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Insertion of a Nontrigonal Phosphorus Ligand into a Transition Metal-Hydride: Direct Access to a Metallohydrophosphorane

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Abstract

The synthesis and reactivity of an NPN-chelating ligand containing a nontrigonal phosphorous triamide center (L1 = P(N(α-N(2-pyridyl)C6H4)2) is reported. Metalation of L1 with RuCl2(PPh3)3 gives RuCl2(PPh3)(L1) (2). By contrast, metalation of L1 with RuHCl(CO)(PPh3)3 yields RuCl(CO)(PPh3)(L1H) (3), a chelated 10-P-5 ruthenahydridophosphorane, via net insertion into the Ru–H bond. Hydride abstraction from 3 with Ph3CPF6 gives [RuCl(CO)(PPh3)(L1)]PF6 (4); reaction of 4 with NaBH4 returns 3.

TOC graphic

Tricoordinate phosphorus (8-P-3) compounds 1-2 are essential donor ligands in transition metal chemistry. 3-6 Within typical (pseudo)threefold symmetry, the Lewis basicity and nucleophilicity of trigonal pyramidal 8-P-3 compounds makes the mixture of a transition metal fragment (M–X) and a phosphine (R3P) a robust and reliable route to the formation of R3P–M–X complexes (Figure 1, left). Contrarily, we describe in this Communication a noncanonical ligation event arising from metalation of a nontrigonal 8-P-3 compound. Specifically, we report the insertion of a distorted 8-P-3 phosphorous triamide center into a transition metal-hydride bond to form a 10-P-5 metallophosphorane7-31 (Figure 1, right) in preference to the typical 8-P-4 complex. Through these results, we realize the merger of phosphorus-based biphilic reactivity 32 with transition metal ligancy and thereby provide a

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Experimental procedures, spectral data (1H, 13C, 31P NMR), cartesian coordinates (.pdf)

Crystallographic files (.cif)

The authors declare no competing financial interests.
new entry point for the study of supporting ligands based on higher coordination number phosphorus fragments.

Nontrigonal tricoordinate phosphorus compounds (e.g. molecular symmetries \(C_{2v}\), \(C_s\)) express enhanced biphilic reactivity. For instance, \(C_s\)-symmetric phosphorous triamide 1 inserts into \(E-H\) bonds (\(E = -\text{OR}, -\text{NHR}\)), in some cases reversibly. This and related \(P\)-centered reactivity have been applied to a variety of stoichiometric and catalytic chemical transformations. In pursuit of transition metal complexation, we elected to embed the nontrigonal phosphorous triamide \(\text{PN}_3\) core within a \(\kappa^3\)-chelating framework in order to afford kinetically stable complexes. To this end, ligand \(\text{L1}\) was designed to incorporate two 2-pyridyl moieties flanking the phosphorous triamide \(\text{PN}_3\) core. Its synthesis was accomplished in two steps from bis(2-aminophenyl)amine by twofold electrophilic heteroarylation with 2-chloropyridine, followed by reaction with \(\text{PCl}_3\) in the presence of \(\text{NEt}_3\) (Scheme 1).

In the solution phase, \(^1\text{H}\) NMR spectra of \(\text{L1}\) exhibit a twofold equivalence of resonances (\(\delta\) 8.26–6.92 ppm), indicating a time-averaged \(C_s\) molecular symmetry or higher. A \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of \(\text{L1}\) displays a singlet at \(\delta 141.7\) ppm (Figure 2a), residing upfield as compared to 1 (\(\delta 159.8\) ppm). Structural analysis suggests the origin of this spectral distinction. X-ray diffraction of a colorless single crystal of the ligand \(\text{L1}\) revealed a solid state structure of approximate \(C_s\) local symmetry (Figure 3a) marked by folding of the phosphorous triamide moiety along the \(P_1-N_1\) axis, in line with previous observations for 1. However, in contrast to 1, the \(\angle N_2-P_1-N_3\) angle for \(\text{L1}\) is decidedly more acute (cf. 108.67(4)° vs. 115.21(7)°) while the bond lengths \(d(P_1-N_{2/3})\) are somewhat longer (Table 1). These structural features can be rationalized qualitatively by reference to Bent’s rule, where the electron-withdrawing 2-pyridyl \(N\)-substituents attract phosphorus \(p\)-character to the \(P_1-N_{2/3}\) bonds, resulting in elongated \(d(P-N_{2/3})\) distances and contracted \(\angle N_2-P_1-N_3\) angles. The complementary accrual of \(s\)-character in the nonbonding \(P\)-based lone pair therefore increases nuclear shielding for \(\text{L1}\) as observed in the \(^{31}\text{P}\{^1\text{H}\}\) NMR chemical shift.

Metalation of \(\text{L1}\) by treatment with \(\text{RuCl}_2(\text{PPh}_3)_3\) was realized in THF at ambient temperature to afford an octahedral complex \(\text{RuCl}_2(\text{PPh}_3)(\text{L1})(\text{2})\). In the resulting \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra, the resonance corresponding to the phosphorus nucleus of \(\text{L1}\) is found downfield (relative to free ligand \(\text{L1}\)) as a doublet at \(\delta 186.8\) ppm with \(J = 49\) Hz; the corresponding coupling partner arising from the phosphorus nucleus of \(\text{PPh}_3\) resonates at \(\delta 42.7\) ppm with complementary \(J = 49\) Hz coupling (Figure 2b). The \(\kappa^3\)-chelating mode is confirmed by X-ray diffraction of a single crystal sample, where the facial coordination of the tridentate \(\text{L1}\) ligand is evident (Figure 3b). The \(\text{Ph}_3\text{P}\) ligand is found \(cis\) with respect to the phosphorus atom in the \(\text{L1}\) fragment, giving a complex of overall \(C_1\) symmetry. The high number of complex overlapping resonances in the aryl region of the solution phase \(^1\text{H}\) NMR spectra for 2 are congruent with the elimination of the symmetry element about the central \(P_1-N_1\) axis of \(\text{L1}\) upon ligation. The \(\angle N_2-P_1-N_3\) angle is broadened (113.94(4)°) as compared to free \(\text{L1}\), braced by the constraint imposed by the chelation of the pyridyl arms to Ru. A distinctive feature of the structure for 2 is the exceptionally short \(d(\text{Ru}_1-P_1)\) bond distance (2.1262(3) Å), which is significantly shorter than the typical range for \(\text{R}_3\text{P–Ru}\).
bonds (2.20 Å < d < 2.45 Å) and only modestly longer than the shortest characterized R₃P–Ru distance (2.0883(6) Å), found for a NPN κ₃-chelate containing a central tricoordinate phosphorus site substituted with electronegative heteroatoms similar to 2. The electronegative substituents probably contribute to the short Ru–P length of 2 by promoting π-backbonding from the metal.46

Metalation of L₁ with RuHCl(CO)(PPh₃)₃ was similarly attempted; however, the expected congener of 2 was not returned. Instead, ³¹P{¹H} NMR spectra (Figure 2c) showed formation of a new complex with a large upfield shift for the phosphorus atom of L₁ at δ ≈ −12.3 ppm and coupling (doublet, J = 29 Hz) to one remaining PPh₃ ligand (δ 54.7 ppm, ²Jₚ₋ₚ = 29 Hz). In the ¹H-coupled ³¹P NMR spectrum, the signal at δ −12.3 ppm is further split into a doublet with a large coupling constant (J = 535 Hz). The magnitude of this coupling constant suggests the formation of a direct P–H bond. Indeed, the corresponding proton coupling partner is found in the ¹H NMR spectrum as a doublet at δ 7.66 ppm (J = 535 Hz), well downfield from the typical range for a Ru(II)–H (i.e. δ < 0 ppm). The formation of P–H bond is also supported by an absorption at 2226 cm⁻¹ in the IR spectrum, which can be assigned to a P–H stretching mode. Together, these spectra suggest that reaction of L₁ with RuHCl(CO)(PPh₃)₃ affords a stable complex in which the hydrido ligand of Ru is transferred to the phosphorus atom, which we formulate as RuCl(CO)(PPh₃)(L₁H) (3, Scheme 1).

The solid-state structure of 3, determined by X-ray diffraction on a single crystal confirms this assignment (Figure 3c). Indeed, the 10-P-5 nature of the phosphorus environment is evident. The geometry about P is described by a distorted trigonal bipyramid (τ₅ = 0.50) with the H and Ru substituents occupying equatorial positions; by consequence, the phosphorous triamide framework is greatly planarized as compared to 2 with the 2-pyridylamides occupying the trans diapical sites (∠N₂–P₁–N₃ = 170.74(7)°). The resulting trigonal bipyramidal geometry contains two electronegative N atoms in diapical positions and electropositive H and Ru atoms in two equatorial positions, which follows a general trend of phosphoranes.49 The ruthenium-phosphorus bond distance (d(Ru₁–P₁) = 2.2509(4) Å) is ca. 0.12 Å longer than in 2. The origin of this change is given at least in part by the ring constraints imposed by the chelating pyridyl arms, which draw the pentacoordinate phosphorus away from an idealized axial octahedral coordination site about ruthenium (compare ∠P₁–Ru–Cl₁ = 168.85(1)° vs. 160.57(2)° for 2 and 3, respectively).

In view of the apparent transferal of hydride from Ru to P in 3, it is instructive to consider the suite of isomeric canonical structures in Figure 4. Examples of the type A (metal-bound terminal hydride) are legion.50-53 Complexes of the type B (bridging hydride) are less common; Schrock has characterized such complexes of Re54 and Mo55 formed by protonation of the progenitor metal-phosphine.56, 57 By contrast, examples of the type C (phosphorus-bound terminal hydride) do not appear to be known.

Neither the downfield ¹H NMR chemical shift of the hydrido ligand (δ 7.66 ppm) nor the long d(Ru₁–H₁) experimental distances (2.980–2.998 Å) seem to indicate significant Ru–H interaction for 3, disfavoring depictions A and B. As a further point of adjudication, the topological properties of the electron density were analyzed within the QTAIM framework.

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A geometry-optimized DFT model (B3LYP/def2-TZVP) of 3 reproduces the experimental structure with good agreement (see SI), and an all-electron single point calculation (B3PW91/def2-TZVP with zero-order regular approximation (ZORA)\(^ {59,60}\) for relativistic effects) was executed. As depicted in the plot of the electron density in the plane containing the Ru, P, and H nuclei (Figure 5), bond paths defined by (3,−1) critical points are found for Ru–P and P–H, but not for Ru⋯H. Moreover, the atomic basins for Ru and H do not abut. Consequently, complex 3 is well-formulated as ruthenahydrophosphorane with a terminal, nonbridging P-bound hydride (type C). The precise mechanism by which the hydride is transferred from Ru to P is under ongoing investigation.

Whereas decades of research have been devoted to understanding tricoordinate phosphorus compounds as supporting ligands in transition metal chemistry, higher coordination number phosphorus compounds are comparatively poorly-recognized transition metal substituents.\(^ {61-64}\) That said, well-defined and structurally characterized examples of 10-P-5 metallophosphoranes are known, primarily from the work of Riess,\(^ {11-12}\) Nakazawa,\(^ {22,26,64}\) and Lattmann.\(^ {14-20}\) Among these reported metallophosphoranes, complex 3 is the first to contain a terminal P-bound hydride, and the first to be formed directly by net insertion of a trivalent phosphorus center into an existing metal-ligand bond. The interconversion of 8-P-4 and 10-P-5 complexes by intramolecular ligand migration is known,\(^ {65}\) and has been invoked to rationalize metal-phosphine catalyst decomposition pathways.\(^ {66,67}\) In such transformations, there is an apparent connection to be made to migration reactivity to/from lower coordinate phosphorus ligands (i.e. phosphenium,\(^ {68-70}\) phosphide\(^ {71,72}\), phosphinidene\(^ {73-76}\)).

With respect to reactivity, complex 3 exhibits hydridic character; treatment with triphenylcarbenium hexafluorophosphate (Ph\(_3\)CPF\(_6\)) leads to hydride abstraction and conversion to [RuCl(CO)(PPh\(_3\))(L1)]PF\(_6\) (4) (eq. 1). The abstraction of hydride was confirmed by the disappearance of the IR band corresponding to P–H stretching and a hypsochromic shift of the C=O stretching band (\(\nu_{co} = 1957\) cm\(^{-1}\) (3) vs. 2027 cm\(^{-1}\) (4); \(\Delta \nu_{CO} = 70\) cm\(^{-1}\)). Moreover, the \(\text{\textsuperscript{31}P}\) NMR spectra for 4 (6 187.3 ppm (L1); 5 42.5 ppm (PPh\(_3\)); \(^2J_{P-P} = 43\) Hz for the couple) no longer exhibit \(^1J_{P-H}\) coupling. All attempts to deprotonate the P–H in 3 by treatment with base (e.g. KHMDS, KH/18-crown-6) have been unsuccessful to date; the acidity of P–H moiety is apparently quite low. However, the treatment of 4 with an exogenous hydride donor (NaBH\(_4\)) returns 3, indicating the bidirectionality of the phosphorus-centered hydride reactivity and the pronounced electrophilicity of the distorted phosphorous triamide center.

\[
\begin{align*}
\text{3} & \quad \text{Ph}_3\text{CPF}_6 \quad \text{CH}_2\text{Cl}_2, \text{rt} \\
\text{3} & \quad \text{NaBH}_4 \\
\text{3} & \quad \text{THF}, \Delta \\
\text{4} & \quad \text{NaBH}_4
\end{align*}
\]
Taken together, these results demonstrate that geometrically deformed tricoordinate phosphorus ligands may exhibit properties that diverge from the traditional view of phosphines as spectator ligands. The observation of robust chelation during the course of ligand-based abstraction/addition reactivity manifests the colocalized donor and acceptor behavior that is expressed by the descriptor ‘biphilic’. Moreover, the flexibility of the phosphorus center in nontrigonal phosphorous triamide L1 to adopt various geometries and coordination numbers calls to mind a connection to the functional participation of ligands as found in metal-ligand cooperative chemistry. In this vein, the relative ease with which metallophosphorane 3 is accessed motivates us therefore to pursue additional study on higher coordination number phosphorus-based chelating ligands, and these investigations are an ongoing matter.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Divergent metalation of trigonal and nontrigonal 8-P-3 compounds.
Figure 2.
$^{31}$P NMR spectra of (a) $\text{L1}$, (b) 2 and (c) 3 in CDCl$_3$. Units are ppm relative to 85% H$_3$PO$_4$. 
Figure 3.
Thermal ellipsoid plots rendered at the 50% probability level for (a) L1, (b) 2·CH$_2$Cl$_2$ and (c) 3. Hydrogen atoms except H(1) of 3 are omitted for clarity. Solvent molecules of crystallization (2) and phenyl rings of PPh$_3$ ligands (2 and 3) are also omitted. For 3, only one of the three independent molecules contained in the unit cell is shown; see SI for full details.
Figure 4.
Canonical structures corresponding to hydride transfer from M→P.
Figure 5.
Calculated electron density for 3 in the plane defined by Ru–P–H coordinates. Electron density contours (—), gradient vector field (—), bond paths (—), bond critical points (.), and atomic basins (----) are depicted. Units are Å.
Scheme 1.
Synthesis of Chelating Ligand L1 and Related Ru Complexes 2 and 3.
Table 1
Selected Bond Distances (Å) and Angles (°) for 1, L1, 2, and 3.

| Metric          | 1a  | L1   | 2    | 3    |
|-----------------|-----|------|------|------|
| d(Ru1–P1)       | 2.126(3) | 2.2509(4) |
| d(Ru1–P2)       | 2.3329(3) | 2.3359(4) |
| d(Ru1–Cl1)      | 2.4836(3) | 2.4749(4) |
| d(P1–N1)        | 1.7610(12) | 1.7485(8) | 1.7085(9) | 1.7178(14) |
| d(P1–N2)        | 1.7190(13) | 1.7341(8) | 1.7280(9) | 1.8362(14) |
| d(P1–N3)        | 1.7014(14) | 1.7786(8) | 1.7135(9) | 1.8193(15) |
| θ(Ru1–P1–N1)    | 147.62(3) | 140.14(6) |
| θ(P1–Ru1–Cl1)   | 168.851(10) | 160.569(16) |
| θ(N2–P1–N3)     | 115.21(7) | 108.67(4) | 113.94(4) | 170.74(7) |
| θ(N1–P1–N2)     | 90.08(6)  | 90.56(4)  | 91.40(4)  | 86.59(7)  |
| θ(N3–P1–N3)     | 90.51(6)  | 89.45(4)  | 92.04(4)  | 87.25(7)  |

*Data from Ref. 38.*