Organometallics **1997,** *16,* 3579−3581

Bridged Hemilabile Allylphosphonate Ligand: Synthesis and Crystal Structure of a New Binuclear Rhodium Complex

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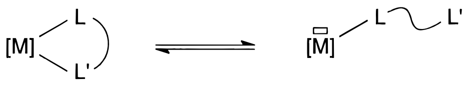
Received March 5, 1997⊗

Summary: The reaction of 2 equiv of the allylphosphonate $CH_2{=}CH{-}CH_2{-}P(O)(OEt)_2$ with $[Rh(Cl)(CO)_2]_2$ results in the formation of a new binuclear rhodium complex with two bridged bidentate allylphosphonate ligands in cis positions, reaction with carbon monoxide induces the lability of the phosphonate moiety, which is reversible.

Introduction. Bidentate ligands with two types of donor sites are well-known and have been the subject of many reports.[1] Transition-metal complexes containing hemilabile bidentate ligands are of great potential interest in homogeneous catalysis: with one strong and one weak donor function, they give the possibility for a substrate to displace the weaker donor, whereas the chelate effect confers stability on the catalyst precursor in the absence of the substrate (eq 1).[2]



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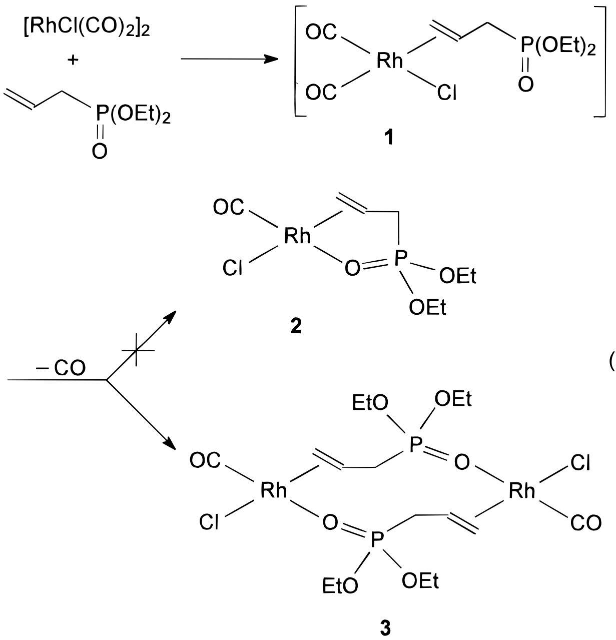
As part of our research program concerning the role of hemilabile ligands on the hydroformylation of simple olefins, we were interested in complexes of rhodium incorporating bidentate olefin ligands where a heteroatom is bound to the olefin by a carbon chain to yield a chelate ligand. Olefinic phosphines[3] and olefinic amines[4] have been shown to give rise to such chelate complexes; meanwhile, no study of the potential hemilability of these bidentate ligands has been reported. New hemilabile rhodium complexes with phosphonate−phosphine ligands $(RO)_2P(O)(CH_2)_nPPh_2$ have been recently shown as promising catalyst precursors because of the easy ring opening of the chelate structure by decoordination of the phosphonate moiety.[5]

We report here the study of the ability of allylphosphonates $CH_2{=}CH{-}CH_2{-}P(O)(OR)_2$ to function as a hemilabile chelating ligand. Because of the great lability of the phosphonate groups,[5] the complexes would provide ideal models for the proposed intermediates in homogeneous catalytic reactions such as hydrogenation, hydroformylation, and isomerization of olefins.

Results and Discussion. Treatment of $[Rh(Cl)(CO)_2]_2$ with 2 equiv of the allylphosphonate $CH_2{=}CH{-}CH_2{-}P(O)(OEt)_2$ in CH_2Cl_2 at room temperature first leads to an unstable derivative whose IR data are typical of *cis* mononuclear $Rh(Cl)(CO)_2(L)$ complexes.[6] This compound **1**, which has no indication of coordinated phosphonate in the IR or the ^{31}P NMR spectrum,[6] rapidly undergoes a decarbonylation process to give rise to a chelate complex for which the spectroscopic data[8] indicate the coordination of both the olefin and the phosphoryl oxygen atom. This seems in agreement with the structure **2** (eq 2) in which one of the carbonyl ligands of complex **1** is substituted by the phosphonate group. Such mononuclear chelate complexes are typically observed in the reaction of $[Rh(Cl)(CO)_2]_2$ with most of the mixed bidentate ligands L∼L′.[9]



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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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S0276-7333(97)00182-9 CCC: $14.00

Table 1. Crystal Structure Determination and Refinement of 3

formula	$Rh_2Cl_2P_2O_8C_{16}H_{30}$
mol wt	689.08
cryst syst	orthorhombic
space group	*Pbca*
a, Å	13.289(3)
b, Å	17.511(9)
c, Å	22.538(5)
V, Å	5245(3)
Z	8
ρ(calcd), g·cm^{-3}	1.745
F(000)	2752
μ(Mo Kα), cm^{-1}	16.00
T, K	293
cryst size, mm	0.15 × 0.30 × 0.40
radiation	Mo Kα
max 2θ, deg	50
range of *hkl*	0–15; 0–20; 0–26
no. of reflns measured	5124
no. of reflns obsd ($I > \sigma(I)$)	2603(4.0σ)
N(obs)/*N*(var)	2603/256
R	0.061
R_w[a]	0.048
S_w	3.37
max residual, e Å^{-3}	0.48
α/σ	0.02

[a] $a_w = 1/\sigma(F_o)^2 - [\sigma^2(I) + (0.04F_o{}^2)^2]^{-1/2}$

After evaporation of the reaction mixture to dryness, the residue gives yellow crystals on recrystallization from hexane–dichloromethane (2:1).

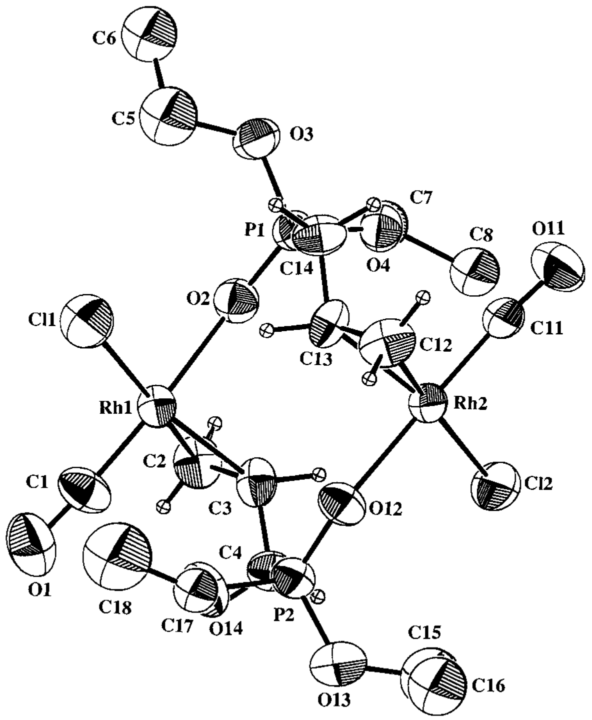

Figure 1. Molecular structure of **3**. Selected bond lengths (Å): Rh(1)–Cl(1), 2.327(3); Rh(1)–O(2), 2.092(7); Rh(1)–C(1), 1.76(1); Rh(1)–C(2), 2.12(1); Rh(1)–C(3), 2.13(1). Selected bond angles (deg): Cl(1)–Rh(1)–O(2), 90.6(2); Cl(1)–Rh(1)–C(1), 92.0(4); Cl(1)–Rh(1)–C(2), 165.9(3); Cl(1)–Rh(1)–C(3), 155.6(3); O(2)–Rh(1)–C(1), 175.1(4); C(2)–Rh(1)–C(3), 38.1(4).

Surprisingly, the X-ray radiocrystallographic study[10] (Table 1) shows that the chelate complex is not **2** but the dimeric compound **3** (eq 2) formed by two {Rh(Cl)(CO)(CH_2=CH–CH_2–P(O)$(OEt)_2$} entities in which the allylphosphonate ligands are bridging the two metal centers. The two allylphosphonates are *cis* to each other, and the oxygen atom of the phosphonate group is *trans* to the carbonyl ligand (Figure 1). This molecular structure reveals that the molecule is quasi centrosymmetric, and the coordination about each rhodium atom can be described as square planar. Slight distortions of the square plane are justified by consideration of the angles defined by the ligands surrounding the central rhodium of Cl(1)–Rh(1)–O(2) = 90.6(3)°, Cl(1)–Rh(1)–C(1) = 92.0(4)°, Cl(2)–Rh(2)–O(12) = 89.0(2)°, and Cl(2)–Rh(2)–C(11) = 90.6(4)°. The ethylene C=C groups are approximately orthogonal to the coordination square plane, and the Rh–C(2) (C(12)) and Rh–C(3) (C(13)) distances are equivalent. The C=C lengths (1.38 and 1.39 Å) are similar to those found in other Rh–olefin complexes.[4b,12] The parameters involving the chlorine and carbonyl ligands are not unusual. Indeed, the Rh–Cl bond lengths (2.327 and 2.333 Å) are normal for Rh–Cl bonds *trans* to a π olefin,[4b,13] and the Rh–CO lengths (1.76, 1.73 Å) are equivalent to the one found for a carbonyl *trans* to a phosphine oxide[14] or a phosphonate[15] group.

To our knowledge, **3** is the first bimetallic complex of rhodium bearing chlorine and carbonyl ligands and two bridging mixed bidentate ligands in *cis* positions.[16] The distance between the allyl and phosphonate groups does not seem to be responsible for the formation of **3** since the cyclic monomeric complex [Rh(Cl)(L)(CH_2=CH–CH_2–NHPh)], bearing a shorter bidentate ligand, has been described.[4c]

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(6) IR (CH_2Cl_2): ν(CO) 2063, 1998 cm^{-1}; ν(PO) = 1252 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 27.3. The observation of two almost equally intense bands in the ν(CO) region of the infrared spectrum is in accord with the *cis*-Rh(Cl)$(CO)_2$(L) complex.[7] The IR ν(PO) and the ^{31}P NMR signal are similar to those observed for the free ligand, indicating uncoordination of the phosphonate moiety.

(7) (a) Pribula, A. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 2784. (b) Poilblanc, R.; Gallay, J. *J. Organomet. Chem.* **1971**, *21*, C53.

(8) **3**: IR (CH_2Cl_2) ν(CO) 2005 cm^{-1}; ν(PO) 1145 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 33.6. The IR shift in the stretching band of the phosphoryl group ν(PO) to lower value and the ^{31}P NMR shift downfield from the corresponding resonance of the uncoordinated phosphonate are observed, indicating the coordination of the oxygen of the P=O group.

(9) Sharp, P. R. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Ed.; Pergamon: Oxford, 1995; Vol. 8, pp 115–302.

(10) A parallelepiped crystal of dimensions 0.15 × 0.30 × 0.40 mm was selected and studied on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods with the program SHELX-86.[11] A total of 5124 reflections were collected, of which 2603 ($I > 2\sigma(I)$) were used to give R = 0.061 and R_w = 0.048.

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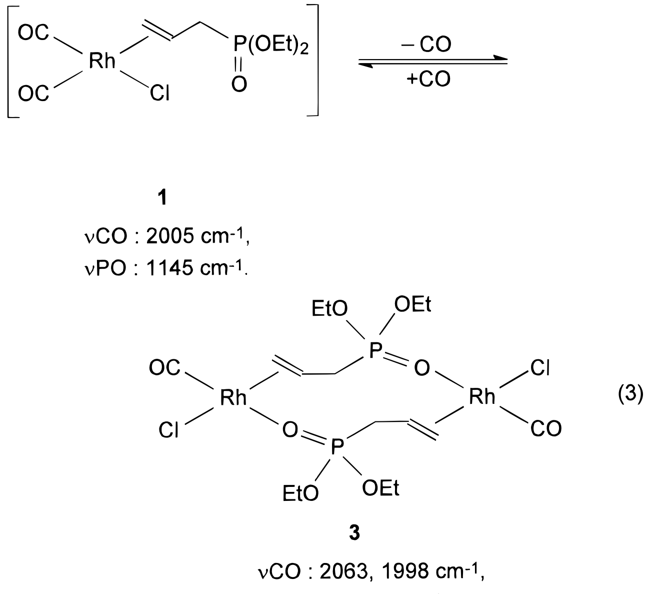
(16) Reaction of $[Rh(Cl)(CO)_2]_2$ with $Ph_2PCH_2P(S)Ph_2$ (dppms) leads to the dimeric complex [Rh(Cl)(CO)(μ dppms)$_2$Rh(Cl)(CO)] with the phosphine *trans* to the thiophosphoryl.[17] Similarly, reaction of the rhodium carbonyl chloride dimer with Ph_2PCH_2SMe has been shown to give the binuclear face-to-face complex with the phosphine *trans* to the thioether group.[18] Furthermore, in this case, the formation of this dimeric bis(phosphinothioether) depends on the ligand length, the introduction of a second methylene group in the bridge giving monomeric cyclic Rh(Cl)(CO)(Ph_2P–CH_2–CH_2–S–Me).[18]

(17) Blagborough, T. C.; Davis, R.; Ivison, P. *J. Organomet. Chem.* **1994**, *467*, 85.

(18) Anderson, G. K.; Kumar, R. *J. Organomet. Chem.* **1988**, *342*, 263.

The hemilabile behavior of the allylphosphonate ligands in complex **3** is illustrated by its reaction with carbon monoxide: bubbling CO at room temperature through a dichloromethane solution of **3** affords mononuclear complex **1** bearing a monodentate allylphosphonate ligand for which reversible coordination of the oxygen is observed, whereas the metal–olefin bond remains intact (eq 3). Despite several attempts, it was impossible to obtain complex **1** completely free from the binuclear compound **3**, as indicated by the IR data. Purging with nitrogen regenerates complex **3**, indicating that the reaction is reversible (eq 3).



1

νCO : 2005 cm-1,
νPO : 1145 cm-1.

(3)

3

νCO : 2063, 1998 cm-1,
νPO : 1252 cm-1.

To our knowledge, this reaction is the first example that shows the hemilability of a mixed bidentate ligand with an allyl moiety. Consequently, this new type of complex represents an interesting potential model for the study of catalytic functionalizations of olefins. Reactions of this new dimeric rhodium compound are currently under investigation.

Experimental Section. All manipulations were performed under an atmosphere of nitrogen with standard Schlenk techniques, and all solvents were distilled under an inert atmosphere from an appropriate drying agent.[19]

Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer. The ^{1}H (300 MHz), ^{13}C (75.47 MHz), and ^{31}P (121.49 MHz) spectra were obtained on a Bruker AC300 spectrometer with the chemical shifts reported in δ values relative to the residual protonated solvent (^{1}H), the solvent resonance (^{13}C), or using 87% H_3PO_4 as an external standard (^{31}P). The starting reagents were obtained from commercial sources and used without purification.

Preparation of $CH_2{=}CH{-}CH_2{-}P(O)(OEt)_2$. To a suspension of 32.8 mmol (750 mg) of sodium in 20 mL of THF at 0 °C was added 32.8 mmol (4.2 mL) of HP(O)(OEt)$_2$. The mixture was maintained overnight at 25 °C and then slowly added at 0 °C to a solution of 1 equiv (3 mL) of $CH_2{=}CH{-}CH_2{-}I$ in 10 mL of THF. After 2 h of stirring, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 and distilled. $CH_2{=}CH{-}CH_2{-}P(O)(OEt)_2$: 40 °C under 2.5×10^{-3} Torr (Yield: 70%). ^{1}H NMR ($CDCl_3$): δ 1.30 (6H, t, $J_{H-H} = 7.1$ Hz), 2.59 (2H, dd, $J_{H-P} = 21.9$ Hz, $J_{H-H} = 7.3$ Hz), 4.09 (4H, m), 5.20 (2H, m), 5.78 (1H, m). ^{13}C NMR ($CDCl_3$): δ 16.5 (d, $^{3}J_{C-P} = 6$ Hz), 31.8 (d, $^{1}J_{C-P} = 139.0$ Hz), 61.8 (d, $^{2}J_{C-P} = 6.6$ Hz), 119.6 (d, $^{3}J_{C-P} = 14.4$ Hz), 127.3 (d, $^{2}J_{C-P} = 11.2$ Hz). ^{31}P NMR ($CDCl_3$,): δ 26.9.

Preparation of Binuclear Complex 3. To a solution of 0.25 mmol (97.3 mg) of $[Rh(Cl)(CO)_2]_2$ in 10 mL of CH_2Cl_2 at room temperature was added a solution of 2 equiv (0.50 mmol, 89.0 mg) of $CH_2{=}CH{-}CH_2{-}P(O)(OEt)_2$ in 5 mL of CH_2Cl_2. After 10 min of stirring, an IR spectrum of the solution showed the formation of the intermediary complex **1**,[6] which rapidly underwent a decarbonylation process. Then, a new band appeared on the IR spectrum in the ν(CO) area. The solvent was removed after 30 min of stirring, and the yellow-brown residue was taken up with hexane–CH_2Cl_2 (2:1). Complex **3** was recrystallized from this mixture at −30 °C and obtained as yellow microcrystals (yield: 75% vs $[Rh(Cl)(CO)_2]_2$). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2005, ν(PO) 1145. ^{1}H NMR ($CDCl_3$, 263 K): δ 1.32 (6H, t, $J_{H-H} = 7.0$ Hz), 2.63 (2H, br, $J_{H-P} = 21.6$ Hz), 4.15 (4H, m), 3.71 (2H, m), 4.43 (1H, m). ^{13}C NMR ($CDCl_3$, 263 K): δ 16.2 (d, $^{3}J_{C-P} = 6.5$ Hz), 33.0 (d, $^{1}J_{C-P} = 144.7$ Hz), 63.5 (br), 63.6 (d, $^{1}J_{C-Rh} = 8.2$ Hz), 64.4 (d, $^{2}J_{C-P} = 6.4$ Hz), 182.7 (dd, $^{1}J_{C-Rh} = 79.3$ Hz, $^{3}J_{C-P} = 9.1$ Hz). ^{31}P NMR ($CDCl_3$, 263 K): δ 33.6.

Study of the Lability of the Phosphonate Group on 3. A solution of 0.1 mmol (68.9 mg) of **3** in 10 mL of CH_2Cl_2 was placed under a carbon monoxide atmosphere. The reaction was monitored by IR spectroscopy. After 30 min of stirring, the IR spectrum taken from the solution showed the formation of complex **1** (ν(CO) 2063, 1998 cm^{-1}) together with a small amount of **3** (ν(CO) 2005 cm^{-1}), which was quantitatively regenerated after purging with nitrogen.

Crystal Structure Analysis for 3. The data were collected on a CAD-4 Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation. Table 1 gives the experimental data for the crystal structure of **3**. The cell parameters are obtained by least-squares fitting of a set of 25 high-θ reflections. After Lorenz and polarization corrections, the structure was solved with direct methods, scale factor refinement, and Fourier differences. After the isotropic ($R = 0.095$) and then anisotropic refinements ($R = 0.072$), the hydrogens were located with a difference Fourier map. The entire structure was refined by full-matrix least-squares techniques. Atomic scattering factors were taken from ref 20. All calculations were performed on a digital Microvax 3100 computer with the MolEN package (Enraf-Nonius, 1990).

Supporting Information Available: Text giving details of the X-ray structure determination and tables of crystal data, bond distances and angles, and positional and thermal parameters for **3** (9 pages). Ordering information is given on any current masthead page.

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