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Selective Cleavage of P–N Bonds and the Conversion of Rhodium *N*-Pyrrolyl Phosphine Complexes into Diphosphoxane-Bridged Dimers

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Rhodium(I) complexes *trans*-$[RhCl(CO)(PR_2\{NC_4H_3C(O)Me\text{-}2\})_2]$ (R = Ph, NC_4H_4) react with water to give the diphosphoxane-bridged dimers $[Rh_2Cl_2(CO)_2(\mu\text{-}PR_2OPR_2)_2]$ following cleavage of the P–N bonds to the 2-acetyl-*N*-pyrrolyl groups. The two dimers have been crystallographically characterized and show a number of structural differences, with the PPh_2OPPh_2 compound possessing semibridging chloride and carbonyl ligands whereas the $P(NC_4H_4)_2OP(NC_4H_4)_2$ compound contains only terminal chlorides and carbonyls. No evidence for cleavage of the P–N bonds involving the unfunctionalized *N*-pyrrolyl groups in *trans*-$[RhCl(CO)(P\{NC_4H_4\}_2\{NC_4H_3C(O)Me\text{-}2\})_2]$ was observed.

Recently, *N*-pyrrolyl phosphines have attracted attention due to their electronic properties, being excellent π-acceptor ligands.[1] Although functionalities have been added with a view to enhancing this ability,[2] exploitation of the pyrrolyl group as a framework for bifunctional phosphines has been relatively neglected.[3] We recently reported[4] the synthesis of the pyrrole-based ketophosphine $PPh_2\{NC_4H_3C(O)Me\text{-}2\}$ $\mathbf{L^1}$ and demonstrated that it can act as a hemilabile ligand on molybdenum. In this communication we report how hydrolysis of the P–N bond in rhodium complexes of both $\mathbf{L^1}$ and the related ligand $P(pyr)_2\{NC_4H_3C(O)Me\text{-}2\}$ $\mathbf{L^3}$ (pyr = NC_4H_4, *N*-pyrrolyl) lead to the formation of dimers containing bridging diphosphoxane ligands.

The yellow complex *trans*-$[RhCl(CO)(\mathbf{L^1})_2]$ **1** was formed in high yield from the reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with $\mathbf{L^1}$ in toluene. The value of $\nu(C{=}O)$ (1650 cm^{-1}) is consistent with noncoordination of the oxygen atom whereas the value of $\nu(CO)$ (1981 cm^{-1}) suggests $\mathbf{L^1}$ to be less electron withdrawing than $PPh_2(pyr)$, despite the presence of the acyl substituent. Complex **1** is stable in the solid state, but dissolution in dichloromethane at room temperature led to a slow darkening of color and the precipitation of red crystals of **2**. The IR spectrum of **2** showed the presence of both terminal and bridging carbonyl bands (1964, 1793 cm^{-1}), but no peak in the $\nu(C{=}O)$ region. The ^1H NMR spectrum showed broad signals that can be assigned to the phenyl groups and the absence of the characteristic signals of the pyrrole ring, in agreement with the loss of the 2-acetylpyrrolyl functionality. The very low solubility of **2** prevented a satisfactory $^{31}P\{^1H\}$ NMR spectroscopic analysis, and only a weak broad resonance could be observed after 18 h of acquisition time, suggesting fluxionality in solution. The spectroscopic evidence indicated that a major reorganization of the ligand had occurred, with the formation of a polynuclear species. Structural characterization by X-ray crystallography[5] identified **2** as the dimeric compound $[Rh_2Cl_2(CO)_2(\mu\text{-}\mathbf{L^2})_2]$ ($\mathbf{L^2}$ = PPh_2OPPh_2) (Figure 1). The oxygen atom in $\mathbf{L^2}$ is believed to originate from adventitious water, and this was confirmed by an increase in the rate of formation of **2** from **1** on use of wet dichloromethane. The identity of the solvent is not an important factor in the reaction, and **2** can also be prepared from **1** using wet toluene.

The coordination geometry around each rhodium center in **2** is distorted trigonal bipyramidal, with two phosphorus atoms from different bridging $\mathbf{L^2}$ ligands arranged trans to each other in the axial positions. The equatorial positions are occupied by one terminal and two semi-bridging ligands, which were identified as carbonyls and chlorides, disordered equally between the terminal and bridging positions.

Although a 1:1 mixture of $[Rh_2(CO)_2(\mu\text{-}Cl)_2(\mu\text{-}\mathbf{L^2})_2]$ and $[Rh_2Cl_2(\mu\text{-}CO)_2(\mu\text{-}\mathbf{L^2})_2]$ cannot be eliminated on the basis of the X-ray analysis, a simpler model contains one compound, $[Rh_2Cl(CO)(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}\mathbf{L^2})_2]$, present in two positions with equal likelihood (**2′** and **2″** in Figure 2). The

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(5) X-ray data for **2**: $C_{50}H_{40}Cl_2O_4P_4Rh_2\cdot CH_2Cl_2$, $M = 1190.42$, $T = 293(2)$ K, monoclinic, $P2_1/n$, $a = 14.394(2)$ Å, $b = 9.683(2)$ Å, $c = 17.287(3)$ Å, $\beta = 92.93(2)°$, $V = 2406.3(7)$ Å^3, $Z = 2$, $\rho_c = 1.599$ g cm^{-3}, $\mu = 1.081$ mm^{-1}; 4539 reflections collected of which 4230 independent [$R_{int} = 0.0167$]. Final R indices [$I > 2\sigma(I)$] R1 = 0.0475, wR2 = 0.1165.

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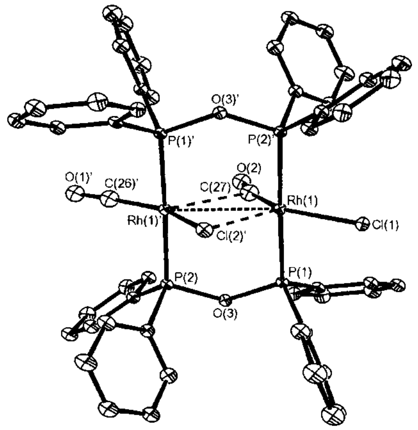
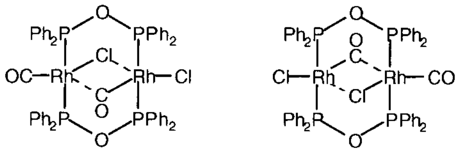


Figure 1. Molecular structure of **2**, with carbonyls and chlorides shown in one of the two positions. Selected bond lengths (Å) and angles (deg) Rh(1)−Rh(1)′ 2.8683(9), Rh(1)−P(1) 2.292(1), Rh(1)−P(2)′ 2.299(1), Rh(1)−Cl(1) 2.361(5), Rh(1)−Cl(2) 2.464(5), Rh(1)−C(26) 1.83(2), Rh(1)−C(27) 1.84(2), P(1)−O(3) 1.636(3), P(2)−O(3) 1.651(3), P(1)−O(3)-P(2) 125.9(2). Primed atoms generated by symmetry transformation $-x + 1$, $-y$, $-z$.



2' **2"**

Figure 2. Orientations of $[Rh_2Cl(CO)(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}\mathbf{L}^2)_2]$ required to give the observed disordered structure of **2**.

related cationic complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}L)_2]^+$ (L = dppm, PPh_2NHPPh_2) have previously been structurally characterized.[6]

Compound **2** is the first reported example of a rhodium dimer containing bridging PPh_2OPPh_2 ligands, though rhodium dimers incorporating the related bridging ligand bis(diphenylphosphino)methane (dppm) have been widely studied.[7] Analysis of the Rh−Rh distances from complexes containing the $Rh_2(\mu\text{-}dppm)_2$ skeleton shows that the distance in **2** [2.8683(9) Å] lies within the ranges observed both for compounds which contain a Rh−Rh bond [2.52−3.01 Å (mean 2.77 Å)][8] and for those in which a Rh−Rh bond is absent [2.83−3.47 Å (mean 3.16 Å)]. The P···P separation between the phosphorus atoms of the same ligand (2.93 Å) is longer than the Rh−Rh distance, indicating compression along the Rh−Rh internuclear axis, though this may be due to the presence of the bridging ligands. These bridges are highly unsymmetric, with Rh−C(27) distances of 1.84(2) and 2.69(3) Å and Rh−Cl(2) distances of 2.464(5) and 2.889(6) Å, respectively; hence the ligands are best described as semibridging. This is further reflected in the bond angles, with the bridging carbonyl ligands [Rh(1)−C(27)−O(2) 165.7(12)°] showing a relatively small deviation from the linear conformation observed for the terminal carbonyl [O(1)−C(26)−Rh(1) 176.3(13)°]. Similar semibridging carbonyl ligands were observed in the structure of $[Rh_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$.[9] The two diphosphoxane oxygen atoms are pointed in opposite directions in **2**, giving a chair conformation for the $Rh_2P_4O_2$ ring, as opposed to the boat conformation observed in the majority of $M_2P_4C_2$ rings.[10]

Although uncoordinated $\mathbf{L}^1$ is slowly hydrolyzed to form $PPh_2P(O)Ph_2$, hydrolysis of **1** is much faster under similar conditions, suggesting the reaction to be metal-promoted. The chelate complex $[RhCl(PPh_3)(\mathbf{L}^2)]$ has previously been prepared from a metal-promoted rearrangement and disruption of mutually cis $Ph_2PO_2CCH{=}CH_2$ ligands.[11] The trans orientation of the $\mathbf{L}^1$ ligands in **1** disfavors formation of the analogous monomer $[RhCl(CO)(\mathbf{L}^2)]$ on hydrolysis, instead promoting formation of the dimer **2** in which the trans orientation of the phosphorus donors is maintained.

In order to examine the generality of diphosphoxane dimer formation, the ligand $P(pyr)_2\{NC_4H_3C(O)Me\}$ $\mathbf{L}^3$ was prepared from the reaction of $P(pyr)_2Cl$ with 2-acetylpyrrole in the presence of base and the analogous rhodium chemistry studied. The reaction of $\mathbf{L}^3$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ gave $[RhCl(CO)(\mathbf{L}^3)_2]$ **3**, and IR spectra demonstrated the presence of both ν(CO) (1997 cm^{-1}) and ν(C=O) (1653 cm^{-1}). On stirring complex **3** in wet toluene at 60 °C, a darkening of color was observed, and on standing, deep red crystals of **4** precipitated. The IR spectrum of **4** showed the presence of a terminal carbonyl (2031 cm^{-1}) and the absence of the acetyl stretch. ^1H NMR spectroscopy again showed loss of the 2-acetylpyrrole functionality. The $^{31}P\{^1H\}$ NMR spectrum consists of a broad apparent doublet of triplets consistent with a dimeric structure.[12]

The identity of **4** was confirmed crystallographically[13] as $[Rh_2Cl_2(CO)_2(\mu\text{-}\mathbf{L}^4)_2]$ [$\mathbf{L}^4$ = $P(pyr)_2OP(pyr)_2$] (Figure 3). In contrast to **2**, the chloride and carbonyl ligands are terminally coordinated and there is no disorder in the structure. The geometry around each rhodium center is square-planar, and the Rh···Rh distance, 3.1177(3) Å, is considerably longer than that observed in **2** and clearly indicates the absence of a Rh−Rh bond. This was also the case in the structure of $[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$, though for this compound the Rh···Rh distance is still longer [3.2386(5) Å].[14] The angle between the mean plane of the rhodium coordination sphere [Rh(1), C(17), Cl(1), P(1), and P(2)′] and the mean plane of the dimer framework [Rh(1), P(1), P(2), Rh(1)′, P(1)′, and P(2)′] in **4** is 82°, and the deviation of the $\mathbf{L}^4$ oxygen atom

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(13) X-ray data for **4**: $C_{34}H_{32}Cl_2N_8O_4P_4Rh_2{\cdot}C_7H_8$, M = 1109.44, T = 293(2) K, monoclinic, $C2/c$, a = 19.8250(2) Å, b = 11.8230(2) Å, c = 20.9580(3) Å, β = 110.9461(7)°, V = 4587.74(11) Å^3, Z = 4, ρ_c = 1.606 g cm^{-3}, μ = 1.025 mm^{-1}; 26407 reflections collected of which 5218 independent [R_{int} = 0.0487]. Final R indices [$I > 2\sigma(I)$] R_1 = 0.0283, wR_2 = 0.0752.

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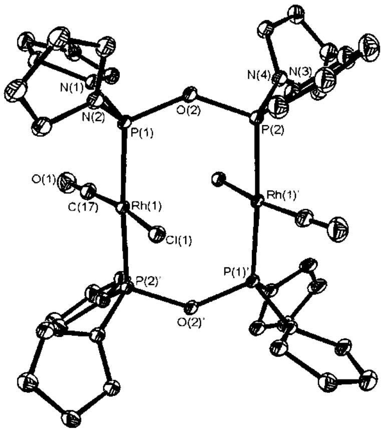

Figure 3. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg) Rh(1)⋯Rh(1)′ 3.1177(3), Rh(1)−C(17) 1.839(3), Rh(1)−P(1) 2.2664(5), Rh(1)−P(2)′ 2.2624(5), Rh(1)−Cl(1) 2.3719(5), P(1)−O(2) 1.618(2), P(2)−O(2) 1.627(2), P(2)−N(3) 1.695(2), P(2)−N(4) 1.672(2), P(1)−O(2)-P(2) 132.4(1). Primed atoms generated by symmetry transformation $-x + {}^{1}/_{2}, -y + {}^{1}/_{2}, -z$.

from this latter plane is 0.08 Å, much less than the analogous distance (0.32 Å) in **2**.

Searches of the Cambridge Crystallographic Database[8] and Chemical Abstracts suggest that compounds **2** and **4** are the first examples of transition metal dimers in which metal centers are bridged by two diphosphoxane ligands. While structural comparisons are limited by the disorder in **2**, it is evident that replacing phenyl groups with *N*-pyrrolyl groups has a marked effect on the structure of the rhodium dimer.

Despite the presence of three P−N bonds in **L**^{3}, the bond to the 2-acetylpyrrolyl group is selectively cleaved during conversion of **3** to **4**. Both *trans*-[RhCl(CO){PPh$_2$(pyr)}$_2$] and *trans*-[RhCl(CO){P(pyr)$_3$}$_2$] have been previously prepared,[1] and neither has been reported to undergo a reaction to give **2** or **4**. Partial delocalization of the negative charge onto the carbonyl group leads to 2-acetylpyrrolyl being a better leaving group than pyrrolyl. This observation is likely to be significant in the development of chemistry based on functionalized *N*-pyrrolyl phosphines.

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Supporting Information Available: Synthetic information for compounds **L**^{3} and **1**−**4**. Crystallographic information for complexes **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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