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Phosphorus Complexes

$[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$: A Phospha-Organometallic Complex Obtained by the Transition-Metal-Mediated Activation of the Heptaphosphide Trianion**

*Caroline M. Knapp, Bethan H. Westcott, Melissa A. C. Raybould, John E. McGrady, and Jose M. Goicoechea**

The chemical activation of white phosphorus by transition-metal complexes is a versatile albeit often unpredictable route to compounds containing homoatomic phosphorus ligands with nuclearities ranging between 1 and 29.[1] In principle, many of the same transformations available for P_4 should also be possible employing other closely related cage compounds, such as the bare Group 15 Zintl anion $[P_7]^{3-}$, although the products resulting from the activation of these anionic cages have little in common with those typically observed for white phosphorus. In most instances, heptapnictide $[E_7]^{3-}$ anions (E = P, As, Sb) react with metal reagents by maintaining their structure and nuclearity or undergoing the activation of a single E–E bond, resulting in a geometric change of the starting nortricyclane-like cage (C_{3v}) to a geometry reminiscent of norbornadiene (C_{2v}).[2,3] More extensive $[E_7]^{3-}$ activation reactions have been reported on a handful of occasions for the heavier Group 15 elements (E = As, Sb), yielding species with increased cluster nuclearities and often unprecedented geometries.[3–10] Such transformations are entirely without precedent for the $[P_7]^{3-}$ cage, however, which is presumably due to the greater bond dissociation energy of the P–P single bond.[11]

Herein we report the chemical activation of the heptaphosphide trianion, $[P_7]^{3-}$, by the transition-metal complex $[Co(mes)_2(PEt_2Ph)_2]$ (mes = 2,4,6-trimethylphenyl) to yield the novel anionic species $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$ (**1**; Figure 1). To our knowledge, this reaction is the first example of a transformation involving the chemical activation of an $[E_7]^{3-}$ cage where the nuclearity of the heptaphosphide starting material remains the same but where a significant alteration of the nortricyclane-like cage geometry has resulted. The chemical activation of neutral systems with related topologies has been reported previously.[12] Coordination to the cobalt metal center has allowed us to "trap" the known cyclopentaphosphide ligand $[P_5]^-$ alongside the diphosphene-like moiety $P_2H(mes)$. The isolobal relationship between phosphorus atoms and C–H fragments has led to phosphorus being referred to as the carbon copy.[13] This relationship makes $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$ a model system for the unknown family of anionic 18-electron organometallic complexes $[Co(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2C{=}CHR)]^{2-}$, which are in turn closely related to cobalt(I) bis(alkene) complexes, such as [CpCo(cod)] (cod = 1,5-cyclooctadiene) and Jonas's reagent.[14,15]

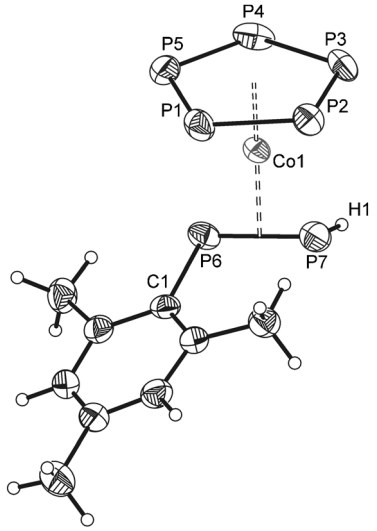

Figure 1. The $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$ dianion in **1**. Ellipsoids are set at 30% probability. All hydrogen atoms were assigned idealized coordinates and are shown as spheres of arbitrary radii. H1 could not be located in the Fourier difference map and was subsequently modeled at 50% occupancy over two positions (*cis* and *trans*). Selected bond distances [Å]: Co1–P1 2.305(1), Co1–P2 2.365(1), Co1–P3 2.346(1), Co1–P4 2.332(1), Co1–P5 2.350(1), Co1–P6 2.270(1), Co1–P7 2.278(1), P1–P2 2.103(1), P1–P5 2.129(2), P2–P3 2.121(1), P3–P4 2.133(2), P4–P5 2.110(2), P6–P7 2.141(1), P6–C1 1.876(3).

Reaction of an ethylenediamine (en) solution of K_3P_7 with one molar equivalent of $[Co(mes)_2(PEt_2Ph)_2]$ yielded the heteroatomic ion $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$. Monitoring of the crude reaction mixture by ^{31}P NMR spectroscopy reveals the presence of other minor unidentified phosphorus-containing side-products in addition to $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$. The $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^{2-}$ cluster anion can be isolated as a pure compound by crystallization (25–30%

[*] C. M. Knapp, B. H. Westcott, M. A. C. Raybould, Dr. J. E. McGrady, Dr. J. M. Goicoechea
Department of Chemistry
University of Oxford, Inorganic Chemistry Laboratory
South Parks Road, Oxford, OX1 3QR (UK)
E-mail: jose.goicoechea@chem.ox.ac.uk
Homepage: http://research.chem.ox.ac.uk/jose-goicoechea.aspx

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yields) and was crystallographically characterized in [K(2,2,2-crypt)]$_2$[Co(η^5-P$_5$)\{η^2-P$_2$H(mes)\}] (**1**). The asymmetric unit of **1** contains a single crystallographically unique [Co(η^5-P$_5$)\{η^2-P$_2$H(mes)\}]$^{2-}$ dianion and two [K(2,2,2-crypt)]$^+$ cations (both of which exhibit rotational disorder). The dianion in **1** reveals a central cobalt atom, which is coordinated by an η^5-pentaphosphide anion and an η^2-P$_2$H(mes) moiety. The position of the proton in the diphosphene moiety could not be located crystallographically and therefore it is unclear whether we have trapped the *cis* or *trans* isomeric form of P$_2$H(mes). DFT level calculations reveal that the *trans*-alkene complex is 15.07 kJ mol^{-1} lower in energy than the *cis* isomer.

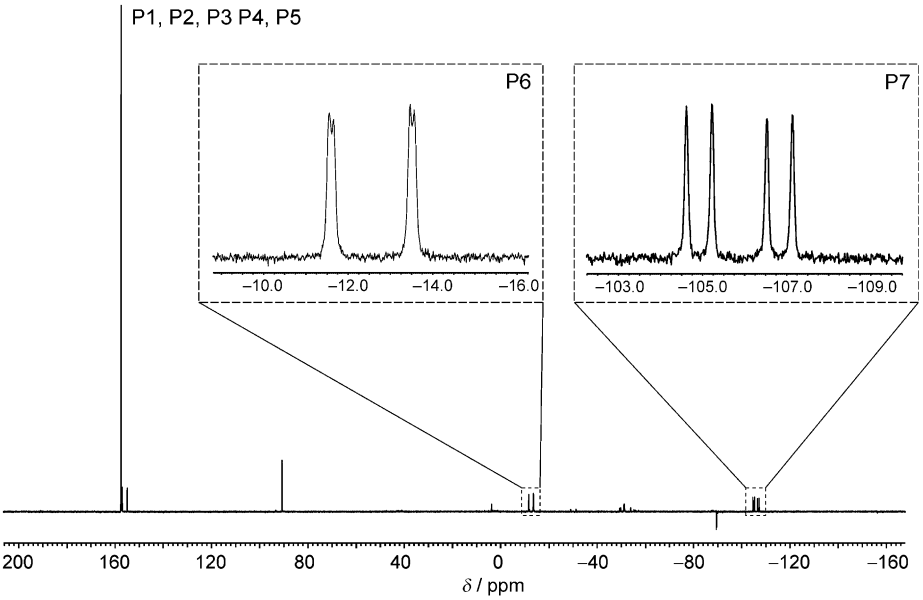

Figure 2. ^{31}P NMR spectrum of a [D$_5$]pyridine solution of [K(2,2,2-crypt)]-**1**. Unlabeled signals arise from an unidentified decomposition product.

The cyclopentaphosphide anion was first observed in solution by NMR spectroscopy,[16] and its coordination chemistry towards transition metals was studied by Scherer and co-workers.[1g,17] However, despite being extensively documented, the number of structurally corroborated examples of isolated transition-metal complexes containing [η^5-P$_5$]$^-$ ligands is limited. There are a handful of examples of transition-metal complexes bearing both the [P$_5$]$^-$ ligand and η^5-cyclopentadienide-type ligands.[18] To date, only one sandwich-type compound solely containing [P$_5$]$^-$ rings has been reported, the inorganic metallocene complex [Ti(P$_5$)$_2$]$^{2-}$.[19] The [η^5-P$_5$]$^-$ moiety has also been structurally observed in a variety of triple-decker complexes, for example, [\{(η^5-Cp*)Cr\}$_2$(μ^2,η^5-P$_5$)] and [(η^5-Cp*)Fe(μ^2,η^5-P$_5$)Sm(DIP$_2$pyr)(thf)$_2$],[20] and the remarkable supramolecular structures reported by Scheer and co-workers synthesized using [FeCp*(η^5-P$_5$)] as a building block.[21]

Metal complexes of P$_2$R$_2$ (R = H, alkyl or aryl functionalities) diphosphene ligands have also been previously reported. The reported complexes can largely be divided into two categories: 1) terminal systems,[22] in which the P$_2$R$_2$ moiety is bonded to a single metal center; and 2) bridging systems in which the P$_2$R$_2$ fragment bonds to two metal centers in a μ^2,η^2-mode.[23] It is interesting to note, however, that no asymmetrically substituted P$_2$RR′-type systems have been reported to date.

The dianion species **1** was characterized in solution by multielement NMR spectroscopy. The ^{31}P\{^{1}H\} NMR spectrum revealed three signals at δ = 157.6, −12.6, and −105.9 ppm in a 5:1:1 ratio. The two doublets at δ = −12.6 and −105.9 ppm correspond to the diphosphaalkene moiety HP = P(mes) and exhibit a ^1J(P-P) coupling constant of 387 Hz. A proton-coupled ^{31}P NMR experiment (Figure 2) allowed us to assign the signal at δ = −105.9 ppm as that corresponding to the phosphorus nucleus directly bonded to the proton (^1J(H-P) = 119 Hz). The signal at δ = −12.6 ppm also shows evidence of weak proton coupling with a ^2J(H-P) coupling constant of 22 Hz. The *H*P = P(mes) proton signal was observed as a doublet of doublets centered at δ = 2.13 ppm. ^{1}H NOE experiments irradiating the *ortho* methyl group resonance (δ = 2.09 ppm) show no contact with the diphosphaalkene proton. However, owing to the proximate chemical shifts of these two signals there is still some ambiguity as to whether or not a single isomer of **1** is present in solution. Further characterization of **1** in solution was carried out by means of electrospray mass spectrometry. In the negative-ion mode spectrum, a mass envelope was observed at *m*/*z* of 395.8 corresponding to the molecular anion [Co(η^5-P$_5$)\{η^2-P$_2$H(mes)\}]$^-$. Similarly, in the positive-ion mode, two peaks were observed at *m*/*z* values of 1227.1 and 1641.4 corresponding to the ion-paired species \{[K(2,2,2-crypt)]$_2$[Co(η^5-P$_5$)\{η^2-P$_2$H(mes)\}]\}$^+$ and \{[K(2,2,2-crypt)]$_3$[Co(η^5-P$_5$)\{η^2-P$_2$H(mes)\}]\}$^+$, respectively.

By analogy with the Dewar–Chatt–Duncanson model, the electronic structure of the [Co(η^5-P$_5$)\{η^2-P$_2$H(mes)\}]$^{2-}$ dianion can be discussed within the boundaries set by two limiting formulations: a Co^{-I} complex of the cyclopentaphosphide anion and an alkene-like diphosphene HP = P(mes), or alternatively as a Co^{I} complex of [P$_5$]$^-$ and a diphosphandiide [HP-P(mes)]$^{2-}$.[24] The P–P bond distance of 2.141(1) Å in the diphosphene unit of **1** lies somewhere in between the additive covalent radii for phosphorus atoms with single (2.22 Å) and double bonds (2.04 Å).[25] Thus it can be rationalized as a singly bonded diphosphandiide dianion that is contracted somewhat owing to the reduction of electrostatic repulsion between phosphorus atoms (for comparison, the P–P distance in the lithium salt of diphenylphosphandiide is 2.244(3) Å).[26] Alternatively, it can be interpreted in terms of extensive π-backbonding from a very electron-rich Co^{-I} center into the π*-antibonding LUMO of a diphosphene.

The DFT-optimized geometries for **1** with both *cis*- and *trans*-P_2H(mes) moieties show bond metrics that are closely related to the crystallographically determined structure (see the Supporting Information for further details). The frontier orbitals of these species are typical of half-sandwich type complexes with significant d-orbital parentage, although there is significant mixing of ligand p-orbitals from both the $[P_5]^-$ and P_2H(mes) moieties. An analysis of the computed charge density ($\rho(\mathbf{r})$) for **1** using Bader's atoms-in-molecules (AIM) methodology[27] was also conducted (see the Supporting Information). The results obtained are consistent with a significant degree of metallacyclic character in the CoP_2 moiety, indicating that whilst phosphorus may formally be a carbon copy, the bonding in **1** is substantially more covalent than that in the hypothetical organometallic complex.[28]

The synthesis and isolation of compound **1** represents an exciting new prospect for Zintl ion chemistry, indicating that low-valent, low-coordinate organometallic complexes may be employed to activate Zintl cluster anions for the synthesis of complexes containing novel phospha-organic moieties. Additional studies investigating the reactivity of alternative transition metal reagents with Group 14 and 15 Zintl ions are currently ongoing.

Experimental Section

$[K(2,2,2\text{-crypt})]_2[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]$: K_3P_7 (23.9 mg, 0.072 mmol), $[Co(mes)_2(PPhEt_2)_2]$ (42.4 mg, 0.067 mmol), and 2,2,2-crypt (61.6 mg, 0.164 mmol) were dissolved in ethylenediamine (ca. 2 mL) to form a brown solution, which was stirred under argon for two hours. The solution was then filtered into a crystallization ampoule, layered with toluene, and left to crystallize. After several days, 26.2 mg (30% yield) of dark red/brown block-like crystals formed. The crystals were characterized by single-crystal X-ray diffraction as $[K(2,2,2\text{-crypt})]_2[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]$. Anal. calcd. (%) for $C_{45}H_{84}CoK_2N_4O_{12}P_7$: C 44.03, H 6.90, N, 4.57; found: C 43.89, H 6.58, N 4.62. ESI-MS (negative-ion mode, DMF): *m/z* 395.8 $[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]^-$. ESI-MS (positive-ion mode, DMF): *m/z* 1227.1 $\{[K(2,2,2\text{-crypt})]_2[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]\}^+$, 1641.4 $\{[K(2,2,2\text{-crypt})]_3[Co(\eta^5\text{-}P_5)\{\eta^2\text{-}P_2H(mes)\}]\}^+$. ^{1}H NMR (500 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 6.72$ (s, 2H; *m*-CH), 3.39 (s, 24H; 2,2,2-crypt), 3.33 (t, ^3J(H-H) = 5 Hz, 24H; 2,2,2-crypt,), 2.31 (t, ^3J(H-H) = 5 Hz, 24H; 2,2,2-crypt,), 2.13 (dd, ^1J(H-P) = 119 Hz, ^2J(H-P) = 22 Hz, 1H, *H*P = P(mes)), 2.09 (s, 6H; *o*-C*H*$_3$), 2.05 ppm (s, 3H; *p*-C*H*$_3$). ^{31}P NMR (202.4 MHz, [D$_5$]pyridine, 25 °C, 85% H_3PO_4): δ = 157.6 (s, 5P; η^5-P_5), −12.6 (dd, ^1J(P-P) = 387 Hz, ^2J(H-P) = 22 Hz, 1P; HP = *P*(mes)), −105.9 ppm (dd, ^1J(H-P) = 119 Hz, 1P; H*P*=P(mes)). ^{13}C NMR (125.7 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 143.2$ (*C*$_6$-(CH$_3$)$_3$H$_2$), 130.9 (*C*$_6$(CH$_3$)$_3$H$_2$), 129.8 (*C*$_6$(CH$_3$)$_3$H$_2$), 128.7 (*C*$_6$-(CH$_3$)$_3$H$_2$), 70.8 (2,2,2-crypt), 68.0 (2,2,2-crypt), 54.3 (2,2,2-crypt), 28.2 (*o*-CH$_3$), 21.5 ppm (*p*-CH$_3$). A full description of experimental methods is provided in the Supporting Information.

Single-crystal X-ray diffraction data were collected using an Enraf–Nonius Kappa-CCD diffractometer and a 95 mm CCD area detector with a graphite-monochromated molybdenum K_α source ($\lambda = 0.71073$ Å). Crystals were selected under Paratone-N oil, mounted on MiTeGen loops, and quench-cooled using an open flow N_2 cooling device.[29] Data were processed using the DENZO-SMN package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALEPACK within DENZO-SMN).[30] Structures were subsequently solved using direct methods, and refined on F^2 using the SHELXL 97-2 package.[31]

$[K(2,2,2\text{-crypt})]_2$-**1**: $C_{45}H_{84}CoK_2N_4O_{12}P_7$, $M_r = 1227.08$, $0.30 \times 0.24 \times 0.13$ mm^3, dark brown–orange blocks; triclinic, space group: $P\bar{1}$ (no. 2); $a = 11.1630(1)$, $b = 12.2130(2)$, $c = 22.7373(2)$ Å, $\alpha = 92.758(1)$, $\beta = 103.630(1)$, $\gamma = 94.379(1)°$, $V = 2996.77(6)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.360$ g cm^{-3}, $\mu = 0.669$ mm^{-1}, $T = 150(2)$ K, $T_{max}/T_{min} = 0.92/0.82$, $2\Theta_{max} = 25.00°$; 19484 reflections collected; 10441 independent reflections; $R_{int} = 0.0268$; $R_1 = 5.03$, and $R_2 = 13.98$ for $I \geq 2\sigma(I)$; $R_1 = 6.53$ and $R_2 = 14.85$ for all data, min./max. residual electron density −0.46/0.83 e Å^3; GoF = 1.050. CCDC 883130 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Positive- and negative-ion mode electrospray mass spectra were recorded on DMF solutions (10–20 μm) on a Masslynx LCT time-of-flight mass spectrometer with a Z-spray source (150 °C source temperature, 200 °C desolvation temperature, 2.4 kV capillary voltage, and 25 V cone voltage). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe. Samples were introduced directly with a 1 mL SGE syringe and a syringe pump at 0.6 mL h^{-1}.

^{1}H, ^{13}C and ^{31}P NMR spectra were acquired at 500.0, 125.7, and 202.4 MHz, respectively, on a Varian Unity Plus 500 NMR spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to the most downfield solvent resonance (^{1}H NMR [D$_5$]pyridine: $\delta = 8.74$ ppm; ^{13}C NMR [D$_5$]pyridine: $\delta = 150.35$ ppm). ^{31}P spectra were externally referenced to an 85% solution of H_3PO_4 in H_2O ($\delta = 0$ ppm).

Elemental analyses were carried out by Elemental Microanalysis Ltd. (Devon, U.K.). Samples (ca. 5 mg) were submitted in sealed Pyrex ampoules.

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