

## A Thermally Stable and Sterically Unprotected Terminal Electrophilic Phosphinidene Complex of Cobalt and Its Conversion to an $\eta^1$ -Phosphirene

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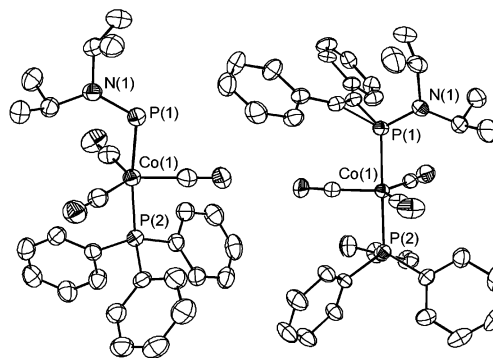
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Since their discovery by Lappert in 1987,<sup>1</sup> stable terminal phosphinidene complexes of transition metals have remained relatively rare.<sup>2</sup> Like carbenes, terminal phosphinidene complexes can be roughly divided into electrophilic or nucleophilic categories on the basis of their reactivities.<sup>3</sup> Until recently, all examples of stable phosphinidene complexes could be categorized as nucleophilic, although transient electrophilic phosphinidene complexes have been studied extensively.<sup>4,5</sup> We have developed a successful route to electrophilic aminophosphinidene complexes via chloride abstraction from chloroaminophosphido complexes and have used it to synthesize stable electrophilic phosphinidene complexes of molybdenum, tungsten, and ruthenium.<sup>6,7</sup> The ruthenium complex was the first example of a stable phosphinidene involving a late transition metal. The amino substituent on phosphorus in these complexes stabilizes the electrophilic phosphorus center via a nitrogen lone pair to phosphorus  $\pi$  donor interaction, which is analogous to the heteroatom to carbon donor interaction observed in Fischer-type carbene complexes.<sup>8</sup> Since that report, there has been an increased interest in the synthesis of terminal late metal phosphinidene complexes, and examples of sterically congested nickel<sup>9</sup> and iridium<sup>10</sup> complexes have recently been reported. In this communication, we report the synthesis and characterization of the first terminal phosphinidene complex of cobalt and the first sterically unhindered late transition metal phosphinidene complex.

The terminal cobalt chloroaminophosphido complex  $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{P}(\text{Cl})\text{N}^i\text{Pr}_2\}]$  (**1**) was formed via reaction of  $\text{K}[\text{Co}(\text{CO})_4]$  with the dichloroaminophosphine  $^i\text{Pr}_2\text{NPCl}_2$  in the presence of triphenylphosphine.<sup>11</sup> Reaction of **1** with aluminum trichloride results in abstraction of chloride from the chloroaminophosphido ligand to form the aminophosphinidene complex  $[\text{Co}(\text{CO})_3(\text{PPh}_3)(\text{PN}^i\text{Pr}_2)][\text{AlCl}_4]$  (**2**).<sup>12</sup> Compound **2** has been structurally characterized, and an ORTEP diagram of the cation is shown in Figure 1. The geometry at cobalt is trigonal bipyramidal with the two phosphorus ligands occupying the axial positions and three carbonyl ligands occupying equatorial positions. The phosphinidene ligand is staggered with respect to the equatorial carbonyl ligands, with  $\text{N}-\text{P}(1)-\text{Co}-\text{C}(1)$  and  $\text{N}-\text{P}(1)-\text{Co}-\text{C}(3)$  torsion angles of  $59.0(1)^\circ$  and  $58.4(1)^\circ$ . The  $\text{P}(1)-\text{Co}-\text{P}(2)$  angle of  $172.82(3)^\circ$  is distorted from the ideal trigonal bipyramidal geometry, likely to avoid steric interaction of the di-isopropylamino group with the equatorial carbonyl ligands.

The triphenylphosphine phosphorus–cobalt distance is  $2.2633(7)$  Å, while the phosphinidene  $\text{P}-\text{Co}$  distance is  $2.1875(8)$  Å. Other than cobalt, the phosphorus is bound only to the nitrogen atom with a  $\text{P}(1)-\text{N}$  distance of  $1.626(2)$  Å and an angle at phosphorus of  $115.41(8)^\circ$ . The methyl groups of the isopropyl group proximal to the metal are directed away from the metal and toward the distal isopropyl group, minimizing steric interaction with the equatorial carbonyls. The methyl groups of the distal isopropyl group are



**Figure 1.** ORTEP diagrams of the cations of  $[\text{Co}(\text{CO})_3(\text{PPh}_3)(\text{PN}^i\text{Pr}_2)]^+[\text{AlCl}_4]^-$  (**2**) and  $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{P}(\text{N}^i\text{Pr}_2)\text{C}(\text{Ph})\text{C}(\text{Ph})\}]^+[\text{AlCl}_4]^-$  (**3**). Hydrogen atoms have been omitted, and thermal ellipsoids are shown at the 50% level.

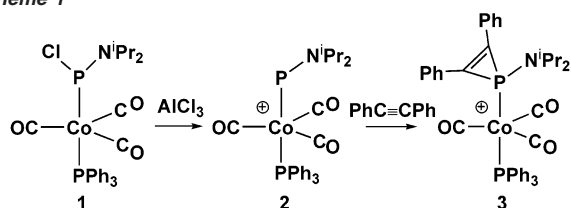
directed away from the proximal isopropyl group. The geometry at nitrogen is planar within experimental error (Scheme 1).

The  $^{31}\text{P}$  NMR spectrum of **2** shows a high-field resonance at  $\delta$  861.2 in the typical region for terminal phosphinidene complexes,<sup>2,7</sup> as well as a peak at  $\delta$  47.6 which corresponds to the triphenyl phosphine ligand. No coupling is observed between the two phosphorus nuclei despite their trans relationship. The  $^1\text{H}$  NMR spectrum of **2** shows two inequivalent isopropyl groups, indicating that there is a barrier to rotation about the PN bond.

Like Fischer carbene complexes, electrophilic phosphinidene complexes are generally considered to be formally derived from the singlet state of free phosphinidene in which the phosphorus atom has two lone pairs and an empty p orbital perpendicular to the plane of the substituent and the lone pairs. Coordination of this moiety to a transition metal results in donation of one lone pair to an appropriate empty metal orbital. Metal to phosphorus  $\pi$ -back-donation to the empty phosphorus p orbital competes with nitrogen lone pair to phosphorus donation.<sup>3</sup> The structural and spectroscopic parameters of compound **2** are clearly consistent with this formulation. The  $\text{Co}-\text{P}$  bond length is longer than expected for a cobalt–phosphorus double bond<sup>13</sup> and is in fact only slightly shorter than typical cobalt–trimethylphosphine bond lengths.<sup>14</sup> The  $\text{P}-\text{N}$  bond is intermediate between PN single and PN double bonds and is similar to those in recently characterized Mo, W, and Ru amino-phosphinidene complexes.<sup>7</sup> This bond length, along with the planarity at nitrogen and the restricted PN rotation, indicates the presence of a significant N to P donor interaction.

An examination of the structure of **2** reveals that the two-coordinate phosphorus center has very little steric protection. In contrast, other late metal phosphinidene complexes of iridium and nickel required the stabilizing effects of bulky ligands on the metal and sterically demanding substituents on phosphorus. The successful isolation of complex **2** clearly shows that given sufficient  $\pi$ -donation

Scheme 1



to phosphorus from the metal or the phosphorus substituent, electrophilic terminal phosphinidene complexes, even of first row metals, are not fundamentally unstable.

The electrophilicity of complex **2** has been demonstrated by its reaction with diphenyl acetylene to form the phosphirene complex  $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{P}(\text{N}^i\text{Pr}_2)\text{C}(\text{Ph})\text{C}(\text{Ph})\}][\text{AlCl}_4]$  (**3**).<sup>15</sup> This reactivity toward alkynes thus parallels the behavior of transient electrophilic phosphinidene complexes.<sup>4,16,17</sup> An ORTEP diagram of the cation of **3** (Figure 1) again displays trigonal bipyramidal geometry at cobalt with the two phosphorus ligands occupying the axial positions. The alkyne has added to the phosphinidene phosphorus, forming a three-membered ring. The Co–P(1) distance of 2.2235(3) Å is very close to the cobalt–triphenylphosphine distance of 2.2320(3) Å. The P–C distances within the ring are 1.7635(6) and 1.7561(6) Å, and the C=C distance is 1.3396(9) Å. The angles within the ring are 67.34(3)°, 67.92(3)°, and 44.74(3)°, respectively, at C(11), C(12), and P(1). The diisopropyl-amino group is oriented similar to that in **2**, and the P–N bond distance of 1.659(2) Å is now consistent with a single bond, indicating that N to P donation is no longer necessary to stabilize the phosphorus center.

The <sup>31</sup>P NMR spectrum of **3** shows two doublets with a peak at δ –76.6 showing the characteristic high-field shift of the phosphorus nucleus in a phosphirene ring.<sup>18</sup> The coupling constant is 140 Hz, typical of a trans arrangement of the phosphorus ligands. The <sup>1</sup>H NMR spectrum shows single resonances for the CH and CH<sub>3</sub> hydrogen atoms of the isopropyl groups, indicating free rotation about the PN bond, again consistent with a P–N single bond.

In summary, the first terminal cobalt phosphinidene complex has been isolated. The complex is stable despite a lack of steric protection, and its structural and spectroscopic parameters clearly show that the phosphinidene ligand is stabilized by a donor interaction with the amino substituent. The electrophilicity of the phosphinidene complex has been demonstrated in its reaction with diphenylacetylene.

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**Supporting Information Available:** Synthetic procedures, analytical, spectroscopic, and crystallographic data for compounds **1–3** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Data for  $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{P}(\text{Cl})\text{N}^i\text{Pr}_2\}]$  (**1**): <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) δ 7.4–7.7 (m, 15H, PPh<sub>3</sub>), 4.1 (b, 2H, CH), 1.43 (d, 6H, <sup>3</sup>J(HH) = 6.7 Hz, CH<sub>3</sub>), 1.26 (d, 6H, <sup>3</sup>J(HH) = 6.7 Hz, CH<sub>3</sub>). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ) δ 282.8 (d, P(Cl)-N<sup>i</sup>Pr<sub>2</sub>), 54.1 (d, PPh<sub>3</sub>), <sup>2</sup>J(PP) = 24 Hz. IR ( $\nu_{\text{CO}}$ ) 2000m, 1977s, 1967s  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{31}\text{NO}_3\text{P}_2\text{Cl}_2\text{Co}$ : C, 51.20; H, 4.76; N, 2.13. Found: C, 51.58; H, 5.31; N, 2.21. X-ray data: monoclinic,  $P2(1)/n$ ,  $a = 11.8269(8)$ ,  $b = 19.988(1)$ ,  $c = 14.214(1)$ ,  $\beta = 112.229(1)$ ,  $V = 3110.5(4)$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.402$ ,  $T = 173(2)$  K, 8041 independent reflections [ $R(\text{int}) = 0.0343$ ],  $R = 0.0393$ ,  $wR2 = 0.0974$ .
- (12) Data for  $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{P}(\text{N}^i\text{Pr}_2)\}][\text{AlCl}_4]$  (**2**): <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) δ 7.4–7.7 (m, 15H, PPh<sub>3</sub>), 5.66 (sept., 1H, <sup>3</sup>J(HH) = 6.3 Hz, CH), 4.75 (b, 1H, CH), 1.67 (d, 6H, <sup>3</sup>J(HH) = 6.3 Hz, CH<sub>3</sub>), 1.58 (d, 6H, <sup>3</sup>J(HH) = 6.5 Hz). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ) δ 861.2 (s, PN<sup>i</sup>Pr<sub>2</sub>), 47.6 (PPh<sub>3</sub>). IR ( $\nu_{\text{CO}}$ ) 2029s, 2017s  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{29}\text{NO}_3\text{P}_2\text{AlCl}_4\text{Co}$ : C, 45.99; H, 4.14; N, 1.99. Found: C, 45.53; H, 4.25; N, 2.06. X-ray data: orthorhombic,  $P2(1)2(1)2(1)$ ,  $a = 12.5260$ ,  $b = 12.8291(6)$ ,  $c = 20.424(1)$ ,  $V = 3282.1(3)$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.427$ ,  $T = 173(2)$  K, 8516 independent reflections [ $R(\text{int}) = 0.0392$ ],  $R = 0.0379$ ,  $wR2 = 0.0819$ .
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- (15) Data for  $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{P}(\text{N}^i\text{Pr}_2)\text{C}(\text{Ph})\text{C}(\text{Ph})\}][\text{AlCl}_4]\cdot\text{CH}_2\text{Cl}_2$  (**3**): <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) 7.3–7.9 (m, 25H, Ph), 3.80 (d septets, 2H, <sup>3</sup>J(HH) = 6.7 Hz, <sup>3</sup>J(HP) = 6.2 Hz, CH), 1.25 (d, 12H, <sup>3</sup>J(HH) = 6.7 Hz). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ) δ 54.4 (d, PPh<sub>3</sub>), <sup>2</sup>J(PP) = 140 Hz), –76.6 (d, PC<sub>2</sub>, <sup>2</sup>J(PP) = 140 Hz). IR ( $\nu_{\text{CO}}$ ) 2019s, 2001s  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{41}\text{O}_3\text{P}_2\text{NAlCl}_4\text{Co}$ : C, 52.09; H, 4.27; N, 1.45. Found: C, 51.26; H, 4.66; N, 1.55. X-ray data: triclinic,  $P-1$ ,  $a = 12.3668(5)$ ,  $b = 13.0461(6)$ ,  $c = 15.9147(7)$ ,  $\alpha = 88.193(1)$ ,  $\beta = 75.292(1)$ ,  $\gamma = 73.836(1)$ ,  $V = 2383.2(2)$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.290$ ,  $T = 173(2)$  K, 12 275 independent reflections [ $R(\text{int}) = 0.0284$ ],  $R = 0.0487$ ,  $wR2 = 0.1650$ .
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