Communications

Bifunctional Imidazolylphosphine Ligands as Hydrogen Bond Donors Promote N−H and O−H Activation on Platinum

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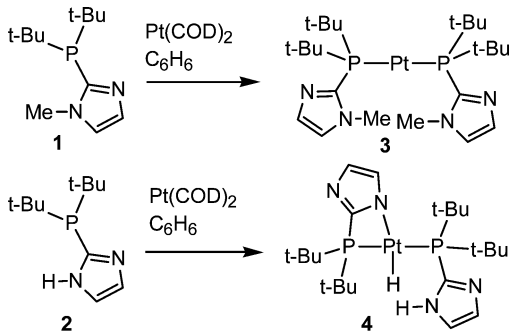
Summary: The NH moieties of two imidazolylphosphine ligands on Pt(II) facilitate formation of trans-(hydrido)(R^1O)bis-(phosphine)Pt(II) species from R^1OH (R^1 = CF_3CO, CH_3CO, Ph, CH_3, H). Evidence points to formation of a reliable binding pocket for coordinated R^1O by hydrogen bond donation from the two NH groups.

C−H activation by transition metal complexes has received intense scrutiny.[1] Though less studied, N−H[2] and O−H bond activation[3] are of great interest for functionalization of organic substrates with nitrogen- or oxygen-containing functional groups. Among reactants that may undergo O−H activation, water is of special interest because of its importance in green chemistry and useful processes such as the Wacker oxidation or hydration of unsaturated species.

Control of substrate binding and activation and catalytic activity and selectivity by enzymatic[4] and synthetic[5] systems can be achieved by using several interactions in concert. The reactivity of O−H and N−H compounds with organometallic complexes can be affected profoundly by the use of ligands containing basic or acidic sites. Heterocyclic phosphine ligands lead to greatly enhanced rate and selectivity in alkyne addition reactions such as hydration[6] and alkoxycarbonylation.[7] Continuing studies of the former[5d] show that the heterocycle may be important as a neutral acceptor of a proton or hydrogen bond, or in *protonated* form as a donor. Here, we report dramatic changes in substrate interaction with Pt as a function of whether a *neutral* imidazolylphosphine ligand (e.g., **1**) bears an N-methyl (N as hydrogen bond acceptor) or N−H group (e.g., **2**, N as donor).

Scheme 1. Different Products as a Function of N-Substituent



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† San Diego State University.
‡ University of California. X-ray crystal structures.

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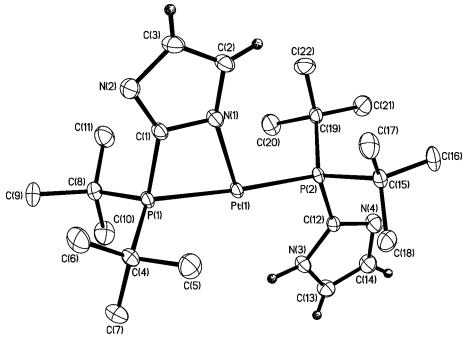

Figure 1. Molecular structure of **4**.

Reaction of related ligands **1** and **2** with $Pt(COD)_2$ led to very different products. In the case of **1**, the two-coordinate Pt(0) complex **3** was formed in 66% yield.[8] Its $^{31}P\{^1H\}$ NMR spectrum exhibited one sharp singlet with Pt satellites (J_{Pt-P} = 4247.1 Hz). There is no spectroscopic evidence for agostic interactions of the N-methyl group hydrogens with the metal, so we conclude that its structure is like that recently reported for the Pd analogue.[9]

In contrast, when **2** is reacted with $Pt(COD)_2$, ligand N−H activation is observed, leading to Pt(II) species **4** in 71% yield. The unsymmetrical nature of **4** was revealed by two $^{31}P\{^1H\}$ doublets (δ 52.6 and 39.4 ppm, $^2J_{P-P-trans}$ = 327.8 Hz) with Pt satellites (J_{Pt-P} = 2940.3 and 2341.2 Hz, respectively). Key proton NMR resonances include a broad one-proton signal at δ 10.57 (N−*H*) and a sharp doublet (Pt−*H*, J_{PH} = 20.5 Hz) at −19.17 ppm with satellites (J_{Pt-H} = 1169.3 Hz).

Clarification of which NMR resonances were associated with the monodentate and bidentate phosphines in **4** came from decoupling experiments. The hydride proton was coupled only to the ^{31}P nucleus with downfield chemical shift, which has a value of J_{Pt-P} (2940.3 Hz) normal for a Pt(II) complex with two phosphines mutually trans, and thus is assigned to the monodentate phosphine. In the chelate, the effects of the constrained four-membered ring on the ^{31}P nucleus within it include a small value of J_{Pt-P} (2341.1 Hz)[10] and the lack of observable coupling to the hydride proton.[10c]

N−H activation of heterocycles on low-valent metals including Pt(0) is known to form metal hydride complexes.[2d,l] Interestingly, as seen in the X-ray diffraction structure of **4** in Figure 1,[11] although the hydride could not be located with certainty, the imidazole N−H could be, and the fact that it is directed toward the apparently vacant site on Pt is consistent with interaction of the form M−H- - -H−N, studied in detail by a number of other groups.[12] Reasonably assuming a Pt−H distance of 1.6 Å and two equal P−Pt−H angles leads to a calculated H- - -H distance of 1.80 Å and H- - -H−N angle of 128°, which are consistent with known values for such systems.[12] Although interesting, this interaction is not responsible for O−H activation of water or methanol using **4**, according to data presented below.

Compared under identical conditions (0.05 M complex in C_6D_6 unless otherwise stated), the reactivities of **3** and **4** with O−H-containing compounds of acidity ranging from that of trifluoroacetic acid to water were quite different. Complex **3** reacted significantly only with more acidic species, whereas **4** gave O−H activation with all compounds tested. Moreover, whereas **4** gave symmetrical *trans*-$L_2Pt(H)(OR^1)$ complexes **5** with all O−H-containing compounds and under nearly all conditions, in several cases **3** also gave unsymmetrical species **6** formed by dissociation of the anionic ligand OR.[1]

The first set of experiments involved more acidic reactants, with pK_a less than 10. For example, adding acetic acid (1.0 equiv) to complex **3** in C_6D_6 led to a mixture containing unreacted **3** (38%) and one new complex, **5-Me-b** (62%). The symmetry of the latter was identified in ^1H NMR spectra by a triplet at δ −22.60 ppm (J_{P-H} = 14.6 Hz, J_{Pt-H} = 1077.4 Hz) and in $^{31}P\{^1H\}$ by a singlet with reduced J_{Pt-P} (2949.7 vs 4247.1 Hz for **3**). When another equivalent of acid was added, the reaction mixture still contained 62% of **5-Me-b**, but less of **3** (17%) and in addition **6-Me-b** (21%). In another experiment, dissolving **3** in acetic acid-d_4 led to complete conversion to **6-Me-b**-d_4. The unsymmetrical nature of **6-Me-b** was revealed by two $^{31}P\{^1H\}$ doublets, $^2J_{P-P-trans}$ = 321.8 Hz, at δ 52.5 (J_{Pt-P} = 2348.2 Hz) and 43.9 ppm (J_{Pt-P} = 2938.8 Hz). Formation of **6-Me-b** from **5-Me-b** with increasing amount of acid may be viewed as an effect of stabilizing ionic species **6-Me-b** through hydrogen bonding of excess acid to the carboxylate anion. Similarly, with CF_3CO_2H (1.0 equiv), **3** was completely converted to **5-Me-a** (80%) and **6-Me-a** (20%).

In sharp contrast, reaction of **4** in C_6D_6 with either CF_3CO_2H or CH_3CO_2H (1.0 equiv) gave only **5-H-a** or **5-H-b**.[13a] Remarkably, even in pure CD_3CO_2D, **4** was converted to **5-H-b**-d_4 (90%), with only 10% of an unsymmetrical species, either **4** or **6-H-b**-d_4.

With phenol (5.0 equiv), a mixture of unreacted **3** (45%) and **6-Me-c** (55%) was produced without detectable amounts of **5-Me-c**.[13a] In contrast, reaction of **4** with phenol (2 equiv) gave a mixture of **4** (39%) and **5-H-c** (61%), without **6-H-c**.[13a]

Thus, whereas both **3** and **4** react with phenol and carboxylic acids, as do several known phosphine−Pt(0) complexes,[14] **3** without NH moieties leads to mixtures of **5-Me** and **6-Me** in varying amounts, whereas **4** shows a pronounced ability to form symmetrical species **5-H** in a predictable manner.

Perhaps the most remarkable differences between **3** and **4** are reactivities toward methanol and water, which are both O−H compounds of low acidity. *Whereas **3** is completely unreactive toward either of these reagents*,[13b] even after days at 85 °C, ***4** reacts reversibly at 25 °C within minutes*. Starting with **4** in C_6D_6, methanol (5 equiv) gave **4** (50%) and **5-H-d** (50%). In the product, the Pt−O−CH_3 moiety produced a singlet at 3.43 ppm with Pt satellites ($^3J_{Pt-H}$ = 25.6 Hz). Starting with **4** in C_6D_6, water (5 equiv) gave **4** (33%) and **5-H-e** (67%). Although formation of **5-H-e** is reversible, a successful X-ray diffraction study of this product (Figure 2)[11] verified its identity as a square-

(8) See Supporting Information for details.

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(11) For **4**: monoclinic, $P2_1$, colorless, 0.32 × 0.20 × 0.04 mm, a = 8.0597(4) Å, b = 13.7541(6) Å, c = 12.0198(5) Å, β = 105.7600(10)°, V = 1282.35(10) Å^3, Z = 2, T = 218(2) K, D_{calc} = 1.602 g/cm^3, R1 = 1.96% for 5228 independent reflections, GOF = 0.819. For **5-H-e**: monoclinic, $P2_1$, colorless, 0.10 × 0.10 × 0.05 mm, a = 15.938(2) Å, b = 11.0650(15) Å, c = 16.233(2) Å, β = 110.883(2)°, V = 2674.7(6) Å^3, Z = 4, T = 100(2) K, D_{calc} = 1.583 g/cm^3, R1 = 2.38% for 11 778 independent reflections, GOF = 0.821. Hydrogen atoms involved in hydrogen bonding were located from the difference map and refined isotropically.

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(13) (a) In these experiments, it is estimated that as little as 5% of **6** could have been detected. (b) As little as 1% of **5** could have been seen.

(14) Examples: (a) Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *Organometallics* **1982**, *1*, 819. (b) Thomas, K.; Dumler, J. T.; Renoe, B. W.; Nyman, C. J.; Roundhill, D. M. *Inorg. Chem.* **1972**, *11*, 1795. (c) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371; also ref 2a.

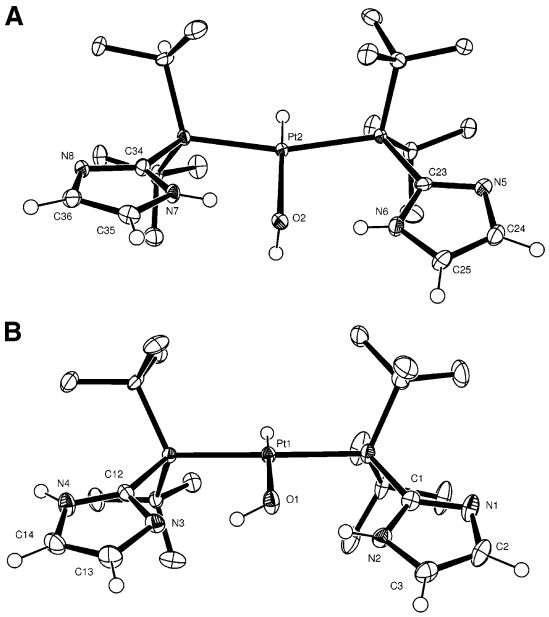


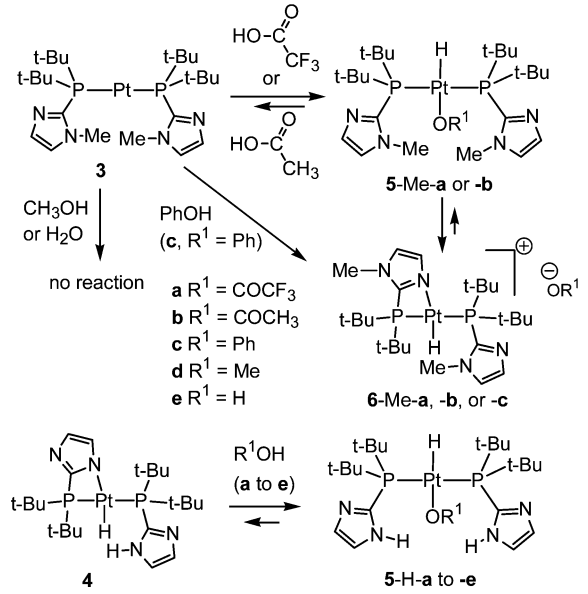
Figure 2. Conformers of **5-H-e**. The three interactions of form N−H- - -O have N−H−O angles 160(4)−166(5)°, N- - -O distances 2.545(4)−2.596(5) Å, and for the O−H- - -N interaction in **B**, O−H−N = 154.3° and O- - -N = 2.567(5) Å.[8] Hydrogen atoms involved in hydrogen bonding were located from the difference map and refined isotropically.

planar species with a hydroxo ligand and trans phosphines. Significantly, evidence for the effects of the ligand NH moieties could be gathered. Two distinct conformers (**A** and **B**) appear in the unit cell. In **A**, both imidazole NH units donate a hydrogen bond to the hydroxo oxygen, whereas in **B**, there is only one such interaction, and the other imidazole acts as an acceptor of a hydrogen bond donated by the hydroxo ligand. Both cases show interactions between the imidazoles and the hydroxo ligand rather than with the hydride as in **4** (Figure 1).

We conclude by noting that because water, all O−H species, and most heterocyclic N−H compounds are at least somewhat acidic (having pK_a values below 20), their bond activations by necessity must be considered from the viewpoint of acid−base chemistry. Both **3** and **4** react with the stronger acids in this study (carboxylic acids or phenol) to give hydridic products (**5-Me** and **6-Me** from **3**, only **5-H** from **4**).[15] In contrast, only **4** reacts with water or methanol. From both these reactivity data and the structure of **5-H-e** in Figure 2, we conclude that the function of the ligand NH moieties is not to increase the proton-

(15) The reversibility of the O−H bond activations in this work precluded a facile comparison of the pK_a values of **5** and **6**.

Scheme 2. Reactivity Depends on Imidazole Substituents



accepting ability of the metal center, but rather to create a reliable binding pocket for the formally anionic oxygenated ligands on Pt through hydrogen bonding. A relevant control experiment started with **3**, which is incapable of hydrogen bond donation, and water (10 equiv) under the same conditions as in Scheme 2. The strong acid CF_3SO_3H (1 equiv) was added; remarkably, 90% of **3** remained unreacted, whereas the remaining 10% formed the unsymmetrical cation of **6-Me**. There was no evidence[13b] of a product containing a coordinated water molecule.

In summary, the results presented here show that ligands **1** and **2** produce very different behavior of Pt centers toward O−H bonds. The effects of NH moieties provided by ligand **2** on Pt include N−H activation in the formation of **4** and stabilization of H−Pt−OR^1 units in **5-H-a** to **-e** by hydrogen-bonding interactions with the oxygen atom of the attached ligand. Further exploration and utilization of phosphine substituents as hydrogen bond donors and acceptors is under active investigation in these laboratories and is expected to be useful in fields such as catalysis, small molecule activation, and molecular recognition.

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Supporting Information Available: Compound preparation, characterization, selected spectra, hydrogen bonding in **5-H-e**, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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