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On the coordination chemistry of phosphinecarboxamide: Assessing ligand basicity

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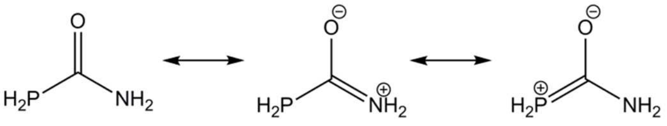
Abstract. We describe the coordination chemistry of the primary phosphine $PH_2C(O)NH_2$ (phosphinecarboxamide) towards group 6 transition-metals. Experimental and theoretical studies reveal that this novel species has comparable electronic properties to PH_3.

We recently reported the synthesis of the novel primary phosphine, $PH_2C(O)NH_2$ (phosphinecarboxamide; a phosphorus-analogue of urea).[1] In contrast to the vast majority of primary phosphines,[2] phosphinecarboxamide is relatively air- and moisture-stable (it does not combust on exposure to air and is stable in solution for several days). In principle, some degree of stabilization to oxidation may result from delocalization of the phosphorus lone-pair into the amide functionality (Scheme 1, right), although the spectroscopic properties, bond metric data and computed electronic structure all suggest that the phosphorus lone pair is reasonably isolated from the amide functional group in the ground state of $PH_2C(O)NH_2$. For example, the HOMO was computed to have considerable phosphorus lone pair character (44.38%),[1] implying that phosphinecarboxamide should be able to act as a Lewis base. With this in mind we set out to study the coordination chemistry of this novel ligand and assess its relative σ-donor/π-acceptor ability compared to that of other phosphines.



Scheme 1. Resonance forms of phosphinecarboxamide.

Phosphines (PR_3) are one of the most important classes of L-type ancillary ligands in inorganic chemistry.[3] Understanding their stereo-electronic properties and the nature of the metal–phosphine bond has historically attracted considerable attention and no little controversy.[4] Amongst the most well-established means of quantifying the strength and character of the metal–phosphine interaction are Tolman's Electronic Parameter (TEP; χ_i) and Cone Angle (TCA; θ).[5] While the latter is widely accepted as a valid measure of steric bulk, the interpretation of the electronic parameter remains controversial, and several alternatives have also been proposed.[6] The problem in finding an unambiguous measure of the electronic properties of a phosphine lies in the separation of the (often) complementary effects resulting from the participation of σ-donor and π-acceptor orbitals (the so-called σ/π controversy).[4] Nevertheless, such methods remain commonly employed despite their limitations, and are very insightful to interpret net effects such as *trans*-influence. So much so, that many of these concepts have since been extended to other families of supporting ligands such as N-heterocyclic carbenes.[7]

The TEP is defined through the influence of the PR_3 ligand on the A_1-symmetric CO stretching frequency of the prototype system $Ni(CO)_3(PR_3)$.[5] However, the high toxicity of the $Ni(CO)_4$ precursor makes the generation of such complexes undesirable, and as a result numerous alternative metal fragments have been employed. Two such systems are $W(CO)_5(PR_3)$ and *cis*-$Mo(CO)_4(PR_3)_2$. In both cases the presence of carbonyl ligand(s) *trans*- to the phosphine(s) allows their *trans*-influence to be measured through both bond metric and IR spectroscopic data.[8,9] The *cis*-$Mo(CO)_4(PR_3)_2$ complexes are particularly relevant because of a well-argued report by Anton and Crabtree which shows that the A_1 carbonyl stretching frequencies in these compounds are linearly related to those in $Ni(CO)_3(PR_3)$ through the expression $\nu_{Ni} = 0.593\nu_{Mo} + 871$ (in units of cm^{-1}).[10] The data for *cis*-$Mo(CO)_4(PR_3)_2$ can therefore be mapped directly onto Tolman's original work on the extended phosphine family in $Ni(CO)_3(PR_3)$.

We first synthesized $W(CO)_5(PH_2C(O)NH_2)$ (**1**) by photolysis of a solution of $PH_2C(O)NH_2$ and $W(CO)_6$ in THF. However, ^{31}P NMR spectroscopy revealed that the major product was decomposition of phosphinecarboxamide to give phosphine (PH_3). To avoid exposure of $PH_2C(O)NH_2$ to photolytic conditions, the substitutionally labile $W(CO)_5(THF)$ species was synthesized *in situ*, and $PH_2C(O)NH_2$ subsequently added to afford the ligand exchange product **1**.

The formation of **1** from $PH_2C(O)NH_2$ and $W(CO)_5(THF)$ in d_8-THF results in a downfield shift of 34.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum which is in agreement with donation of the phosphorus lone pair into the tungsten 5d t_{2g} orbitals.[11] Coupling of the ^{31}P nucleus to ^{183}W ($I = ½$) gives rise to tungsten satellites with a $^1J_{W-P}$ coupling of 216 Hz. This value is identical to that reported for $W(CO)_5(PH_3)$ which is unsurprising as the magnitude of the $^1J_{W-P}$ coupling constant is known to be strongly dependent on the electronegativity of the substituents on the phosphine.[12] An increase in $^{1}J_{P-H}$ was observed in the ^{31}P NMR spectrum from 209 to 347 Hz which is characteristic of complex formation (*i.e.* going from a 3-coordinate to 4-coordinate phosphorus atom). The Fermi contact interaction, a through-bond interaction, is large if the wavefunction of the valence electrons approaches the nucleus. As a result, high s-orbital character in bonds gives rise to larger $^{1}J_{X-Y}$ coupling constants.[13] As a representative example, PH_3 has a H–P–H bond angle close to 90°; the P–H bonds are high in p-orbital character and the lone pair is predominantly s-orbital based.[14,15] Upon coordination, the phosphorus atom effectively “re-hybridises” to a more tetrahedral sp^3 geometry, and the s-orbital character in the P–H bonds increases, which gives rise to a larger coupling constant. A similar argument can be made for phosphinecarboxamide, where the H–P–H angle increases from 93 to 97° on coordination according to the optimized computed geometries of $PH_2C(O)NH_2$ and **1** (see Electronic Supplementary Information; ESI). The ^{1}H NMR spectrum shows a doublet for the phosphine protons centred at 5.22 ppm, which collapses to a singlet on broadband ^{31}P decoupling. The ^{13}C NMR spectrum of **1** reveals two resonances attributable to the carbonyl ligands at 196.2 and 192.5 ppm, corresponding to the ligands *trans*- and *cis*- to phosphinecarboxamide, respectively.

The solution phase IR spectra of **1** in THF showed a pseudo-A_1 carbonyl stretch of the $W(CO)_5$ fragment at 2077 cm^{-1}. Related A_1 stretching frequencies for selected complexes of the type $W(CO)_5(PR_3)$ are given in Table 1. Phosphinecarboxamide shows diminished π acceptor properties compared to the phosphorus trihalides, and has a similar electronic parameter to phosphine (PH_3) and triethylphosphite ($P(OEt)_3$). Surprisingly, removal of the solvent from a solution of **1** under a dynamic vacuum resulted in the decomposition of the complex, indicating that the phosphine is only weakly bonded to the metal centre. Despite repeated attempts, isolation of single crystals of **1** was not possible, in part due to the high solubility of the species.

Table 1. The pseudo-A_1 stretch for selected phosphine complexes $W(CO)_5(PR_3)$ (cm^{-1}).

Phosphine	Pseudo-A_1 stretch	Reference
PMe_3	2070	9
$PH_2C(O)NH_2$	2077	this work
$P(OEt)_3$	2078	16
PH_3	2080	17
$P(OMe)_3$	2081	18
PCl_3	2094	9
PF_3	2101	8

The novel complex *cis*-$Mo(CO)_4(PH_2C(O)NH_2)_2$ (**2**) can be prepared by reaction of $Mo(CO)_4(COD)$ with two equivalents of $PH_2C(O)NH_2$ in non-coordinating solvents (such as CH_2Cl_2). The ^{31}P NMR spectrum of **2** displays a multiplet resonance which collapses to a singlet at −64.9 ppm on proton decoupling (Figure 1). The multiplet resonance was assigned using calculated coupling constant values followed by a least squares simulation of the spectrum (see ESI for full details). The ^{13}C NMR spectrum reveals two different resonances at 212.1 and 206.8 ppm, arising from the *cis*- and *trans*-carbonyl ligands, respectively (the latter exhibits $^{2}J_{P-C}$ coupling of 9 Hz). An additional resonance arising from the $PH_2C(O)NH_2$ ligands was recorded at 171.9 ppm. ^{1}H NMR spectroscopy shows two broad resonances at 6.71 and 5.92 ppm arising from the amide protons, as well as a second order multiplet at 5.00 ppm ($^{1}J_{P-H}$ = 328 Hz; $^{3}J_{P-H}$ = 9 Hz), which collapses to a singlet on broadband decoupling of the ^{31}P resonance.

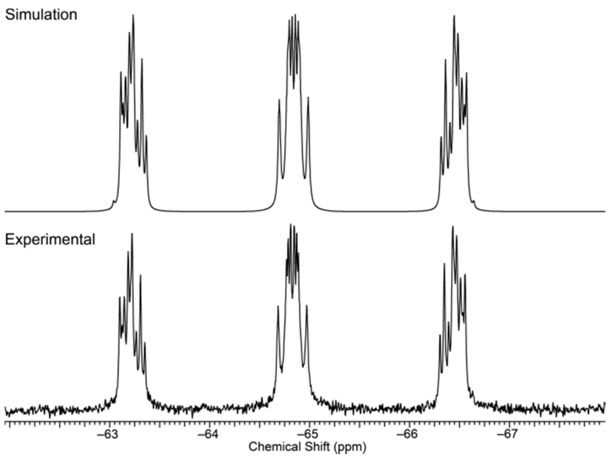


Figure 1. Simulated (top) and experimentally determined (bottom) ^{31}P NMR spectra for **2**. $^{1}J_{P-H}$ = 328 Hz , $^{2}J_{P-P}$ = −25 Hz, $^{3}J_{P-H}$ = 18 Hz, $^{3}J_{P-H}$ = 9 Hz.

The highest absorption in the carbonyl stretching region of the IR spectrum of **2** was observed at 2040 cm^{-1}. Using Crabtree’s formula (*vide supra*), the corresponding TEP is 2081 cm^{-1} which places phosphinecarboxamide in the region of phosphine (2083 cm^{-1}) and trimethylphosphite (2080 cm^{-1}) in terms of its electronic properties (ligands that are traditionally argued to be weakly σ-donating/π-accepting).[5] This is in agreement with the IR spectroscopic results obtained for **1** (*vide supra*).

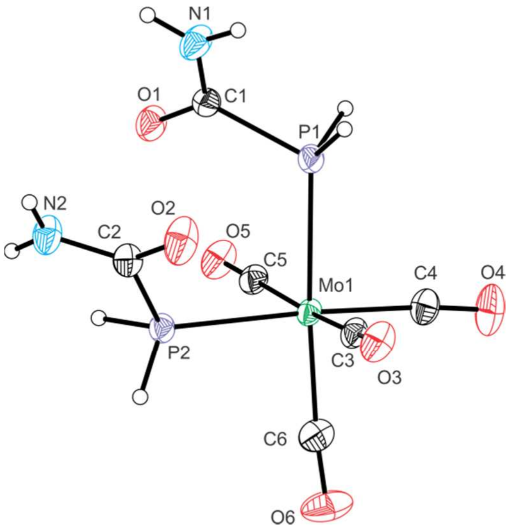


Figure 2. Molecular structure of **2** (anisotropic displacement ellipsoids pictured at 50% probability level). Selected inter-atomic distances (Å) and angles (°): Mo1–P1: 2.481(1); Mo1–P2: 2.480(1); Mo1–C3: 2.044(2); Mo1–C4: 1.997(2); Mo1–C5: 2.041(2); Mo1–C6: 1.995(2); P1–C1: 1.870(2); C1–O1: 1.230(2); C1–N1: 1.325(2); P2–C2: 1.871(2); C2–O2: 1.226(2); C2–N2: 1.328(2); P1–Mo1–P2: 91.73(1); P1–Mo1–C3: 86.56(4); P1–Mo1–C4: 92.49(5); P1–Mo1–C5: 87.60(4); P2–Mo1–C3: 89.47(4); P2–Mo1–C5: 85.33(4); P2–Mo1–C6: 91.62(5); C3–Mo1–C4: 94.27(6); C3–Mo1–C6: 91.60(6); C4–Mo1–C5: 91.35(6); C4–Mo1–C6: 84.28(7); C5–Mo1–C6: 94.54(6).

Crystals of **2** were grown from a concentrated CD_2Cl_2 solution (Figure 2).† The structure of the complex, as determined by single-crystal X-ray diffraction studies, confirms a *cis*-arrangement of the two $PH_2C(O)NH_2$ ligands. The Mo–P bond distances, 2.481(1) and 2.480(1) Å, are identical within experimental error and slightly shorter than the mean value for other *cis*-$Mo(CO)_4L_2$ type systems (2.504 Å).[19] A survey of the chemical literature reveals that short M–P bond distances are typically associated with relatively strong π-interactions (*e.g.* for $Mo(CO)_4[P(OPh)_3]_2$, $d_{Mo–P}$ = 2.432(1)/2.436 (1) Å),[20] while systems that are strong σ-donors and negligible π-acceptors such as PMe_3 and PCy_3 give rise to longer Mo–P bonds (2.522(1)/2.522(1) and 2.649(4)/2.659(4) for $Mo(CO)_4(PMe_3)_2$ and $Mo(CO)_4(PCy_3)_2$, respectively).[21,22] In the latter case, the steric demand of PCy_3 (TCA(PCy_3) = 170° vs. TCA(PMe_3) = 118°) has a notable influence on Mo–P bond distances. Clearly there are numerous different steric and electronic factors contributing to the length of the Mo–P bonds. As a result, the use of such values for the assessment of "bond strength" must be done with caution. That being said, previous reports have noted an inverse relation between M–PR_3 bond distances and bond energies.[23] Mo–CO bond distances vary depending on whether the carbonyl ligands are located *cis*- or *trans*- to $PH_2(CO)NH_2$. Thus CO ligands that are *trans*- to other carbonyls typically have longer Mo–CO bonds (2.044(2) and 2.041(2) Å) than those that are *trans*- to $PH_2C(O)NH_2$ (1.997(2) and 1.995(2) Å). This is consistent with a greater *trans*-influence for CO relative to phosphinecarboxamide due to its superior σ-donating and/or π-acceptor ability.

An electronic structure analysis of W–PR_3 bonds in $W(CO)_5L$, L = PMe_3, PH_3, $PH_2C(O)NH_2$ and PF_3, using density functional theory further reinforces the similarity between $PH_2C(O)NH_2$ and PH_3.[24] In these calculations we have adopted a fragment-based approach to focus on the strength of the W–P bond. The structure of the $W(CO)_5L$ molecule is first freely optimized and then single point calculations are performed on the separate $W(CO)_5$ and PR_3 moieties frozen in the geometries found in $W(CO)_5(PR_3)$. The two fragments are then brought together, the total interaction energy, ΔE_{tot}, giving a measure of the W–P bond strength. We have also repeated the final step (*i.e.* the merging of the two fragments) after removing all virtual (vacant) orbitals on each one of the fragments. Removing the vacant orbitals on the PR_3 unit effectively blocks transfer of electron density from the metal to the π* orbitals of the phosphine (*i.e.* back-bonding) while removing the vacant orbitals on $W(CO)_5$ blocks σ-donation from ligand to metal (forward-bonding). By comparing the interaction energies with and without subsets of vacant orbitals, it is therefore possible to separate the contributions of forward- and back-bonding to the W–P bond. A full summary of the optimized geometries and various components of the interaction energy is presented in the ESI, along with a more detailed description of the computational procedure. The key conclusion is that back-bonding contributes 38% of the total orbital interaction between the $W(CO)_5$ and PR_3 fragments in both $W(CO)_5(PH_3)$ and $W(CO)_5(PH_2(CO)NH_2)$, compared to 33% in $W(CO)_5(PMe_3)$ and 44% in $W(CO)_5(PF_3)$. The same is also true for σ-donation from ligand to metal; PH_3 and $PH_2C(O)NH_2$ have identical forward-bonding contributions, while those of PMe_3 and PF_3 are higher and lower, respectively. The overall picture that emerges from this analysis is therefore consistent with the available spectroscopic evidence that $PH_2C(O)NH_2$ is similar to PH_3, in so much as it is a moderate σ-donor and π-acceptor.

In summary, we have reported the first transition-metal complexes of the novel primary phosphine $PH_2C(O)NH_2$. Data for both complexes indicate that the electronic properties of phosphinecarboxamide are very similar to those of PH_3 and trialkylphosphites such as $P(OMe)_3$ and $P(OEt)_3$, placing $PH_2C(O)NH_2$ in an intermediate family of phosphines with relatively average σ-donor and π-acceptor properties. This is consistent with the observation that the phosphine may be removed from a metal centre under a dynamic vacuum and that binding to coordinatively unsaturated metals is often difficult in the presence of donor solvents.

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Notes and references

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† Crystal data for **1**. Formula: $C_6H_8MoN_2O_6P_2$; Mr = 362.02; crystal size: 0.14 × 0.05 × 0.05 mm; crystal description: colourless plate; monoclinic; space group: $P2_1/n$ (no. 15); a = 7.1284(2); b = 9.7853(2) Å; c = 18.2084(5); β = 94.130(2)°; V = 1266.80(6) Å^3; Z = 4; ρ_{calcd} = 1.898 g cm^{-3}; μ = 11.075 mm^{-1}; T = 150(2) K; T_{max}/T_{min} = 0.306/0.607; $2\Theta_{max}$ = 38.43°; 25541 reflections collected; 2649 independent reflections; R_{int} = 0.0316; R1 = 1.87 and R2 = 5.07 % for I ≥ 2σ(I); R1 = 1.93 and R2 = 5.12 % for all data; Min./max. residual electron density –0.70/0.34 e Å^3. GoF = 1.073. CCDC 1014321 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.

Electronic Supplementary Information (ESI) available: Full experimental details, single crystal X-ray diffraction data, NMR and IR spectra, and computational details are provided. See DOI: 10.1039/c000000x/

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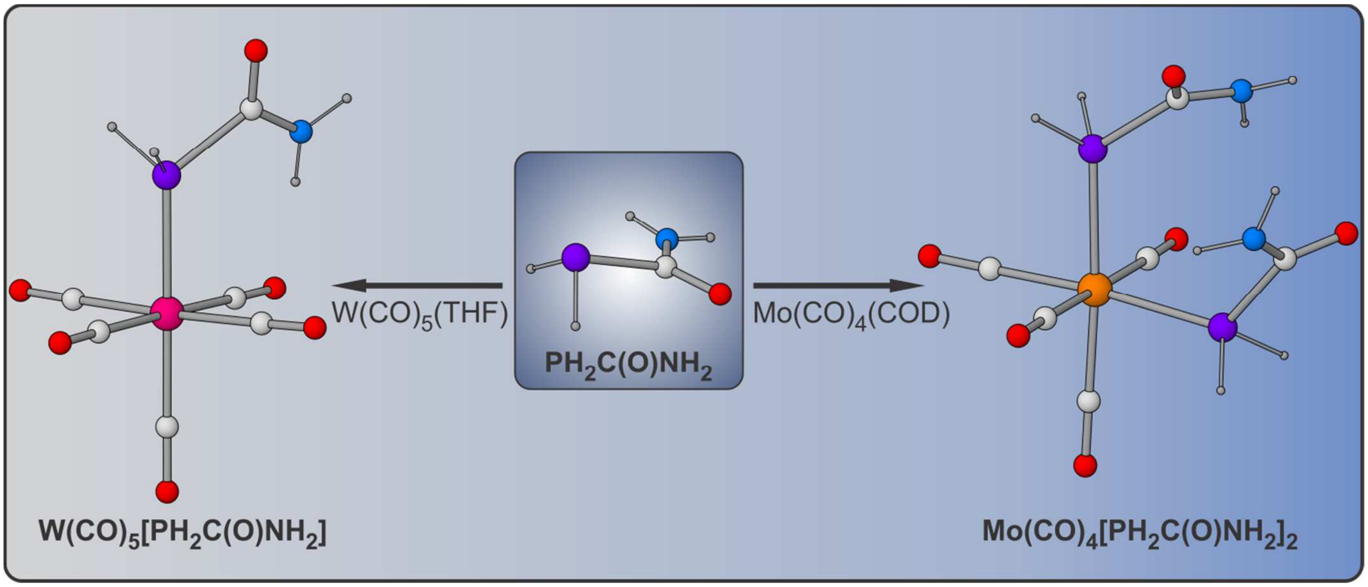

We describe the coordination chemistry of the primary phosphine $PH_2C(O)NH_2$ (phosphinecarboxamide) to form the novel complexes $W(CO)_5(PH_2C(O)NH_2)$ (**1**) and *cis*-$Mo(CO)_4(PH_2C(O)NH_2)_2$ (**2**).