ORGANOMETALLICS

Coordination of an N-Heterocyclic Phosphenium Containing Pincer Ligand to a Co(CO)₂ Fragment Allows Oxidation To Form an Unusual N-Heterocyclic Phosphinito Species

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S Supporting Information

ABSTRACT: A tridentate pincer ligand featuring a central Nheterocyclic phosphenium (NHP⁺) donor has been coordinated to a $Co(CO)_2$ fragment to generate the Co NHP complex [PPP]Co(CO)₂ (2). The NHP unit adopts an unusual pyramidal geometry with a relatively long Co–P distance, suggesting a stereochemically active nonbonding phosphorus lone pair. Interestingly, treatment of 2 with trimethylamine *N*-oxide affords [P(P=O)P]Co(CO)₂ (3), in which the Co-bound central phosphorus donor has been oxidized to an unprecedented N-heterocyclic phosphinito



species. The bonding and electronic properties of these complexes are discussed in the context of DFT and NBO computational data.

While N-heterocyclic carbene ligands (NHCs) have become ubiquitous in the field of transition metal and organo-catalysis,¹⁻⁵ far less focus has been placed on the potential applications of their isovalent group 15 analogues, Nheterocyclic phosphenium cations (NHPs).⁶⁻¹⁰ First reported in 1972,^{11,12} theoretical investigations of the electronic structure of NHPs have shown that they are poor σ donors but excellent π acceptors, in contrast to NHCs, which are very good σ -donors and poor π -acceptors. Recent advancements in the chemistry of NHPs include new preparative methods¹³⁻¹⁶ and new reactivity patterns,^{13,17-19} but the coordination chemistry and catalytic capabilities of NHPs are relatively unexplored compared to their NHC counterparts.

One of the more interesting aspects of NHP ligands is their ability to adopt different binding modes toward transition metals depending on the electronic nature of the transition metal center. Most commonly, when binding to an electronpoor fragment, NHPs act as both σ -donors and π -acceptors, leading to a planar geometry at the phosphorus atom (NHP⁺ description). However, when binding to an electron-rich fragment, NHPs adopt a pyramidal geometry indicative of a nonbonding phosphorus lone pair. Two limiting descriptions for the bonding in such pyramidal NHPs have been suggested: (1) the Lewis acidic NHP phosphorus acts solely as an electron pair acceptor (NHP^+/M^n) and (2) the bonding between the metal and the NHP is covalent and the NHP is best described as a phosphido ligand (NHP⁻/ M^{n+2}). In this sense, a convincing analogy between NHPs and nitrosyls, which can adopt either linear or bent geometries, can be made,¹⁷ highlighting the potential noninnocent character of these ligands and bringing about potential ambiguities in the formal metal oxidation state. Key advantages of phosphenium ligands

over their noninnocent nitrosyl counterparts are (1) the ability to modify their steric and electronic properties via derivatization and (2) the ability to incorporate these ligands into chelating frameworks. These strategies may also be effective at imparting stability in transition-metal NHP complexes and protecting them from nucleophilic attack. Transition-metal complexes of multidentate ligands featuring NHPs are noticeably absent from the literature, particularly in comparison to the growing number of NHC-containing chelating ligands.^{20,21}

We recently reported the synthesis of a cationic N-heterocyclic phosphenium-containing pincer ligand [PPP]⁺ in which the central NHP unit is linked to two phosphine side arms via aryl linkers.²² As a result of the electrophilicity of the central phosphenium center, coordination to transition metal halide starting materials proved problematic, leading to chlorophosphine complexes. Herein, we turn our attention to a different synthetic strategy, utilizing NaCl extrusion from a monoanionic transition metal starting material and a chlorophosphine precursor as a driving force to synthesize a bona fide metal NHP complex featuring our new chelating ligand. A similar metal coordination strategy has been utilized previously to synthesize metal NHP complexes, including $Cp*Fe(CO)_2(NHP^{Me}).^{23}$

Treatment of the PPP-Cl precursor 1 with Na[Co(CO)₄] in THF cleanly generates the neutral red complex [PPP]Co(CO)₂ (2) in 95% yield (Scheme 1). Complex 2 is characterized by two ³¹P NMR signals at 286.4 (triplet) and 29.9 ppm (doublet), corresponding to a Co-bound central NHP and

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Received:August 31, 2011Published:October 5, 2011
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Scheme 1



two Co-bound phosphine donors, respectively. The infrared spectrum of 2 reveals two ν (CO) stretches at 1981 and 1926 cm⁻¹, implying that two CO ligands remain bound to Co.

X-ray crystallography of single crystals of **2** confirms the tridentate binding mode of the NHP-diphosphine ligand and the presence of two remaining carbonyl ligands (Figure 1). The



Figure 1. Displacement ellipsoid representations of 2 and 3. For clarity, only one of the two independent molecules in the asymmetric unit of 2 is shown and hydrogen atoms and a THF solvate molecule have been omitted. Relevant interatomic distances (Å) are as follows. For 2: Co1–P102, 2.2386(6); Co1–P101, 2.2083(6); Co1–P103, 2.1988(5); Co1–C139, 1.792(2); Co1–C140, 1.765(2). For 3: Co1–P2, 2.1675(5); Co1–P1, 2.1791(5); Co1–P3, 2.1853(5); Co1–C39, 1.7773(19); Co1–C40, 1.7793(19); P2–O1, 1.4875(13).

geometry about Co is intermediate between square pyramidal and trigonal bipyramidal ($\tau = 0.56$),²⁴ with the central NHP occupying a position essentially trans to a CO ligand (P-Co- $C \approx 167^{\circ}$). More interesting, however, is the geometry about the central phosphorus of the NHP unit. Unlike the standard planar geometry expected for an N-heterocyclic phosphenium moiety, the NHP adopts a distinctly pyramidal geometry. Of the two molecules in the asymmetric unit, the average angle between the N-P-N plane and the Co-P bond vector is ~114°. Such a pyramidal geometry implies the presence of a lone pair on the central NHP phosphorus, suggesting that the complex may be described as either an NHP⁻ phosphido ligand coordinated to a Co^I center or an NHP⁺ phosphenium ligand acting as an electron pair acceptor to Co^{-I}. Several Co NHP complexes have been structurally characterized to date: an asymmetric $\text{Co}_2(\text{CO})_5(\mu\text{-NHP}^{\text{Me}})_2$ dimer²⁵ and $(\text{CO})_3\text{Co (NHP^R)$ (R = ^tBu, Mes).²⁶ The Co-P^{NHP} distance in 2 (2.2386(6) Å) is relatively long compared to the Co-P^{NHP} distances in the planar phosphenium complexes $Co_2(CO)_5(\mu$ - NHP^{Me} ₂ (2.05 Å)²⁵ and (CO)₃Co(NHP^R) (2.04 and 2.00 Å for R = ^tBu, Mes).²⁶ This longer distance is compatible with the absence of multiple Co-P bond character. Interestingly, of the ~20 structurally characterized transition-metal terminal NHP complexes, complex 2 joins $Cp^*Fe(CO)_2(NHP^{Me})$ as only the second example of a pyramidal NHP coordination mode.²³ The latter compound was described by Paine and co-workers as an adduct between an $Fe^0 [Cp_2^*Fe(CO)_2]^-$ fragment and an NHP^{Me+} phosphenium ligand.

In an effort to promote carbonyl dissociation, complex 2 was treated with trimethylamine *N*-oxide at room temperature. Rather than oxidation of CO and extrusion of CO_2 , the new dicarbonyl product 3 was obtained (Scheme 2). The triplet

Scheme 2



signal for the central phosphorus in the ³¹P NMR spectrum of **3** is shifted substantially upfield (81.8 ppm) compared to that of 2, while the doublet for the phosphine side arm donors is similar (27.8 ppm). X-ray diffraction of single crystals revealed 3 to be the product of oxidation of the central NHP phosphorus, $[P(P=O)P]Co(CO)_2$ (Figure 1), to generate an N-heterocyclic phosphinito complex. While there are many examples of metal-bound phosphorus oxidation by trimethylamine N-oxide, 27-29 to our knowledge, this is the first isolated example of an oxidized NHP. The most striking feature of the solid-state structure of 3 is a $Co-P^{NHP}$ distance significantly shorter than that observed in the phosphorus(III) precursor 2 (2.1675(5) Å vs 2.2386(6) Å). We attribute this phenomenon to increased Co to P^{NHP} back-bonding upon phosphorus oxidation, and a similar unusually short M-P distance has been observed in a Pd-P(O)(NR₂)₂ species.³⁰ Consistent with this explanation, the $Co(CO)_2$ -derived IR stretches of 3 are shifted ~ 20 cm⁻¹ higher in energy than those of 2 (2000, 1949 cm⁻¹), suggesting decreased Co \rightarrow CO π back-bonding as a result of increased $Co \rightarrow P$ back-bonding. Similarly, the CO stretching frequencies of $CpFe(CO)_2(P(CF_3)_2)$ have been shown to increase upon oxidation to $CpFe(CO)_2(O=P(CF_3)_2)$ with a corresponding contraction of the Fe-P bond by 0.07 Å.³¹ While one would typically compare P-N distances between 2 and 3 to assess the extent of metal-phosphorus back-donation, this comparison is rendered invalid by the different oxidation states of phosphorus in these two compounds. The P(P=O)Pligand in 3 is similar to an oxidized phosphido PP(O)P pincer ligand recently reported by Bourrisou.³²

To investigate the electronic structure and bonding in 2 and 3, a computational investigation was undertaken using density functional theory (DFT, Gaussian 09) and natural bond orbital (NBO) analysis (Figure 2). The Co–P^{NHP} NBO in complex 2 is predicted to be essentially covalent, with 46.3% contribution from Co and 53.7% contribution from P. Upon phosphorus oxidation in complex 3, the NBO remains covalent, but with slightly more contribution from P (Co, 41.0%; P, 59.0%). Notably, there is considerably more phosphorus s character involved in the Co–P NBO of 3 than in 2. While the natural charges of Co in both complexes are predicted to be identical (-1.52), the charge on phosphorus increases from 1.12 in 2 to 2.05 in 3, consistent with oxidation from phosphorus(III) to phosphorus(V).

For comparison, calculations were also performed on two model compounds: $(Me_2P)Co(PPh_3)_2(CO)_2$ (4), a bona fide phosphido analogue of 2, and $(NHP^{Me})Co(PPh_3)_2(CO)_2$ (5; see the Supporting Information). The phosphide Co–P NBO of 4 has a constitution remarkably similar to that in 2, with 46.2% contribution from Co and 53.8% contribution from P. These observations are in line with assignment as an NHP



Figure 2. Computed Co–P natural bond orbitals (NBOs) of **2** and **3**. **2**: 46.3% Co, 53.74% P (85.5% p, 14.2% s). **3**: 41.0% Co, 59.0% P (64.1% p, 35.4% s).

phosphido ligand, since a dative donor-acceptor interaction from Co to P would be expected to have significantly more contribution from Co. Interestingly, the Co- P^{NHP} NBO in **5** is calculated to be made up of 53.2% Co and 46.8% P character and, thus, more in line with a donor/acceptor bonding description. The natural charge on Co in **2** is computed to be -1.52, only slightly more negative than that of the Co center in **4** (-1.31).

An additional convincing piece of evidence for NHP⁻ phosphido character comes from the calculated Co-CO vibrational frequencies for 2 compared to those in 4 and 5. While the computed values do not match experimental values, comparisons between other computed values remain valid. The infrared CO stretches calculated for 2 are 1928 and 1885 cm^{-1} while those predicted for phosphido complex 4 are 1925 and 1856 cm⁻¹, suggesting a similar Co oxidation state (Co^I) in these two complexes. On the other hand, the CO stretching frequencies predicted for 5 are 1894 and 1812 cm⁻¹, indicative of a more electron-rich Co center involved in a donor/acceptor interaction with the NHP without fully undergoing twoelectron oxidation. Thus, our findings from DFT and NBO studies suggest that the bonding in 2 is best described as an NHP⁻ phosphide ligand bound to a formally Co^I center. The NHP⁻ phosphido bonding description renders these PPP ligands analogous to a family of bis(phosphine)phosphido ligands reported in recent years.^{33–36} The difference between the bonding of the chelating NHP-diphosphine ligand and the monodentate NHP^{Me} in model complex 5 is intriguing and may be related to the enforced planarity of the N-aryl substituents, delocalizing the nitrogen lone pairs responsible for stabilizing the singlet state of the phosphenium.

In summary, sodium-halogen exchange has proven to be a useful synthetic route to a cobalt complex coordinated by our previously reported NHP-diphosphine chelating ligands. Upon NHP coordination, however, the NHP unit adopts an unusual pyramidal geometry indicative of a NHP⁻ phosphido description and a two-electron-oxidized Co center. Consistent with this description, oxidation with trimethylamine *N*-oxide leads exclusively to oxidation of the central NHP phosphorus to generate an unprecedented metal-bound N-heterocyclic phosphinito species. Future investigations will focus on the coordination chemistry of the NHP-diphosphine ligand and its oxidized derivative with additional transition metal fragments in an effort to evaluate the factors that govern planar vs pyramidal coordination modes in these sterically and electronically modifiable nitrosyl analogues.

ASSOCIATED CONTENT

Supporting Information

Text, tables, and figures giving experimental procedures, computational data, and additional spectral data and CIF files giving crystallographic details and data for **2** and **3**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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ACKNOWLEDGMENTS

C.M.T. is grateful for a 2011 Sloan Research Fellowship. We also thank Brandeis University for funding this project.

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