*Inorg. Chem.* **2005**, *44*, 7708–7710


# Palladium and Rhodium Ureaphosphine Complexes: Exploring Structural and Catalytic Consequences of Anion Binding

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Received July 4, 2005

The addition of a chloride ion to Pd and Rh complexes supported by the ureaphosphine ligand **L** results in the formation of chelating diphosphine complexes that retain some catalytic activity.

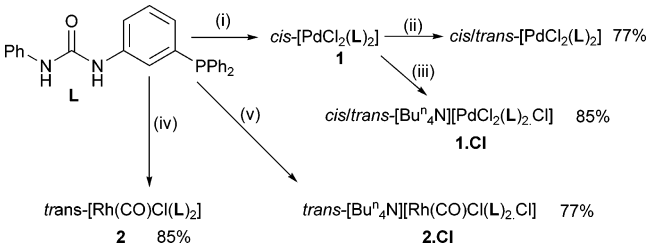
Chelating diphosphines are ubiquitous as ligands that stabilize and define transition-metal centers during important catalytic processes. Interwoven variables such as bite angle, steric demand, and electronic effects are key to catalyst efficacy and have led to the generation of a myriad of elegantly designed, chelating diphosphine ligands for use in catalytic processes.[1] Recently, two new and potentially versatile supramolecular approaches to chelating diphosphine ligands were reported in which (i) direct hydrogen-bonding interactions between 2-pyridone- and 2-hydroxypyridine-phosphine tautomers[2] and (ii) the assembly of monomeric, pyridine-functionalized phosphines on a bis[zinc(II) porphyrin] template[3] both resulted in chelate formation and unique catalytic activity.

As a new supramolecular approach to chelating diphosphine catalysts, we envisaged that anion sequestration by a suitably designed phosphine ligand would result in chelate formation and subsequent control of catalytic activity. While ligands able to act as ionophores for both metal and anion are well-known,[4] to our knowledge, the use of anions as supramolecular constructs in catalyst ligand design has yet to be explored. Significantly, it has been shown that anion-binding ureas can affect the outcome of Pd-catalyzed alkene hydrocarbonylation,[5] and, furthermore, an anion-assisted trans/cis isomerization was observed in acetanilide-functionalized phosphine complexes of Pd.[6] These observations suggest that hydrogen-bonding interactions are sufficiently robust to direct the outcome of catalytic reactions.

We report herein the ability of ureaphosphine ligands to form well-defined chelates at Pd and Rh in the presence of a chloride ion and the apparent retention of this supramolecular interaction during the Rh-catalyzed hydroformylation of octene.

Reaction between the ureaphosphine **L**, generated by the addition of PhNCO to *m*-$H_2NC_6H_4PPh_2$, and $PdCl_2(PhCN)_2$ in $CH_2Cl_2$ results in the rapid formation of the bis(phosphine)palladium complex $PdCl_2(\mathbf{L})_2$ (**1**) in good yield (Scheme 1). If the reaction mixture is rapidly worked up

**Scheme 1.** Synthesis and Anion-Binding Reactions of Ureaphosphine Complexes **1** and **2**[a]




[a] Reagents and conditions: (i) $[PdCl_2(PhCN)_2]$, $CH_2Cl_2$, 5 min; (ii) reaction time 1 h; (iii) $Bu^n_4N{\cdot}Cl$, $CH_2Cl_2$; (iv) $[\{Rh(CO)_2Cl\}_2]$, $CH_2Cl_2$; (v) $[\{Rh(CO)_2Cl\}_2]$, $Bu_4NCl$, $CH_2Cl_2$.

(after ca. 5 min), pure *cis*-**1** is isolated ($\delta_P$ 34.3 ppm[7]). However, prolonged reaction at room temperature results in the precipitation of **1** as a pale-yellow solid in a 1:3 cis/trans isomeric ratio ($\delta_P$ 25.5 ppm [trans]). The insolubility of **1** in common organic solvents can be attributed to polymer

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10.1021/ic051110f CCC: $30.25 
Published on Web 10/06/2005

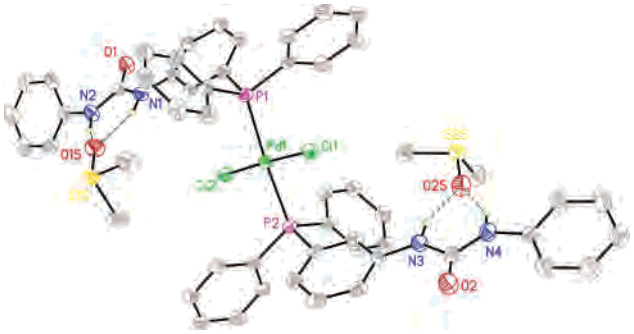


**Figure 1.** X-ray crystal structure of the ureaphosphine complex [$PdCl_2$-(**L**)$_2$]·2DMSO (**1**·2DMSO; 50% displacement ellipsoids). For clarity, all hydrogens except those of the urea nitrogens N1, N2, N3, and N4 are omitted. Selected bond lengths (Å) and angles (deg): Pd1−Cl1 2.2978(11), Pd1−Cl2 2.3036(11), Pd1−P1 2.3509(12), Pd1−P2 2.3268(12); Cl1−Pd1−P1 87.16(4), Cl1−Pd1−P2 90.58(4), Cl2−Pd1−P1 95.40(4), Cl2−Pd1−P2 86.83(4), P1−Pd1−P2 176.13(4), Cl1−Pd−Cl2 177.32(4).

formation due to intermolecular hydrogen bonding. These interactions are disrupted by dissolution in DMSO, so allowing the above NMR data to be acquired. An EXSY NMR experiment showed that no isomer exchange occurs in solution at room temperature, and this contrasts with the allosteric, anion-controlled, cis/trans isomerization seen for Pd complexes of similar acetanilide-functionalized phosphine ligands.[6] Crystals grown from DMSO were analyzed by X-ray crystallography (Figure 1).

It is clear from the solid-state structure that crystallization of *trans*-**1** is favored over that of *cis*-**1** and that intermolecular hydrogen bonding occurs between the urea protons and the DMSO solvent oxygen atoms O1S and O2S [N1−O1S 2.846(5) Å, N2−O1S 2.962(4) Å, N3−O2S 2.819(5) Å, N4−O2S 2.836(4) Å]; the ureaphosphine backbones adopt an anti configuration, presumably for steric reasons. Dissolution of crystalline *trans*-**1** in DMSO-*d* results in rapid equilibration to a 1:3 cis/trans mixture.

Unlike the above, the 1:1 reaction between in-situ-prepared *cis/trans*-**1** and $Bu^n_4N$·Cl in $CH_2Cl_2$ does not result in precipitation due to polymer formation but instead forms the anion-bound adduct *cis*/*trans*-[$Bu^n_4N$][$PdCl_2$(**L**)$_2$Cl] (**1**·Cl) in high yield (Scheme 1); the 1:1 complex/anion ratio was supported by elemental analysis, and no change in the cis/trans isomer ratio was observed upon anion binding. Surprisingly, the addition of $Bu^n_4N$·$H_2PO_4$ to **1** resulted in chloride substitution at Pd and isolation as crystals of substoichiometric amounts of the $Cl^-$-bound adduct **1**·Cl; other Pd species are also formed in the bulk material during this reaction and show $J_{PP}$ coupling in the $^{31}P\{^1H\}$ NMR spectrum that is consistent with metal phosphate coordination. The $^1H$ NMR spectrum of **1**·Cl clearly shows that anion binding has occurred in solution because the resonances attributed to the urea N−H's shift significantly downfield as compared to the resonances of the anion-free complex **1** ($\Delta\delta$[DMSO-*d*] 0.46 ppm) and the ureaphosphine ligand **L** ($\Delta\delta$[DMSO-*d*] 0.58 ppm) (DMSO-*d* was used because **1** and **L** are otherwise insoluble; **1**·Cl is soluble in chlorinated solvents). This interaction was also probed using standard NMR titration methodology (Figure 2), and the Job plots derived from the addition of anion to solutions of both **1**

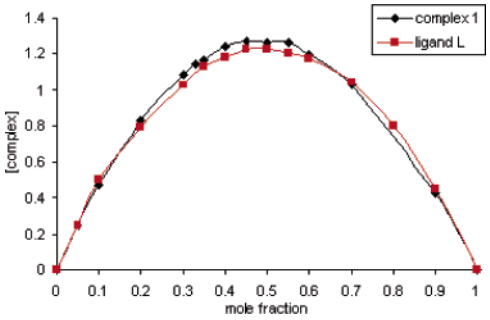


**Figure 2.** Job plots from the addition of [$Bu^n_4$·Cl] to the ureaphosphine ligand **L** and the Pd complex **1**.

and **L** confirm that 1:1 anion binding occurs in solution in both cases. Unfortunately, we have been unable to calculate accurate association constants using these data, possibly as a consequence of competing inter- and intramolecular hydrogen-bonding interactions between **L**, **1**, and the chloride ion.

The inaccuracy of the above calculations and the reality that many metal-catalyzed reactions are conducted at elevated temperature led us to assess the thermal stability of **1**·Cl by $^1H$ NMR spectroscopy in $BrC_6D_5$. Between 300 and 403 K, no significant change in the urea chemical shift was observed [$\delta$(300 K) = 10.41 ppm; $\delta$(403 K) = 10.27 ppm], which suggests that hydrogen bonding to the anion is uncompromised within this temperature range. In contrast, the non-anion-bound complex **1** is completely insoluble in $BrC_6D_5$ at 400 K, and this implies that intermolecular hydrogen-bonding interactions remain dominant in this case.

To classify definitively the nature of anion binding, the solid-state structural determination of *trans*-**1**·Cl was undertaken (Figure 3). Unlike with **1**, *intra*molecular hydrogen-bonding interactions between the hydrogens associated with the urea nitrogen atoms N1 and N2 and their symmetry equivalents and the single chloride ion $Cl_3$ occur [N1−Cl3 3.341(4) Å, N2−Cl3 3.201(4) Å] and result in the formation of an unusual, effectively chelating diphosphine bound to Pd1; this supramolecular interaction between the urea hydrogens and the chloride ion also results in meso stereochemistry at Pd1. It is clear that trans orientation of the ureaphosphine ligands results in a hydrogen-bonding cavity that is suitable for chloride anion binding. This feature is potentially important in the catalytic chemistry of these systems because rhodium complexes of chelating diphosphines that can adopt a range of bite angles or even span trans sites are extremely effective hydroformylation catalysts.[1,8]

To date, we have been unable to crystallize either *cis*-**1** or *cis*-**1**·Cl and so cannot unequivocally define the structural effect of anion binding in this isomer. It is clear, however, that anion binding does occur in solution in both $Pd^{II}$ ($\Delta\delta$ 0.46 ppm) and also $Pd^0$ complexes; preliminary investigations

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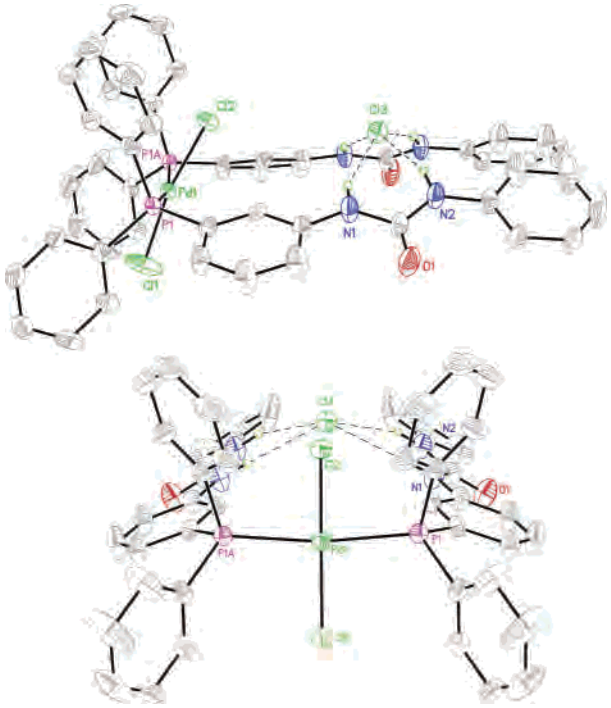


**Figure 3.** X-ray crystal structure of the anion-bound complex $[Bu^n_4N][PdCl_2(\mathbf{L})_2\cdot Cl]$ (**1**·Cl; 50% displacement ellipsoids). For clarity, the $[Bu^n_4N]^+$ cation and all hydrogens except those of the urea nitrogens N1 and N2 are omitted. Selected bond lengths (Å) and angles (deg): Pd1−Cl1 2.2857(18), Pd1−Cl2 2.3007(16), Pd1−P1 2.3484(10); Cl1−Pd1−P1 93.88(3), Cl2−Pd1−P1 87.25(3), Cl1−Pd1−Cl2 169.59(8), P1−Pd1−P1A 165.83(5). The suffix A on atom P1A indicates the symmetry operation ($x$, $^1/_2 - y$, $z$).

suggest that $Pd^0$ complexes such as $[Pd(TCNE)(\mathbf{L})_2]$ (TCNE = tetracyanoethylene) and its anion-bound congener $[Bu^n_4N][Pd(TCNE)(\mathbf{L})_2\cdot Cl]$ can be synthesized and that anion binding is observed in solution [$\Delta\delta(CDCl_3)$ 1.48 ppm].

We have also started to explore the synthesis of $Rh^I$ complexes of **L** and have been able to prepare *trans*-$[RhCl(CO)(\mathbf{L})_2]$ (**2**) and *trans*-$[Bu^n_4N][RhCl(CO)(\mathbf{L})_2.Cl]$ (**2**·Cl) in good yield by ligand substitution from $[\{RhCl(CO)_2\}_2]$ (Scheme 1). The resonances at 30.1 ($J_{Rh-P}$ = 125.7 Hz) and 30.7 ppm ($J_{Rh-P}$ = 126.7 Hz) in the $^{31}P\{^1H\}$ NMR spectra of **2** and **2**·Cl, respectively, are consistent with trans ligand arrangements; no resonances consistent with cis isomers were observed. The elemental analysis of **2**·Cl supports a 1:1 complex/anion ratio, and anion binding in solution is inferred from the $^1H$ NMR spectrum of **2**·Cl, which shows that the urea N−H's shift to higher frequency upon anion addition [$\Delta\delta$(**2**·Cl vs **2**, DMSO-*d*) 0.39 ppm].

The occurrence of well-defined anion binding in the above $Pd^{II}$, $Pd^0$, and $Rh^I$ complexes led us to undertake a preliminary investigation of the effect of anion incorporation on the catalytic activity of these metal complexes. Catalyst mixtures derived from **L**, palladium(0) dibenzylideneacetone precursors, and with or without $F^-$, $Cl^-$, $Br^-$, $HSO_4^-$, and lactate were assessed for the ambient-temperature allylic alkylation reaction between *rac*-1,3-diphenyl-2-propenyl acetate and dimethyl malonate. While all catalyst mixtures were found to be active and achieved 100% conversion after 18 h, no significant difference was seen with anion present, and no asymmetric induction was observed in the presence of the chiral lactate anion; as such, and in line with the solid-state structure of *trans*-**1**·Cl, it would appear that a meso isomer may be adopted in preference to the rac isomers. The $Rh^I$ complexes **2** and **2**·Cl were assessed as preformed catalysts for the hydroformylation of octene using 1:1 $H_2$/CO syngas at 80 °C, 20 bar, and compared to the commercially available ROPAC catalyst, $[Rh(CO)(acac)(PPh_3)]$. While complete conversion of octene to linear/branched (2.6:1) aldehyde was observed after 1 h using the ROPAC catalyst, both **2** (10 h) and **2**·Cl (24 h) required prolonged reaction times for complete conversion to an aldehyde product of a similar linear/branched ratio (ca. 3:1 in both cases). Reactions carried out for 2, 4, 6, 8, and 10 h using **2** and **2**·Cl were analyzed, and in both cases, a significant induction period was observed (5 h for **2**, >10 h for **2**·Cl). The increased reactivity seen for **2** as compared to that of **2**·Cl suggests that the abstraction of chloride necessary to form a reactive, hydridic intermediate is less hindered in **2** because the urea anion-binding pocket is blocked by a precoordinated chloride ion in **2**·Cl.

We have shown that the new (bis)ureaphosphine complexes **1** and **2** bind a chloride ion to form, primarily, trans-chelating diphosphine ligands at the metal. These supramolecular interactions are observed both in solution and in the solid state (for **1**·Cl) and appear to be retained at the elevated temperatures required for many catalytic reactions. $Pd^0$ complexes derived from $Pd^0$ precursors, **L**, and additional anion act as catalysts for allylic alkylation, although no product discrimination is observed in the presence of added anion. However, the presence of anion does appear to decrease the efficacy of **2** in the rhodium-catalyzed hydroformylation of octene.

**Acknowledgment.** We thank the University of Nottingham and the EPSRC for support and the EPSRC National Crystallography Service for collecting the diffraction data for complex **1**.

**Supporting Information Available:** Experimental details for all complexes and catalytic reactions (PDF) and X-ray crystallographic files for **1** and **1**·Cl (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC051110F