

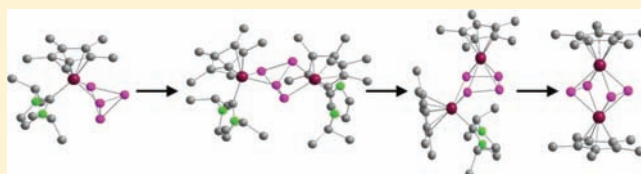
Symmetrical P₄ Cleavage at Cobalt: Characterization of Intermediates on the Way from P₄ to Coordinated P₂ Units[†]

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Supporting Information

ABSTRACT: Degradation of white phosphorus (P₄) in the coordination sphere of transition metals is commonly divided into two major pathways depending on the P_x ligands obtained. Consecutive metal-assisted P–P bond cleavage of four bonds of the P₄ tetrahedron leads to complexes featuring two P₂ ligands (symmetric cleavage) or one P₃ and one P₁ ligand (asymmetric cleavage). A systematic investigation of the degradation of white phosphorus P₄ to coordinated $\mu,\eta^{2:2}$ -bridging diphosphorus ligands in the coordination sphere of cobalt is presented herein as well as isolation of each of the decisive intermediates on the reaction pathway. The olefin complex [Cp*Co(ⁱPr₂Im)(η^2 -C₂H₄)], **1** (Cp* = η^5 -C₅Me₅, ⁱPr₂Im = 1,3-di-isopropylimidazolin-2-ylidene), reacts with P₄ to give [Cp*Co(ⁱPr₂Im)(η^2 -P₄)], **2**, the insertion product of [Cp*Co(ⁱPr₂Im)] into one of the P–P bonds. Addition of a further equivalent of the Co^I complex [Cp*Co(ⁱPr₂Im)(η^2 -C₂H₄)], **1**, induces cleavage of a second P–P bond to yield the dinuclear complex [{Cp*Co(ⁱPr₂Im)}₂($\mu,\eta^{2:2}$ -P₄)], **3**, in which a kinked cyclo-P₄⁴⁻ ligand bridges two cobalt atoms. Consecutive dissociation of the N-heterocyclic carbene with concomitant rearrangement of the cyclo-P₄ ligand and P–P dissociation leads to complexes [Cp*Co($\mu,\eta^{4:2}$ -P₄)Co(ⁱPr₂Im)Cp*], **4**, featuring a P₄ chain, and [{Cp*Co($\mu,\eta^{2:2}$ -P₂)}₂], **5**, in which two isolated P₂²⁻ ligands bridge two [Cp*Co] fragments. Each of these reactions is quantitative if performed on an NMR scale, and each compound can be isolated in high yields and large quantities.



INTRODUCTION

Degradation of white phosphorus (P₄) is a major topic in main-group and transition-metal chemistry.^{1,2} White phosphorus is the classical starting material for industrial synthesis of inorganic and organic phosphorus compounds, and for most transformations an initial chlorination or oxychlorination step to PCl₃, PCl₅, or POCl₃ is required.^{1–3} A considerable challenge, concerning economic and waste disposal aspects, is to avoid this oxidation step by direct catalytic transformation of P₄ into the desired phosphorus compounds. Fragmentation and transformation of white phosphorus using either main-group element compounds¹ or transition-metal complexes² is a feasible method toward the design of novel catalytic reactions that incorporate phosphorus atoms into organic and inorganic compounds. The most interesting organophosphorus compounds contain one or two phosphorus atoms, and therefore, fragmentation of P₄ is essential. Degradation of P₄ in the coordination sphere of transition metals is commonly divided into two major pathways depending on the P_x ligands obtained (see Scheme 1).² Consecutive metal-assisted P–P bond cleavage of four bonds of the P₄ tetrahedron leads to complexes featuring two P₂ ligands (symmetric cleavage, left side of Scheme 1) or one P₃ and one P₁ ligand (asymmetric cleavage; right side of Scheme 1), depending on the exact location of the element–element bond scission.

Symmetrical degradation of the P₄ tetrahedron to P₂ units often results in diphosphorus ligands bridging two metal centers in a $\mu,\eta^{2:2}$ coordination mode, and mechanistic

proposals for this symmetrical degradation have been put forward in various cases. However, only a few mechanistic studies have been carried out explicitly on these P₄ degradation mechanisms.^{2g,4}

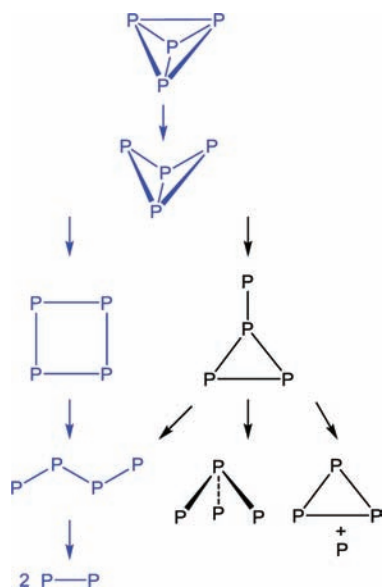
Herein we describe the stepwise degradation of P₄ at the [Cp*Co] (Cp* = η^5 -C₅Me₅) complex fragment as provided by [Cp*Co(ⁱPr₂Im)(η^2 -C₂H₄)], **1** (ⁱPr₂Im = 1,3-di-isopropylimidazolin-2-ylidene), to P₂ ligands as well as isolation and characterization of reaction intermediates.

The P₄ activation chemistry at cobalt half-sandwich precursors is enormously rich, but these investigations have often been hampered by low selectivity, separation problems, and low-yielding syntheses of the complexes. Simon and Dahl reported the first organometallic cobalt complex containing a naked phosphorus atom as a ligand. The tetrameric cobalt complex [{CpCo(μ_3 -P)}₄] (Cp = η^5 -C₅H₅) was prepared by refluxing a toluene solution of [CpCo(CO)₂] and a stoichiometric amount of white phosphorus.^{5a} Subsequent work mainly performed by the groups of Dahl and Scherer, using organometallic cobalt half-sandwich precursors for activation of white phosphorus, clearly demonstrated that subtle variations of the reaction conditions and of the employed ligands have a significant impact on the nature of the reaction product.⁵ Barr and Dahl reported in 1991 the low-yield synthesis of a dinuclear bis(diphosphide)-bridged complex

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Scheme 1. Schematic Representation of the Generation of Phosphorus Units from Formal Stepwise Cleavage of P–P Bonds in the P₄ Tetrahedron

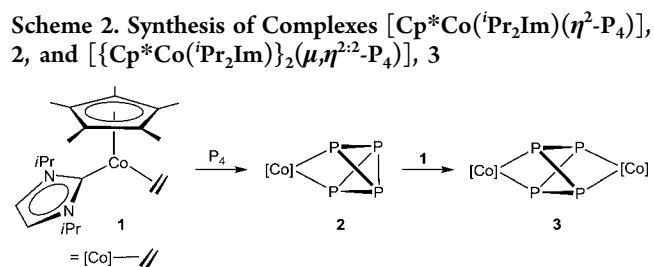


$[(\text{Cp}^*\text{Co})_2(\mu, \eta^{2:2}\text{-P}_2)_2]$ upon photolysis of toluene solutions of $[\text{Cp}^*\text{Co}(\mu\text{-CO})_2]$ with P_4 . Scherer et al. reported the thermolysis of $[\{\text{Cp}^*\text{Co}(\mu\text{-CO})\}_2]$ in toluene with an excess of P_4 to give $[\text{Cp}^*\text{Co}(\text{CO})(\eta^2\text{-P}_4)]$ at 60°C after 30 min and $[\{\text{Cp}^*\text{Co}(\text{CO})\}_2(\mu, \eta^{2:2}\text{-P}_4)]$ after 6 h.^{5d} The reactivity of cobalt half-sandwich complexes bearing bulky alkylated cyclopentadienyl rings toward P_4 , usually in the presence of precursors for organometallic Lewis-acidic complex fragments such as $[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), was investigated by Scheer and co-workers.^{5e–i} This group also reported a systematic study on the replacement of Cp protons with ^tBu groups for the three-component reaction of $[\text{Cp}^R\text{Co}(\mu\text{-CO})_2]$ ($\text{Cp}^R = \text{Cp}, \text{Cp}', \text{Cp}'', \text{Cp}'''$; each prime (') denotes replacement of a Cp proton by ^tBu) with P_4 in the presence of $[\text{Cr}(\text{CO})_5(\text{THF})]$ under UV irradiation. In the course of their studies, Scheer et al. isolated $\text{Cr}(\text{CO})_5$ -stabilized compounds with $[\{\text{Cp}^R\text{Co}(\text{CO})\}_2(\eta^2\text{-P}_4)_2]$ and $[\text{Cp}^R\text{Co}(\eta^4\text{-P}_4)]$ cores as well as dinuclear $[\{\text{Cp}^R\text{Co}(\mu, \eta^{2:2}\text{-P}_2)\}_2]$ and trinuclear $[(\text{Cp}^R\text{Co})_3(\mu_3, \eta^{4:2:2}\text{-P}_4)\{\text{Cp}^R\text{Co}(\mu\text{-CO})\}]$. The latter reveals a distorted planar P_4 ligand capped by a Cp^RCo moiety and a $[(\text{Cp}^R\text{Co})_2(\text{CO})](\text{Co}\text{-Co})$ complex fragment that coordinates three of the four P atoms.^{5e–i} Scherer and co-workers also used thermolytic and photolytic reactions of $[\text{Cp}^R\text{Co}(\mu\text{-CO})_2]$ with white phosphorus to synthesize complexes with P_x ligands of higher nuclearity.^{5j} In a recent contribution the Scheer group reported the advantageous usage of $[(\text{Cp}^R\text{Co})_2(\mu, \eta^{4:4}\text{-C}_7\text{H}_8)]$ as a $[\text{Cp}^R\text{Co}]$ precursor for quantitative synthesis of $[(\text{Cp}^R\text{Co})_2(\mu, \eta^{2:2}\text{-P}_2)_2]$ and for generation of complexes of higher P_n ligands ($\text{P}_8, \text{P}_{12}, \text{P}_{16}$, and P_{24}).^{5k}

RESULTS AND DISCUSSION

In a continuation of our work on NHC-stabilized transition-metal complexes of 3d elements⁶ we recently reported the synthesis of the cobalt half-sandwich complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_4)]$, **1**.⁷ Complex **1** reacts cleanly with P_4 at room temperature with loss of ethylene, affording complexes $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$, **2**, and $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu, \eta^{2:2}\text{-P}_4)]$, **3**, depending on the stoichiometry and reaction conditions employed (see Scheme 2).

$[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$, **2**, and $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu, \eta^{2:2}\text{-P}_4)]$, **3**



Reaction of 1 equiv of **1** with P_4 requires approximately 24 h at room temperature to reach completion and is selective and quantitative if performed on an NMR scale. Complex **2** was isolated as a red solid in 78% yield. Transfer of the $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$ complex fragment to P_4 cleanly leads to insertion of the fragment into P_4 and thus cleavage of one bond of the P_4 tetrahedron. Complex **2** was characterized via ¹H, ¹³C, and ³¹P NMR spectroscopy, IR spectroscopy, elemental analysis, mass spectroscopy, and X-ray crystallography. The ¹H and ¹³C NMR spectrum of the complex shows all the signals expected for a pseudo-C_s-symmetric complex. Most significantly, the ³¹P NMR spectrum of **2** reveals three sets of resonances for the A₂XY spin system: one set at -165.87 ppm (for the P atoms attached to Co), one at -296.88 ppm, and one at -347.59 ppm with coupling constants $J_{\text{P-P}}$ of 149 and 160 Hz. A compound closely related to complex **2**, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})(\eta^2\text{-P}_4)]$, has been previously synthesized by the Scherer group.^{5d} For this compound a very similar ³¹P NMR spectrum was reported, but the resonances are significantly shifted to higher field compared to the resonances observed for **2**.

Crystals of **2** suitable for X-ray diffraction have been obtained from saturated toluene solutions at 0°C (see Figure 1). The X-ray structure confirms that white phosphorus has been activated by cobalt and that one edge of the tetrahedron has been opened and coordinated to the $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$ complex fragment. The phosphorus ligand can be formally considered as P_4^{2-} coordinated to $[\text{Cp}^*\text{Co}^{\text{III}}(\text{iPr}_2\text{Im})]^{2+}$. The Co–P bond lengths

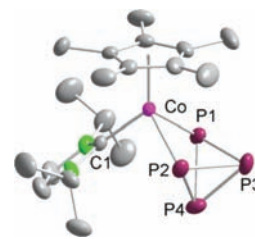


Figure 1. ORTEP diagram of the molecular structure of $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$ **2** in the solid state (ellipsoids set at 50% probability level). The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co–Cp*_{centroid} 1.7657(7), Co–C1 1.935(3), Co–P1 2.2286(8), Co–P2 2.2383(8), P1–P2 2.6398(11), P1–P3 2.2193(11), P1–P4 2.2149(13), P2–P3 2.2220(12), P2–P4 2.2194(13), P3–P4 2.1799(15); C1–Co–P1 94.39(8), C1–Co–P2 93.71(8), P1–Co–P2 72.45(3), P4–P1–P3 58.89(4), P4–P1–P2 53.54(3), P3–P1–P2 53.58(3), P4–P2–P3 58.79(5), P4–P2–P1 53.39(4), P3–P2–P1 53.48(3), P4–P3–P1 60.45(4), P4–P3–P2 60.55(4), P1–P3–P2 72.94(4), P3–P4–P1 60.65(4), P3–P4–P2 60.66(5), P1–P4–P2 73.07(4), C1–Co–Cp*_{centroid} 128.39(1).

of 2.2286(8) and 2.2383(8) Å are similar to those observed in the molecular structure of $[\text{Cp}^*\text{Co}(\text{CO})(\eta^2\text{-P}_4)]$ (2.261(1) Å and 2.255(1) Å).^{5d} The P–P distance between the phosphorus atoms coordinated to cobalt, i.e., P1 and P2, is 2.6398(11) Å, which is commonly considered as nonbonding² and significantly longer than all other P–P distances in the molecule (2.1799(15)–2.2220(12) Å).

Complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$, **2**, reacts cleanly with another equivalent of the ethylene complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_4)]$, **1**, to yield the dinuclear compound $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu,\eta^{2:2}\text{-P}_4)]$, **3**, in which a $\mu,\eta^{2:2}\text{-P}_4$ ligand bridges two $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$ complex fragments (see Figure 3). This

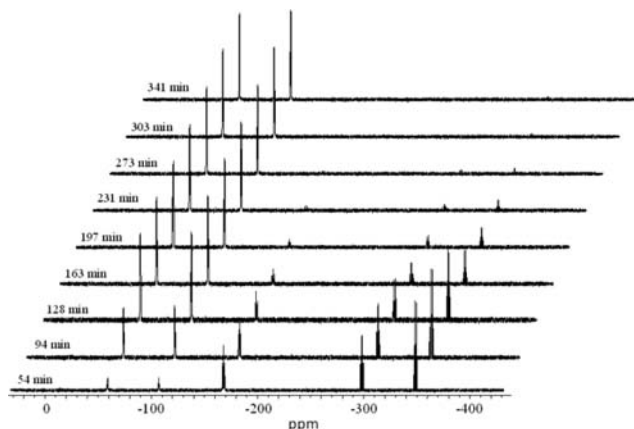


Figure 2. Time-dependent ^{31}P NMR spectra (298 K) of the reaction of $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$, **2**, with $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_4)]$, **1**.

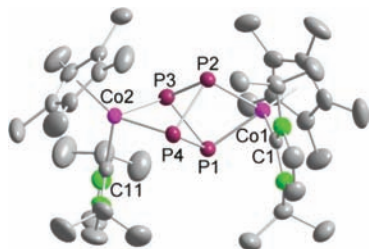


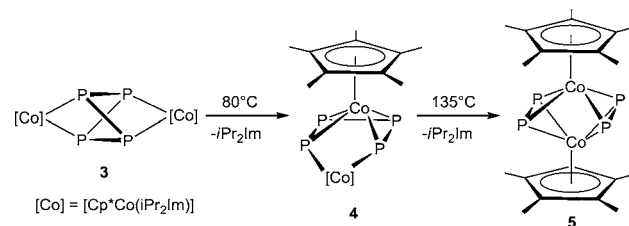
Figure 3. ORTEP diagram of the molecular structure of $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu,\eta^{2:2}\text{-P}_4)]$, **3**, in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1–Cp*_{centroid} 1.7718(7), Co1–C1 1.923(3), Co1–P1 2.2711(13), Co1–P2 2.2480(13), Co2–Cp*_{centroid} 1.7766(7), Co2–C11 1.936(3), Co2–P3 2.2497(15), Co2–P4 2.2659(17), P1–P2 2.6282(18), P3–P4 2.6161(16), P1–P3 2.2341(15), P1–P4 2.2594(17), P2–P3 2.2495(15), P2–P4 2.2358(15), C1–Co1–Cp*_{centroid} 127.477(23), C11–Co2–Cp*_{centroid} 128.18(3), C1–Co1–P1 93.31(9), C1–Co1–P2 96.87(9), P1–Co1–P2 71.12(4), C11–Co2–P3 97.86(10), C11–Co2–P4 92.67(10), P3–Co2–P4 70.81(3), Co1–P1–P2 54.03(4).

reaction is quantitative if performed on the NMR scale. Time-dependent ^{31}P NMR spectra for this conversion at 298 K are depicted in Figure 2. Starting from the three sets of resonances for the A_2XY spin system of **2** at -165.87 , -296.88 , and -347.59 ppm, two new sets of resonances arise cleanly at -58.16 and -107.1 ppm for the $AA'XX'$ spin system of compound **3**. In the product, the bridging ligand gives rise to two multiplets of higher order with coupling constants of $J = 126$ Hz, $J' = -23$ Hz, $J_A = 258$ Hz, and $J_X = 0$ Hz (see Figure S2 of the Supporting Information). Complex **3** can be

advantageously synthesized from reaction of 2 equiv of the half-sandwich complex **1** and 1 equiv of white phosphorus in 82% isolated yield. Heating of the reaction mixture up to 50 °C is recommended to perform this reaction on a convenient time scale, but higher temperatures should be avoided since the complex decomposes (vide infra).

Heating toluene solutions of complex **3** to 80 °C leads to elimination of one of the NHC ligands and rearrangement of the $\mu,\eta^{2:2}\text{-P}_4$ ligand, affording the new complex $[\text{Cp}^*\text{Co}(\mu,\eta^{4:2}\text{-P}_4)\text{Co}(\text{iPr}_2\text{Im})\text{Cp}^*]$, **4**, in quantitative yield (see Scheme 3).

Scheme 3. Synthesis of $[\text{Cp}^*\text{Co}(\mu,\eta^{4:2}\text{-P}_4)\text{Co}(\text{iPr}_2\text{Im})\text{Cp}^*]$, **4, and $[(\text{Cp}^*\text{Co})_2(\mu,\eta^{2:2}\text{-P}_2)]$, **5**, via Thermolysis of $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu,\eta^{2:2}\text{-P}_4)]$, **3****



In the course of the formation of complex **4** the bridging P_4 ligand rearranges to a P_4 chain, which is η^4 -coordinated to $[\text{Cp}^*\text{Co}]$ and η^2 -coordinated to $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$. Complex **4** might be regarded as a metallacyclotetraphosphacyclus which is coordinated by the $[\text{Cp}^*\text{Co}]$ moiety. If the reaction is performed in an NMR tube, all signals of the eliminated, uncoordinated NHC can be detected. The reaction can be easily followed by ^{31}P NMR spectroscopy, since the $AA'XX'$ spin system of the P_4 chain gives rise to two sets of resonances at 142.2 and 252.3 ppm in a completely different region compared to **3** (-58.2 and -107.1 ppm). The coupling constants observed for **4** are $J = 324$ Hz, $J' = 12$ Hz, $J_A = 387$ Hz, and $J_X = 16$ Hz (see Figure S3 of the Supporting Information).

Crystals of **4** suitable for X-ray diffraction have been obtained from saturated benzene solutions at room temperature. Complex **4** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (see Figure 4). The P_4 chain is coordinated to two cobalt atoms, Co1 of the $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$ moiety complex fragment inserted between P1 and P4 and Co2 of the $[\text{Cp}^*\text{Co}]$ moiety that coordinates in an η^4 mode to the P_4 chain. The bond lengths Co1–P1 and Co1–P4 of 2.2407(12) and 2.2298(13) Å are close to the values found for $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$ **2** (2.2286(8) and 2.2383(8) Å) and $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu,\eta^{2:2}\text{-P}_4)]$ **3** (2.2711(13), 2.2480(13), 2.2497(15), and 2.2659(17) Å). All bond lengths and angles of the pseudotetrahedral environment at Co1 closely resemble the $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\text{PP}]$ section of **2** and **3**. The Co2–P distances (Co2–P1 2.3130(14) Å, Co2–P2 2.2865(14) Å, Co2–P3 2.2897(14) Å, Co2–P4 2.2990(12) Å) are slightly longer compared to the Co1–P bond lengths and lie in the narrow range between 2.2851 and 2.3129 Å. The best-fit plane through the Cp carbon atoms at Co2 is close to parallel to that through the planar P_4 chain (intersection angle 5.84°).

The central motif of the molecular structure is the square planar P_4 chain coordinated to both cobalt atoms. The P–P distances within this chain are 2.1777(17) (P1–P2), 2.1748(16) (P3–P4), and 2.1442(19) Å (P2–P3) and thus

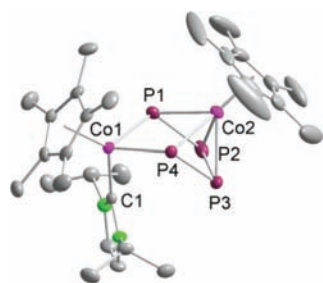


Figure 4. ORTEP diagram of the molecular structure of $[\text{Cp}^*\text{Co}(\mu, \eta^{4:2}\text{-P}_4)\text{Co}(\text{iPr}_2\text{Im})\text{Cp}^*]$, **4**, in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): $\text{Co1}-\text{Cp}^*_{\text{centroid}}$ 1.78538(3), $\text{Co1}-\text{C1}$ 1.932(4), $\text{Co1}-\text{P1}$ 2.2407(12), $\text{Co1}-\text{P4}$ 2.2298(13), $\text{Co2}-\text{Cp}^*_{\text{centroid}}$ 1.7120(3), $\text{Co2}-\text{P1}$ 2.3130(14), $\text{Co2}-\text{P2}$ 2.2865(13), $\text{Co2}-\text{P3}$ 2.2893(14), $\text{Co2}-\text{P4}$ 2.2997(12), $\text{P1}-\text{P2}$ 2.1777(17), $\text{P2}-\text{P3}$ 2.1442(19), $\text{P3}-\text{P4}$ 2.1748(16), $\text{P1}\cdots\text{P4}$ 2.5562(16); $\text{C1}-\text{Co1}-\text{P1}$ 96.46(12), $\text{C1}-\text{Co1}-\text{P4}$ 96.11(13), $\text{C1}-\text{Co1}-\text{Cp}^*_{\text{centroid}}$ 127.53(1), $\text{Co1}-\text{P4}(\text{plane})$ 126.41(2), $\text{P1}-\text{P2}-\text{P3}$ 95.73(7), $\text{P2}-\text{P3}-\text{P4}$ 95.14(7), $\text{Cp}^*_{\text{centroid}}-\text{Co2}-\text{P4}(\text{centroid})$ 174.16(1).

shorter than the 2.219 Å P–P single bond in diphosphine(**4**) but significantly longer than the 2.034 Å P=P double bond in bis(2,4,6-tri-*tert*-butylphenyl) diphosphene.⁸ However, the “short” distances observed are very close to the P–P bond lengths in the cyclo- P_4^{2-} unit in $\text{Cs}_2\text{P}_4\cdot 2\text{NH}_3$ (2.146(1) and 2.1484(9) Å) as reported by Korber and co-workers.⁹ The chain reveals a slight bond contraction at the bond between P2 and P3, as might be expected for a P_4^{4-} ligand isoelectronic to a butadiene dianion. The distance between P1 and P4 of 2.562(16) Å is significantly elongated (approximately 0.4 Å) compared to the average P–P distances of 2.156 Å but lies midway between a regular P–P single-bond length and a van der Waals contact. Facing a similar problem, Scheer, Chisholm, and Eisenstein and co-workers performed theoretical calculations to clarify the bonding situation in the structurally characterized complex $[(\text{Cp}^*\text{Co})(\mu^3, \eta^{4:2:2}\text{-P}_4)\{(\text{Cp}^*\text{Co})_2(\mu\text{-CO})\}]$.^{5h} This compound contains a quasi-planar cyclo- P_4 core with P–P bond lengths in the range 2.161–2.503 Å, and theoretical analysis supported a description of the longest P–P distance (2.503 Å) as a weak bond rather than a van der Waals contact. The structural motif of a P_4 chain has also been found for the higher homologue rhodium in the related complex $[\text{Cp}^*\text{Rh}(\mu, \eta^{4:2}\text{-P}_4)\text{RhCp}^*(\text{CO})]$,¹⁰ for which the “short” P–P distances average to 2.154 Å, whereas the “long” P–P distance of 2.697(3) Å is significantly larger compared to P1–P4 in **4** and was characterized as nonbonding. The difference observed for **4** and the rhodium complex presumably originates merely from the differing radii of the metals that coordinate to P1 and P4, cobalt in **4** and rhodium in $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Rh}(\mu, \eta^{4:2}\text{-P}_4)\text{Rh}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})]$.

Further thermolysis of **4** leads to elimination of the remaining NHC ligand with formation of the complex $[(\text{Cp}^*\text{Co})_2(\mu, \eta^{2:2}\text{-P}_2)]$, **5**, which features two isolated P_2^{2-} ligands. Heating of solutions of **4** in xylene at 135 °C for 7 days leads to quantitative formation of **5**, which was isolated in 94% yield. Complex **5** gives rise to a singlet in the ^1H NMR spectrum at 1.65 ppm for the Cp^* methyl groups, two resonances at 10.43 and 94.59 ppm for the Cp^* carbon atoms in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, and a singlet at –15.1 ppm for the phosphorus atoms in the ^{31}P NMR spectrum. This compound was prepared in the early 1990s by Dahl and co-workers^{5c} in very low yields (7.4%) using photolysis of toluene

solutions of $[\text{Cp}^*\text{Co}(\mu\text{-CO})_2]$ and P_4 and was structurally characterized at that time. A convenient route to closely related $[(\text{Cp}^*\text{Co})_2(\mu, \eta^{2:2}\text{-P}_2)]$ ($\text{Cp}^* = \eta^5\text{-1,2,4-}t\text{Bu}_3\text{C}_5\text{H}_2$) from reaction of $[(\text{Cp}^*\text{Co})_2(\mu, \eta^{4:4}\text{-C}_7\text{H}_8)]$ and an excess of P_4 at room temperature was recently reported by Scheer and co-workers.^{5k} In contrast to the work reported here, complexes of higher nuclearity such as isolated P_{12} and P_8 clusters seem to be important intermediates in this case. It has been shown that the 36 VE cobalt dimer $[(\text{Cp}^*\text{Co})_2(\mu, \eta^{2:2}\text{-P}_2)]$, **5**, consists of two 14-electron $[\text{Cp}^*\text{Co}]$ fragments bridged by two four-electron-donating P_2^{2-} ligands (P–P distances of 2.053(4) and 2.058(4) Å) that are coordinated in a η^2 -fashion to the transition metals.

CONCLUSIONS

For the degradation of P_4 two major pathways are encountered in the literature: the asymmetric pathway leading to P_1 and P_3 phosphide ligands and a symmetric pathway leading to P_2 phosphide ligands (see Scheme 1). Symmetrical degradation of P_4 to P_2 units often results in formation of dinuclear complexes featuring $\mu, \eta^{2:2}$ -bridging diphosphorus ligands. We report here the first systematic investigation on the degradation of white phosphorus P_4 to coordinated P_2 units in the coordination sphere of a transition metal as well as isolation of each of the decisive intermediates. Using the $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$ moiety we establish here the symmetrical pathway for P_4 degradation at this complex fragment, marked in blue in Scheme 1. These results are summarized in Figure 5

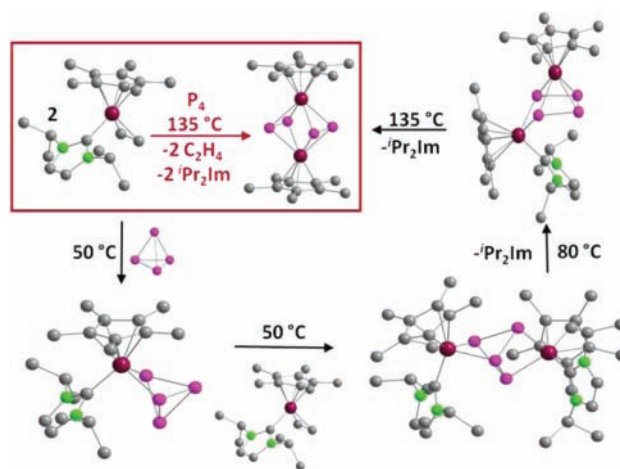


Figure 5. Stepwise degradation of white phosphorus P_4 to coordinated P_2 units using $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_4)]$, **1**.

Starting with the reactive cobalt half-sandwich NHC complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_4)]$, **1**, reaction with P_4 leads to insertion of $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})]$ into one of the P–P bonds to give $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-P}_4)]$, **2**. Further addition of the Co^{I} species affords cleavage of a second P–P bond to give the dinuclear complex $[\{\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})\}_2(\mu, \eta^{2:2}\text{-P}_4)]$, **3**, in which a kinked cyclo- P_4^{4-} ligand bridges both cobalt atoms and acts as a four-electron donor ligand to the cobalt atoms. Consecutive dissociation of the N-heterocyclic carbene ligand occurs with rearrangement of the cyclo- P_4 ligand and P–P dissociation, which leads to complexes $[\text{Cp}^*\text{Co}(\mu, \eta^{4:2}\text{-P}_4)\text{Co}(\text{iPr}_2\text{Im})\text{Cp}^*]$, **4**, featuring a P_4 chain, and $[\{\text{Cp}^*\text{Co}(\mu, \eta^{2:2}\text{-P}_2)\}_2]$, **5**, in which two isolated P_2^{2-} ligands bridge two $[\text{Cp}^*\text{Co}]$ fragments.

Each of these reactions is quantitative if performed on NMR scale, and each compound can be isolated in high yields and

large quantities without further purification such as chromatography or recrystallization, procedures often required in this type of chemistry. Starting from the cobalt ethylene complex **1** and white phosphorus, each of the compounds can be synthesized directly and in high yield if the correct stoichiometry and reaction conditions are employed. Reaction temperatures up to 50 °C and a stoichiometry Co:P₄ of 1:1 or 2:1 lead exclusively to the mononuclear or dinuclear complexes **2** and **3**, reaction temperatures of approximately 80 °C and a stoichiometry ratio Co:P₄ of 2:1 lead to [Cp*Co(μ,η^{4,2}-P₄)Co(Pr₂Im)Cp*], **4**, and reaction temperatures of 135 °C exclusively provide [(Cp*Co(μ,η^{2,2}-P₂))₂], **5**. Thus, these procedures are ideally suited for synthesis of the different complexes at the Cp*Co fragment and studying the reactivity of the different P_n ligands in these compounds.

EXPERIMENTAL DETAILS

General Considerations. All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen atmosphere using standard Schlenk techniques. Elemental analyses were performed in the microanalytical laboratory of the Inorganic Chemistry Departments of the Universities Karlsruhe (TH) and Würzburg. EI mass spectra were recorded on a Varian MAT 3830 (70 eV). NMR spectra were recorded on a Bruker AMX 300 and Bruker AV 400 at 298 K. ¹³C NMR spectra are broad-band proton decoupled (¹³C{¹H}). NMR data are listed in parts per million (ppm) and reported relative to tetramethylsilane. Coupling constants are quoted in Hertz. Spectra are referenced internally to residual protio-solvent resonances (¹H; CDCl₃, 7.24 ppm; C₆D₆, 7.15 ppm) or natural-abundance carbon resonances (¹³C; CDCl₃, 77.0 ppm; C₆D₆, 128.0 ppm). Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 and are reported in cm⁻¹. [(η⁵-C₅Me₅)Co(Pr₂Im)(η²-C₂H₄)]⁺ and Pr₂Im^{6b} were prepared according to literature procedures.

Synthesis of [(η⁵-C₅Me₅)Co(Pr₂Im)(η²-P₄)] (2**).** Complex **1** (1.05 g, 2.80 mmol) and white phosphorus (0.35 g, 2.80 mmol) were suspended in 20 mL of toluene. The reaction mixture was stirred for 24 h at room temperature. A color change from dark red to brown was observed. The solvent was removed in vacuo and the remaining solid was suspended in pentane. The product was filtered off and dried in vacuo to give **2** as a red powder. Yield: 1.03 g, 78%. Crystals of **2** suitable for X-ray diffraction have been obtained from saturated toluene solutions at 0 °C. Anal. Calcd for C₁₉H₃₁N₂P₄Co: C, 48.52; H, 6.64; N, 5.96. Found: C, 48.32; H, 6.73; N, 5.89. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ = 1.04 (d, 6 H, ³J_{HH} = 6.7 Hz, CH₃), 1.44 (d, 6 H, ³J_{HH} = 6.6 Hz, CH₃), 1.53 (s, 15 H, C₅(CH₃)₅), 5.20 (m, 2 H, ¹Pr-H), 6.40 (s, 2 H, NCHCHN). ¹³C{¹H} NMR (100.6 MHz, 25 °C, C₆D₆): δ = 9.6 (C₅(CH₃)₅), 24.5 (¹Pr-CH₃), 26.3 (¹Pr-CH₃), 51.6 (¹Pr-CH), 92.6 (C₅(CH₃)₅), 118.7 (NCCN), 183.6 (NCN, coupling to phosphorus was not observed). ³¹P{¹H} (162 MHz, 25 °C, C₆D₆) δ = -165.87 (dd, 2P, P₄, ¹J_{PP} = 149 Hz, ¹J_{PP} = 160 Hz), -296.88 (dt, 1P, P₄, ¹J_{PP} = 149 Hz, ¹J_{PP} = 160 Hz), -347.59 (q, 1P, P₄, ¹J_{PP} = 149 Hz, ¹J_{PP} = 160 Hz). MS (EI): *m/z* 470.4 (6) [M]⁺, 346.3 (19) [M - P₄]⁺, 304.3 (21) [Cp*Co(Pr₂Im) - (CH₂=CHCH₃)]⁺, 94.2 (13) [Cp*Co]⁺. IR (KBr [cm⁻¹]): 3100 (w), 2970 (m), 2926 (w), 2867 (w), 1631 (w), 1459 (w), 1416 (w), 1397 (m), 1367 (m), 1289 (m), 1207 (m), 1131 (w), 1106 (w), 1078 (w), 1055 (w), 1023 (w), 879 (w), 798 (m), 727 (w), 689 (m), 627 (w), 589 (w), 558 (w), 398 (w).

Synthesis of [(η⁵-C₅Me₅)Co(Pr₂Im)]₂(μ,η^{2,2}-P₄) (3**).** Complex **1** (749 mg, 2.00 mmol) and white phosphorus (124 mg, 1.00 mmol) were suspended in 10 mL of toluene. The reaction mixture was stirred for 24 h at 50 °C. After removing the solvent in vacuo the brown residue was washed with pentane several times. By drying the solid in vacuo compound **3** was obtained as a brown solid. Yield: 670 mg, 82%. Crystals suitable for X-ray diffraction have been grown from hexane solutions of **3** at -30 °C. Anal. Calcd for C₃₈H₆₂N₄P₄Co₂: C, 54.89; H, 7.65; N, 6.36. Found: C, 54.34; H, 7.57; N, 5.91. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ = 1.12 (d, 6 H, ³J_{HH} = 6.7 Hz, CH₃), 1.19 (d, 6 H, ³J_{HH} = 5.7 Hz, CH₃), 1.20 (d, 6 H, ³J_{HH} = 6.4 Hz, CH₃), 1.61 (d, 6 H,

³J_{HH} = 6.6 Hz, CH₃), 1.81 (s, 15 H, C₅(CH₃)₅), 5.64 (m, 2 H, ¹Pr-H), 5.99 (m, 2 H, ¹Pr-H), 6.44 (s, 2 H, NCHCHN). ¹³C{¹H} NMR (100.6 MHz, 25 °C, C₆D₆): δ = 9.7 (C₅(CH₃)₅), 21.2 (¹Pr-CH₃), 24.5 (¹Pr-CH₃), 25.4 (¹Pr-CH₃), 25.7 (¹Pr-CH₃), 50.4 (¹Pr-H), 50.5 (¹Pr-CH), 51.1 (¹Pr-CH), 51.2 (¹Pr-CH), 51.3 (¹Pr-CH), 91.5 (C₅(CH₃)₅), 117.3 (NCCN), 118.1 (NCCN), 186.7 (NCN). ³¹P{¹H} (162 MHz, 25 °C, C₆D₆): δ = -58.16 (m, P₄, J = 126 Hz, J' = -23 Hz, J_A = 258 Hz, J_X = 0 Hz), -107.06 (m, P₄, J = 126 Hz, J' = -23 Hz, J_A = 258 Hz, J_X = 0 Hz). MS (EI): *m/z* 663.0 (98) [M - (Pr₂Im)]⁺, 511.0 (99) [M - 2(Pr₂Im)]⁺, 481.0 (89) [M - 2(Pr₂Im) - P]⁺, 376.0 (79) [Cp*Co(Pr₂Im)(P)]⁺, 346.0 (95) [Cp*Co(Pr₂Im)]⁺, 256.0 (91) [Cp*Co(P₂)]⁺, 194.0 (98) [Cp*Co]⁺. IR (KBr [cm⁻¹]): 2972 (s), 2901 (s), 1638 (w), 1458 (w), 1393 (m), 1365 (m), 1319 (w), 1276 (s), 1211 (vs), 1099 (s), 1021 (vs), 933 (w), 873 (w), 804 (s), 729 (w), 688 (m), 631 (w), 574 (w), 535 (w), 506 (w), 486 (w), 470 (w).

Synthesis of [(η⁵-C₅Me₅)Co(Pr₂Im)]₂(μ,η^{2,2}-P₄)[Co(η⁵-C₅Me₅)] (4**).** Complex **1** (1.00 g, 2.88 mmol) and white phosphorus (178 mg, 1.44 mmol) were suspended in 10 mL of toluene. The reaction mixture was stirred for 3 days at 80 °C. After removing the solvent in vacuo the black residue was washed with pentane several times. By drying the solid in vacuo compound **4** was obtained as a black solid. Yield: 915 mg, 96%. Crystals of **4** suitable for X-ray diffraction have been obtained from saturated benzene solutions at room temperature. Anal. Calcd for C₂₉H₄₆N₂P₄Co₂: C, 52.42; H, 6.98; N, 4.22. Found: C, 52.32; H, 7.00; N, 4.26. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ = 1.02 (d, 6 H, ³J_{HH} = 6.6 Hz, CH₃), 1.62 (s, 15 H, C₅(CH₃)₅), 1.74 (d, 6 H, ³J_{HH} = 6.5 Hz, CH₃), 2.02 (s, 15 H, C₅(CH₃)₅), 5.57 (m, 2 H, ³J_{HH} = 6.4 Hz, ¹Pr-H), 6.44 (s, 2 H, NCHCHN). ¹³C{¹H} NMR (100.6 MHz, 25 °C, C₆D₆): δ = 10.1 (C₅(CH₃)₅), 11.1 (C₅(CH₃)₅), 23.9 (¹Pr-CH₃), 26.3 (¹Pr-CH₃), 52.0 (¹Pr-CH), 93.8 (C₅(CH₃)₅), 95.5 (C₅(CH₃)₅), 117.8 (NCCN), 186.7 (NCN). ³¹P{¹H} (162 MHz, 25 °C, C₆D₆): δ = 142.21 (m, P₄, J = 324 Hz, J' = 12 Hz, J_A = 387 Hz, J_X = 16 Hz), 252.3 (m, P₄, J = 324 Hz, J' = 12 Hz, J_A = 387 Hz, J_X = 16 Hz). MS (EI): *m/z* 663.9 (12) [M]⁺, 512.0 (100) [M - (Pr₂Im)]⁺, 304.1 (25) [Cp*Co(Pr₂Im) - (CH₂=CHCH₃)]⁺, 256.0 (24) [Cp*Co(P₂)]⁺, 194.0 (27) [Cp*Co]⁺ - 2(CH₂=CHCH₃)⁺. IR (KBr [cm⁻¹]): 2977 (s), 2902 (vs), 1635 (w), 1578 (w), 1561 (w), 1464 (m), 1415 (m), 1393 (s), 1369 (vs), 1316 (w), 1278 (s), 1244 (w), 1208 (vs), 1160 (w), 1123 (w), 1101 (w), 1075 (w), 1021 (s), 980 (w), 939 (w), 878 (w), 800 (w), 732 (m), 691 (s), 633 (w), 609 (w), 570 (w), 539 (w), 505 (w), 470 (w), 420 (w), 384 (w), 356 (m), 323 (m).

Synthesis of [(Cp*Co)₂(η^{2,2}-P₂)] (5**).** Complex **1** (375 mg, 1.00 mmol) and white phosphorus (62 mg, 0.50 mmol) were suspended in 10 mL of xylene. The reaction mixture was stirred for 7 days at 135 °C. After removing the solvent in vacuo the black residue was washed with pentane several times. By drying the solid in vacuo compound **5** was obtained as a black solid. Yield: 241 mg, 94%. ¹H NMR (400 MHz, 25 °C, C₆D₆): δ = 1.65 (s, 15 H, C₅(CH₃)₅), 1.3C{¹H} NMR (100.6 MHz, 25 °C, C₆D₆): δ = 10.4 (C₅(CH₃)₅), 94.6 (C₅(CH₃)₅). ³¹P{¹H} (162 MHz, 25 °C, C₆D₆): δ = -15.1 (s, P₂). MS (EI): *m/z* 511.8 (95) [M]⁺, 450.1 (7) [M - P₂]⁺, 377.0 (22) [M - (η⁵-C₅Me₅)]⁺, 329.3 (47) [(η⁵-C₅Me₅)₂Co]⁺, 314.0 (48) [(η⁵-C₅Me₅)₂Co - CH₃]⁺, 256.1 (90) [(η⁵-C₅Me₅)Co(P₂)]⁺. IR (KBr [cm⁻¹]): 2968 (m), 2902 (vs), 1656 (w), 1633 (w), 1618 (w), 1566 (w), 1469 (s), 1428 (m), 1373 (vs), 1255 (w), 1210 (m), 1109 (vs, br), 1023 (vs), 879 (w), 798 (m), 613 (w), 575 (w), 474 (m), 434 (m), 356 (s), 301 (vs).

Crystallography. Crystal data collection and processing parameters are given below. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS diffractometer (Mo Kα radiation) equipped with a FTS AirJet low-temperature device. Data were collected at 203 K. Images were processed with the STOE software packages, and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary, and structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions and refined using a riding model. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package.¹¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms

were assigned to idealized positions and included in structure factors calculations. Some residual electron density of a solvent molecule (presumably hexane) in the cell of compound **2** was difficult to model properly, and the Platon squeeze function was used to eliminate the contribution of the electron density in the solvent region from the intensity data. The solvent-free model was then employed for the final refinement.

Crystal Structure Determination of [Cp*Co(Pr₂Im)(η²-P₄)]2**.** C₁₉H₃₁CoN₂P₄, *M_r* = 470.27, black block, 0.50 × 0.40 × 0.20 mm, monoclinic, space group *Cc*, *a* = 16.394(3) Å, *b* = 9.4038(19) Å, *c* = 17.023(3) Å, β = 118.37(3)°, *V* = 2309.2(8) Å³, *T* = 203 K, *Z* = 4, ρ_{calcd} = 1.353 g·cm⁻³, μ = 1.027 mm⁻¹, *F*(000) = 984, 8075 reflections in *h*(-19/20), *k*(-11/11), *l*(-20/20) measured in the range 4.21° < θ < 25.84°, completeness 94.7%, 4150 independent reflections, 3943 observed reflections (*I* > 2σ(*I*)), 244 parameters, 2 restraints. All data: *R*₁ = 0.0281 and *wR*₂ = 0.0705. *I* > 2σ(*I*): *R*₁ = 0.0255 and *wR*₂ = 0.0664. Goof: 1.080. Largest difference peak/hole: 0.273/-0.231 e Å⁻³.

Crystal Structure Determination of [(Cp*Co(Pr₂Im))₂(μ,η²-P₄)]3**.** C₃₈H₆₂Co₂N₄P₄, *M_r* = 816.66, brown block, 0.35 × 0.15 × 0.12 mm, triclinic, space group *P*-1, *a* = 10.507(7) Å, *b* = 13.924(9) Å, *c* = 17.651(12) Å, α = 101.841(8)°, β = 91.660(7)°, γ = 105.228(7)°, *V* = 2429(3) Å³, *T* = 203 K, *Z* = 2, ρ_{calcd} = 1.116 g·cm⁻³, μ = 0.841 mm⁻¹, *F*(000) = 864, 9617 reflections in *h*(-13/12), *k*(-17/16), *l*(0/22) measured in the range 1.73° < θ < 26.44°, completeness 96.2%, 9617 independent reflections, 7944 observed reflections (*I* > 2σ(*I*)), 451 parameters, 0 restraints. All data: *R*₁ = 0.0601 and *wR*₂ = 0.1263. *I* > 2σ(*I*): *R*₁ = 0.0479 and *wR*₂ = 0.1184. Goof: 1.102. Largest difference peak/hole: 0.590/-0.249 e Å⁻³.

Crystal Structure Determination of [Cp*Co(μ,η^{4,2}-P₄)Co(Pr₂Im)Cp*]4**.** C₂₉H₄₆Co₂N₂P₄, *M_r* = 664.42, red block, 0.80 × 0.80 × 0.30 mm, monoclinic, space group *P*2₁/*c*, *a* = 16.671(3) Å, *b* = 11.665(2) Å, *c* = 17.231(3) Å, β = 108.69(3)°, *V* = 3174.2(11) Å³, *T* = 203 K, *Z* = 4, ρ_{calcd} = 1.390 g·cm⁻³, μ = 1.268 mm⁻¹, *F*(000) = 1392, 26 958 reflections in *h*(-20/20), *k*(-13/13), *l*(-21/21) measured in the range 2.15° < θ < 25.97°, completeness 94.3%, 5863 independent reflections, 5331 observed reflections (*I* > 2σ(*I*)), 348 parameters, 0 restraints. All data: *R*₁ = 0.0553 and *wR*₂ = 0.1368. *I* > 2σ(*I*): *R*₁ = 0.0501 and *wR*₂ = 0.1319. Goof: 1.108. Largest difference peak/hole: 0.627/-0.582 e Å⁻³.

■ ASSOCIATED CONTENT

📄 Supporting Information

Simulation of NMR spectra and details of molecular structure determination. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†Dedicated to Roald Hoffmann on the occasion of his 75th birthday.

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