

Preliminary communication

NMR spectra and crystal structure of a regioselective hydroformylation catalyst complex $\text{RhH}(\text{diphosphite})(\text{CO})_2$

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Abstract

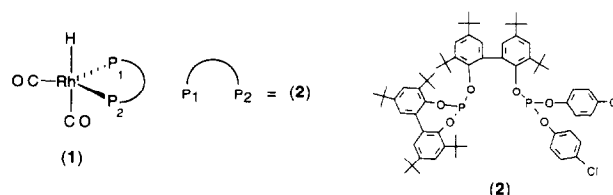
The crystal structure and characterization in solution are described for a very regioselective hydroformylation catalyst, $\text{RhH}(\text{CO})_2(\text{diphosphite})$ with $\{2(3,3',5,5'\text{-tetra-}t\text{-butyl-1,1'-biphenyl-2,2'-diylphosphite}), 2'(\text{bis}(4\text{-Cl-phenyl)phosphite})\text{-3,3,5,5'-tetra-}t\text{-butyl-1,1'-biphenyl}\}$ as the diphosphite. The complex is formed under CO-H_2 pressure from $\text{Rh}(\text{CO})_2\text{Acac}$ and has a distorted TBP geometry with both phosphorus atoms in equatorial positions.

Keywords: Rhodium; Diphosphite; Hydroformylation; Catalysis; Crystal structure

Bidentate phosphorus ligands are widely studied because of their potential as ligands in the hydroformylation of various alkenes [1]. Bryant and coworkers [1a] used bulky diphosphite modified rhodium carbonyl catalysts for the hydroformylation of propene and observed a huge enhancement in the normal-to-branched aldehyde ratio. Cury and Buchwald [1b] reported the selective hydroformylation of functionalized alkenes with one of these catalysts. Casey et al. [1c] showed that a natural bite angle of diphosphines of approximately 120° induces an equatorial–equatorial (ee) coordination of the phosphorus atoms. He and others [1c,d] suggested that this geometry is responsible for the high regioselectivity in the rhodium-catalyzed hydroformylation of hex-1-ene [1e]. Recently we suggested [2] that diphosphite-modified catalysts also require an ee coordination in order to achieve the observed high regioselective [1f] and enantioselectivity [3]. We now report the X-ray structure and the characterization in solution of a diphosphite coordinated rhodium complex **1**, a highly regioselective hydroformylation catalyst [4].

The catalyst complex was obtained by the reaction of $\text{Rh}(\text{CO})_2\text{Acac}$ with $\{2(3,3',5,5'\text{-tetra-}t\text{-butyl-1,1'-biphenyl-2,2'-diylphosphite}), 2'(\text{bis}(4\text{-Cl-phenyl)phosphite})\text{-3,3,5,5'-tetra-}t\text{-butyl-1,1'-biphenyl}\}$ (**2**) under syngas pressure [5]. The ^{31}P NMR spectrum shows that the two phosphorus atoms are almost magnetically degenerate, although they are chemically inequivalent. The small differences in chemical shifts and the large values of $J_{\text{P}(1)\text{P}(2)}$ lead to second-order spectra, as observed for most asymmetric diphosphites [1f].

Fig. 1 shows the observed (m,1H) and simulated hydride region of the ^1H NMR spectrum [7]. The coupling constants of both the phosphorus atoms with the hydride proton (–15 and 66 Hz) do not give an unambiguous indication of the position of the proton in relation to the phosphorus atoms since 66 Hz fits neither



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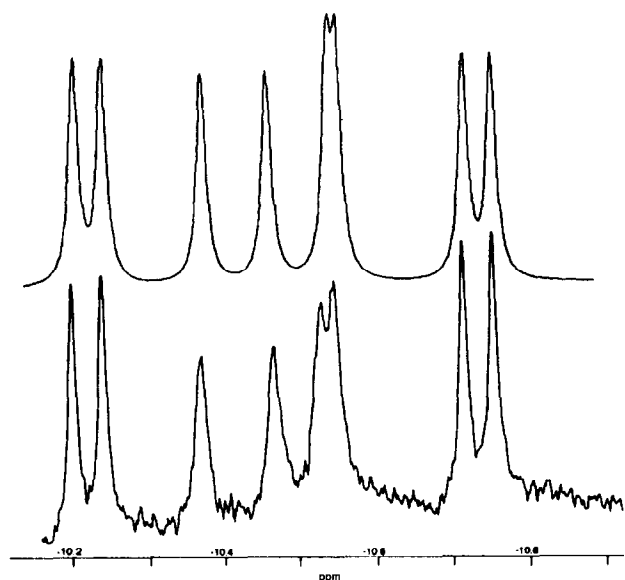


Fig. 1. Measured (lower) and simulated (upper) ^1H NMR spectra of hydride region (100 MHz).³

a *trans* nor a clear *cis* disposition [8]. The ^{13}C NMR spectrum of the ^{13}C -enriched complex reveals the presence of two different CO ligands: one coupled to the phosphorus atoms with relatively large J_{CP} values

($J_{\text{CP}(1)} = 48 \text{ Hz}$; $J_{\text{CP}(2)} = 36 \text{ Hz}$) and the other to the phosphorus atoms with very small J_{CP} values ($J_{\text{CP}(1)} = -2.5 \text{ Hz}$; $J_{\text{CP}(2)} = 14 \text{ Hz}$). IR spectra showed three bands, assigned to the RhH and two CO absorptions [9]. The deuterio analogue shows two CO absorptions in which the peak shifts are in accordance with one CO in an axial and the other in an equatorial position. These data indicate a trigonal bipyramidal (TBP) structure in solution, with two equatorial phosphorus ligands (1).

The X-ray structure of 1 (Fig. 2) reveals a distorted TBP geometry around the rhodium and confirms the suggested structure, although the hydrido ligand could not be located [10]. Both phosphorus atoms occupy equatorial positions; the P(1)–Rh–P(2) angle is $115.95(9)^\circ$. The angles made by the phosphorus atoms with the equatorial CO are $115.2(4)^\circ$ and $118.5(3)^\circ$. The dihedral angles of the diphenyl rings are respectively $60.6(4)^\circ$ for C(29)–C(34) with C(35)–C(40) and $61.9(4)^\circ$ for C(1)–C(6) with C(7)–C(12). The rhodium atom is situated above the equatorial plane ($0.395(1) \text{ \AA}$) and resides towards the axial CO ligand. The axial CO ligand deviates from the molecular axis the P–Rh–C angles are P(1)–Rh–C(ax) = $92.1(3)^\circ$ and P(2)–Rh–C(ax) = $104.2(3)^\circ$. The P–Rh distances are longer than those in the AcacRhP₂ complex [11] (P = bis(phenyl

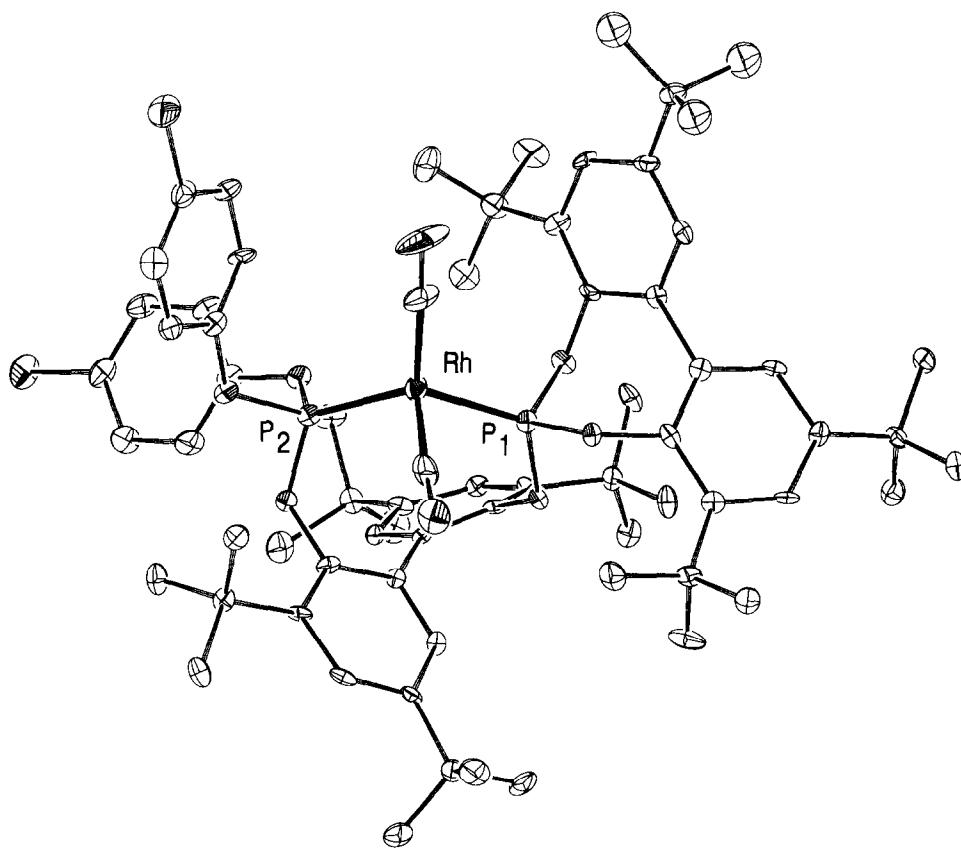


Fig. 2. ORTEP 30% probability plot (PLATON) for RhH(diphosphite)(CO)₂ (1). The hydrido ligand could not be located. Hydrogen atoms are omitted for clarity.

3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-diyl)phosphite) (2.1549(9) and 2.1566(9) Å compared with 2.239(3) and 2.255(3) Å in **1**). Alternatively, the geometry of **1** can be described as highly distorted tetrahedral with a hydride on one of the faces, accounting for the unusual NMR coupling constants [8].

This is the first X-ray structure of a hydrido rhodium diphosphite complex and, to our knowledge, also the first structure of a rhodium hydrido dicarbonyl complex with a bidentate phosphorus ligand. The structure is analogous to that of the [1c] 2,2'-bis(diphenylphosphinomethyl)-(1,1'-biphenyl) (BISBI) coordinated iridium complex. The TBP structure of the diphosphite rhodium complex is more distorted than that of (BISBI)IrH(CO)₂, indicating that there is greater steric crowding around the metal center in **1**. The ee coordination and the steric bulk lead to a high selectivity in the hydroformylation reaction. Little space is available for the incoming substrate to coordinate at the remaining equatorial position. Upon migration of the hydride toward the π -bonded alkene the steric interactions can be most efficiently minimised by the formation of a linear alkyl–rhodium intermediate. [1a,2]. Thus, upon coordination of the substrate and subsequent hydride migration, linear alkyl species are obtained almost exclusively, resulting in a high *n/b* ratio [4]. The importance of both bulk and rigid bite angles in inducing formation of linear alkyl complexes has been revealed by hydroformylation experiments involving less bulky or more flexible (yet ee coordinating) diphosphites, which lead to *n/b* ratios of only 2 and to higher rates [1f].

The new structural data for this active catalyst can be used for parametrization in molecular mechanics calculations. Such calculations are widely used to study structure–performance relationships in hydroformylation, but until now no structural data have been available.

Acknowledgments

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- [4] In a typical experiment an autoclave was charged with 8×10^{-6} mol of Rh(CO)₂Acac, 0.091 g (8×10^{-5} mol) of (**1**), 19 ml of toluene and of CO–H₂ at 20 bar. The autoclave was heated to 60°C and 20 mmol of oct-1-ene and 5.13 mmol of decane (internal standard) were added. Results after 30% conversion: TOF, 460 m m⁻¹ h⁻¹; *n/b* = 15; 7% isomerization products.
- [5] A glass bottle equipped with a stirring bar was filled with 10 mg of Rh(CO)₂Acac, 44 mg of **2** and 2 ml of acetone. When the compounds had completely dissolved, the open vessel was placed in a 200 ml autoclave which was charged with CO–H₂ at 10 bar. The autoclave was heated to 40°C and after 3 h was cooled to room temperature and the pressure released. The white precipitate formed was separated by decanting most of the solvent and Hacac and then allowing the remaining solvent to evaporate. (The microcrystals obtained were air stable during several days.) That the product was indeed the initially formed active hydroformylation catalyst was confirmed by in-situ high pressure NMR and IR spectroscopy in the presence of an excess of **2** [1f].
When the isolated complex is used for the hydroformylation similar results are obtained. To keep all the rhodium coordinated to the diphosphite, additional diphosphite is required [6]. Colorless crystals were obtained by dissolving 10 mg of Rh(CO)₂Acac and 44 mg of **2** in 2 ml of benzene, charging the autoclave to 10 bar, heating it to 60°C and releasing the pressure after 3 h, and when most of the solvent and the formed Hacac evaporated off, and the autoclave cooled to give crystals. Melting point (decomposition above 180°C). Mass spectroscopy (PD): *m/e* 1236 M⁺ – 2CO – H.
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- [7] Simulation of the NMR spectra of RhH(¹²CO)₂(diphosphite) with GeNMR (IvorySoft) produced the following data. ³¹P{¹H} NMR (benzene-*d*₆, 121.5 MHz): δ 160.55 (P(1)), 159.85 (P(2)), *J*_{RhP(1)} = 237 Hz, *J*_{RhP(2)} = 217 Hz, *J*_{P(1)P(2)} = 170.0 Hz ppm. ¹H NMR (benzene-*d*₆, 300.13 MHz): δ –10.40 (m, Rh–H, *J*_{RhH} = 3.5 Hz, *J*_{HP(1)} = –15 Hz, *J*_{HP(2)} = 66 Hz) ppm. ¹⁰³Rh NMR (via 2D-REVERSE, benzene-*d*₆ 100 MHz): δ –1018 (dd) ppm. ¹³C NMR of the ¹³CO labeled complex (benzene-*d*₆, 15 MHz): δ 191.91 (ddd, CO(eq), *J*_{CRh} = 66 Hz, *J*_{CP(1)} = 48 Hz, *J*_{CP(2)} = 36 Hz, 193.38 (ddd, CO(ax), *J*_{CRh} = 54 Hz, *J*_{CP(1)} = –2.5 Hz, *J*_{CP(2)} = 14 Hz) ppm.
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- [9] The IR spectrum of **1** in Nujol showed three bands with equal intensities at 2036, 1997 and 1991 cm⁻¹ assigned respectively to two combination bands of the ν_{CO} and to ν_{MH} . In the deuteride complex the lowest energy band has disappeared, leaving two CO absorption bands at 2062 and 2005 cm⁻¹. No ν_{MD} could be found because of other intense bands in that region.

[10] Crystallographic data for $C_{70}H_{89}Cl_2O_8P_2Rh_1$ were collected at 150 K on an Enraf–Nonius CAD4-Turbo diffractometer on a rotating anode for a transparent crystal ($0.15 \times 0.25 \times 0.50$ mm) with the monoclinic spacegroup $C2/c$ (No. 15), with $a = 40.632(6)$, $b = 13.943(3)$ and $c = 23.645(5)$ Å, $\beta = 92.420(15)^\circ$, $V = 13384(4)$ Å³, $Z = 8$, 10633 reflections measured, 9873 unique, Mo K α (graphite monochromator) radiation and $1.5^\circ < \theta < 23.5^\circ$. The structure was solved by automated Patterson methods (DIRDIF-92). Refinement on F^2 (SHELXL-93). Hydrogen

atoms were placed in calculated positions except for the hydrido atom $wR_2 = 0.164$, $R_1 = 0.0824$ (for 4807 reflections with $I > 2.0\sigma(I)$) for 773 parameters, $S = 0.935$. The values of Rh–C(eq) and Rh–C(ax) (not mentioned in the text), are 1.878(12) and 1.938(9) Å, respectively. One of the *tert*-butyl groups is disordered (C(17), C(18), C(19) and C(20)).

Lists of atomic coordinates, bond angles and distances and H-atom coordinates thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.