, 10, 50019 Sesto Fiorentino (Italy)
Fax: (+39) 055-5225-203
E-mail: mperuzzini@iccom.cnr.it
Homepage: http://www.iccom.cnr.it

Dr. D. Yakhvarov
A. E. Arbuzov Institute of Organic and Physical Chemistry
Russian Academy of Sciences
Arbuzov str. 8, 420088 Kazan (Russian Federation)

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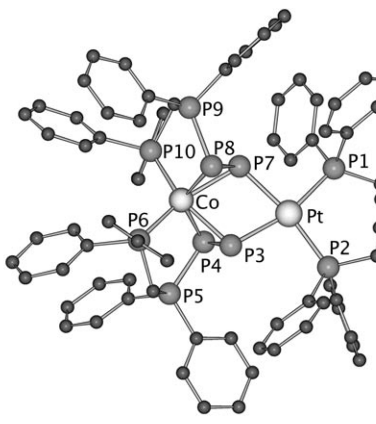

Figure 1. Molecular structure of the heterobimetallic cation $\mathbf{2}^+$. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co–P10 2.226(3), Co–P6 2.216(3), P3–P4 2.179(4), P7–P8 2.185(4), Pt–P7 2.334(3), Pt–P1 2.317(3); P6-Co-P10 110.77(12), P3-Co-P4 56.67(11), P3-Co-P7 74.43(11), P7-Co-P8 56.57(11), P3-P4-P5 89.19(14), P7-P8-P9 90.06(15).

$(PPh_3)_2\}]^+$ cations, and interspersed molecules of ethanol and dichloromethane in 1:1:2:1 ratio.

The original P_6 "zigzag" chain in $\mathbf{1}^+$ has been cleaved upon reaction with the $Pt(PPh_3)_2$ moiety to form two separate P_3 moieties, namely RP5-P4-P3 and RP9-P8-P7, which are nearly identical in light of their bond lengths and angles. This reaction occurs with complete regioselectivity and may be viewed as the formal oxidative cleavage of the internal P–P single bond of the η^4-tetraphosphabutadiene unit $P^{(+)}$–P=P–P=P–$P^{(+)}$. The P3–P7 bond length changes from 2.197(3) Å in $\mathbf{1}^+$ to 2.823(4) Å in $\mathbf{2}^+$ following the insertion of PtL_2, while the P3-Co-P7 angle opens from 57.2(1)° to 74.43(11)°. The distance between P3 and P7 excludes the existence of any residual weak interaction between these two atoms in $\mathbf{2}^+$. The other bond distances (P–P and Co–P) and the P-Co-P bond angles remain virtually unchanged with respect to those in $\mathbf{1}^+$. Thus, with the noticeable exception of atoms P3 and P7, the coordination environment around cobalt in complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ is almost superimposable (see the Supporting Information). The formal oxidative charge at the cobalt center is also maintained in $\mathbf{2}^+$ as for the parent compound $\mathbf{1}^+$, that is, Co^{-I}. The geometry around the cobalt center is a distorted tetrahedron and the core of the bimetallic complex contains a C_2 axis of symmetry, as previously found for complex $\mathbf{1}^+$. The coordination geometry around platinum is square planar. The torsion angles P5-P4-P3-Pt and P9-P8-P7-Pt are 154.03(12)° and 158.23(13)°, respectively.

The most outstanding feature of $\mathbf{2}^+$ concerns the electronic nature of the two P_3 ligands which hold the two metal atoms together. Based on the electron charge distribution, the nature of this ligand can be described as a zwitterionic diphenyl(alkyl)phosphonium(+)diphosphenide(−) molecule, $RPh_2P^{(+)}$-P=$P^{(-)}$ ($R = Ph_2PCH_2$), where the negative charge is placed on the μ-Co,Pt-bridging P atom and the positive one on the opposite PPh_2R phosphonium P atom. The average P=P bond length in the diphosphenide moiety is 2.182(4) which is longer than the value found for the only known phosphanetriylphosphonium cation (2.025(1) Å)[13] and in agreement with the P=P bond length in diphosphenes coordinated to transition metals.[14] In the case at hand, the diphosphenide section of the zwitterion acts as a two-electron π-donor towards Co and, additionally, as a two-electron σ-donor towards Pt^{II}. There is also some back-donation from the cobalt center into the π*-orbital of the P–P=P group.[15] A similar bonding situation has been documented in diphosphene systems by Power and co-workers, who have reported a bimetallic iron complex containing a diphosphene ligand σ,π-bonded to two $Fe(CO)_4$ units with a P=P bond length of 2.184(2) Å, as is the case herein.[16]

In keeping with the solid-state structure and the analysis of the electronic properties of $\mathbf{2}^+$, the $^{31}P\{^1H\}$ NMR spectrum exhibits a temperature-invariant AA′BB′CC′DD′EE′X splitting pattern ($X = {}^{195}Pt$; Figure 2). The relatively high value of the $^1J_{P7,P8}$ and $^1J_{P3,P4}$ coupling constants (289.6 Hz) matches that found in other diphosphene complexes and supports the partial double-bond character of these bonds. The coupling constants of the two naked diphosphene P atoms with platinum ($^1J_{Pt,P3} = {}^1J_{Pt,P7} = 525.0$ Hz), which are much smaller than those with the triphenylphosphine P atoms ($^1J_{Pt,P1} = {}^1J_{Pt,P2} = 2585.0$ Hz), are also worth noticing. A similar behavior has been observed for other compounds containing naked P atoms or units coordinated to the $Pt(PPh_3)_2$ fragment[11] and has been ascribed to the nature of the M–P bond.[17]

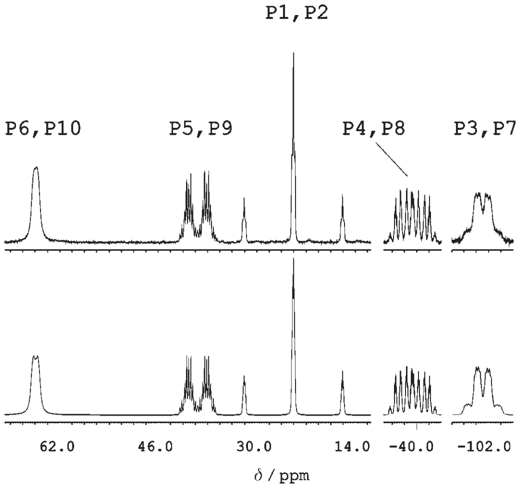

Figure 2. Computed (bottom) and experimental (top) $^{31}P\{^1H\}$ NMR spectra of $\mathbf{2}^+$ (CD_2Cl_2, 161.89 MHz, 294 K). The labeling is the same as in Figure 1.

The μ,$\eta^{1:2:1}$-P_3 ligands found in $\mathbf{2}^+$ belong to a growing and important family of *catena*-phosphorus compounds whose systematization has been proposed recently.[18] Whereas neutral[19] and anionic *catena*-phosphorus species[20] are relatively well known, *catena*-phosphorus cations are still quite rare[18] and no examples of polyphosphorus zwitterions have been reported to date. Additionally, none of the known linear *catena*-phosphorus cations has been so far obtained from white phosphorus.[21]

This work demonstrates that the stepwise cooperation of two different transition metal units may bring about the transformation of P_4 into intriguing organophosphorus compounds. Thus, the known reaction of white phosphorus with

Co^{2+} ions and dppm may be viewed as the first step of a modular process where the carbene-like PtL_2 unit selectively cuts the P_6 chain to yield two doubly metalated *catena*-zwitterionic diphenyl(alkyl)phosphonium(+)diphosphenide(−) ligands. The resulting $RPh_2P^{(+)}{-}P{=}P^{(-)}$ unit is the first example of an unsaturated phosphonium diphosphenide ligand tethering two different metal units and may be a potentially versatile functional organophosphorus group to be used with organic and organometallic species.

Experimental Section

2-BF_4: Addition of solid $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$[22] (90 mg, 0.12 mmol) to a stirred solution of **1**-BF_4 (125 mg, 0.12 mmol) in 10 mL of CH_2Cl_2 under nitrogen at room temperature caused an immediate color change from dark red to dark brown. $^{31}P\{^1H\}$ NMR analysis of this solution showed the complete formation of **2**-BF_4. Addition of ethanol (4 mL) and slow concentration under nitrogen gave dark brown crystals suitable for X-ray crystallography. These crystals were filtered off, washed with *n*-pentane, and dried in a stream of nitrogen. Yield: 168.7 mg (80 %). C,H analysis (%) calcd for $C_{86}H_{74}BCoF_4P_{10}Pt$ (1758.1): C 58.75, H 4.24; found: C 58.94, H 4.29. ESI-MS: m/z (%) 1670.21 (51) $[Co(\mu,\eta^{1:2:1}\text{-}P{=}P\text{-}PPh_2CH_2PPh_2)_2\{Pt(PPh_3)_2\}]^+$, 835.10 (100) $[M^{2+}]$; ^1H NMR (400.13 MHz, CD_2Cl_2, 294 K): $\delta = 7.4\text{–}6.3$ (m, 70H; Ph), 3.2 (m, 2H; CH_2), 2.2 ppm (m, 2H; CH_2); $^{31}P\{^1H\}$ NMR: See Figure 2 and the Supporting Information.

Details of the crystal-structure determinations of **2**-$BF_4\cdot 2\,EtOH\cdot CH_2Cl_2$ are provided in the the Supporting Information, which also includes complete ORTEP drawings, ^{31}P NMR spectroscopic data, and copies of the $^{31}P\{^1H\}$ NMR spectra.

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