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Preliminary Communication

Solution structures of hydrido-rhodium diphosphite hydroformylation catalysts

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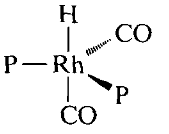
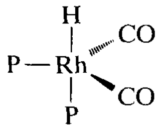
Abstract. The NMR spectroscopy data for five hydroformylation catalysts $RhH(CO)_2(P\text{–}P)$ (P–P = diphosphite bidentate ligand) are reported and interpreted in terms of equatorial and axial coordination of the phosphorus and carbon monoxide ligands in a trigonal bipyramidal structure.

In the last decade the interest in new hydroformylation rhodium catalysts modified with phosphite ligands has enormously increased.[1–8] Especially diphosphites have proven to be extremely useful for obtaining high selectivities to either linear or enantiomerically enriched products.[3,5–7] The structure of these complexes are as yet unknown in open literature, but some preliminary data have been presented.[8]

For rhodium hydrido (di)phosphine complexes evidence has accumulated that in the trigonal bipyramidal complex the hydrido ligand occupies an axial position and the two phosphine ligands should take two equatorial positions if high selectivities to linear products are to be obtained[9,10] (structure **a**). For sterical reasons, the hydro carbyl complexes prefer structure **b**.[9]



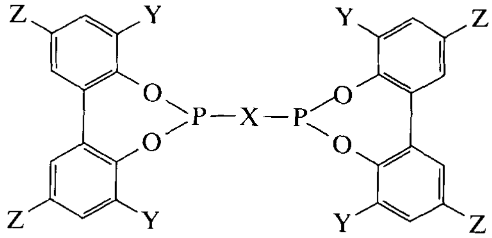
a

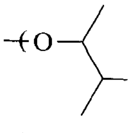


b

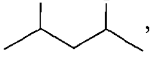
A suitable bridge between the two phosphorus ligands may lead to stabilisation of either structure **a** or **b**. Most bidentate ligands studied sofar have been synthesised aiming at a donor atom - metal - donor atom angle of approximately 90°. Recently a number of diphosphine ligands have been described with a natural bite angle closer to 120°.[10–12] These diphosphines resulted in catalysts with high selectivities to linear products. A striking structural similarity is apparent between these diphosphine ligands and the diphosphite ligands of the new, highly selective catalysts systems. Two general structures[13] seem to induce bite angles which are attractive for selective catalysis in the hydroformylation reaction: a diphenyl bridge with either $-O-PR_2$ or $-CH_2-PR'_2$ donor groups in the 2,2′-positions, or a bridge of five (sometimes four) atoms between the phosphorus atoms (arranged such that interaction between metal and bridge is absent).

We now report structural data of diphosphite complexes indicating that also in these complexes the natural bite angle of the diphosphites is near 120°.[8a] NMR data of five complexes with illustrative ligands are given in table 1. The composition of the complexes is $RhH(P\text{–}P)(CO)_2$.[14a,b]

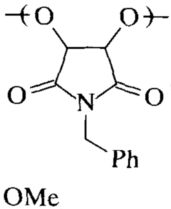


(**1**): X =


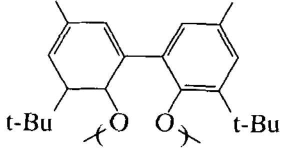
, Y = t-Bu, Z = OMe

(**2**): X =


, Y = t-Bu, Z = OMe

(**3**): X =


, Y = Z = t-Bu

(**4**): X =


, Y = Z = H

(5):

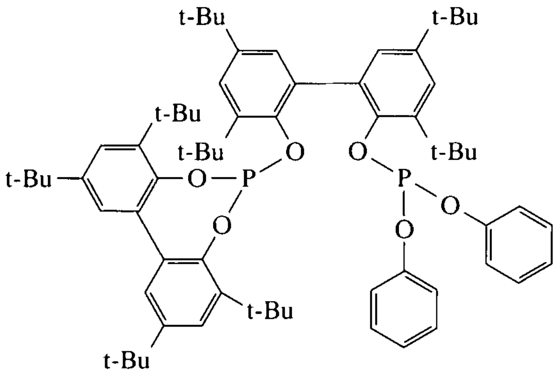


Table I NMR Spectroscopic data for complexes **1–5** [a,b].

PP	δP [c]	δH	$\delta C(^{13}CO)$	$^1J_{Rh-P}$	$^1J_{Rh-H}$	$^2J_{H-P}$
1	156.1	−10.05	n.d. [d]	209	7.2	96
2	158.5	−10.25	n.d.	233	3.0	3
3	158.7	−10.23	n.d.	237	6.0	11
4	174.5	−10.81	194.7	239	3.5	4
5	160.6	−10.35	193.7 C(1) 191.9 C(2)	240	2.3	30

[a] $RhH(P-P)(CO)_2$ complexes **1–5** measured at RT under atmospheric conditions. [b] Spectra recorded on 300 MHz NMR spectrometer, in toluene-*d8*, acetone-*d6* and benzene-*d6*, chemical shifts (δ) in ppm, coupling constants (J) in Hz. [c] ^{31}P spectra recorded ^1H decoupled. [d] Not determined.

The ^1H spectrum of complex **1** has a double triplet hydride signal. The large triplet is an average signal due to very rapid exchange of the two phosphorus donor atoms resulting in broadening of both the ^{31}P doublet and the hydride signal at lower temperatures. Even at 173 K the exchange has not been halted completely although it is clear that in the ^1H spectrum the signal in the slow exchange limit is a double double doublet with one $^2J_{P-H}$ coupling constant close to 190 Hz and one that is very small. We conclude that one phosphorus ligand occupies an axial position (large coupling constant) and the other an equatorial position (structure **b**).[15] The average for $^1J_{P-Rh}$ is 209 Hz. Complex **2** is a clear example of a complex having structure **a**; only small cis coupling constants are observed for $^2J_{H-P}$. Due to C_2 symmetry of the ligand two different ^{31}P chemical shifts may be expected. Indeed at 213 K the fluxionality is frozen out and two ^{31}P signals are observed ($\delta P_1 = 165.3$ ppm, $\delta P_2 = 155.7$ ppm, $^1J_{Rh-P1} = {}^1J_{Rh-P2} = 237$ Hz) with a large $^2J_{P-P}$ coupling constant (236 Hz) which we now think is typical of the equatorial-equatorial relationship. The $^2J_{H-P}$ coupling constants remain small. Similarly, complex **3** shows two equal phosphorus chemical shifts and small $^2J_{H-P}$ coupling constants, indicative of a cis relation between the two phosphorus atoms and the hydrogen (structure **a**). Again at 213 K the fluxionality is frozen out and two ^{31}P signals are observed ($\delta P_1 = 164.6$ ppm, $\delta P_2 = 157.5$ ppm, $^1J_{Rh-P1} = {}^1J_{Rh-P2} = 236$ Hz) with a large $^2J_{P-P}$ coupling constant (327 Hz). Complex **4**, a catalyst giving linear hydroformylation products for a variety of substrates[5], shows similar data. The bisphenol bridge may also lead to diastereotopic phosphorus atoms[16] and inter-conversion could be stopped by cooling, resulting also in two different phosphorus atoms ($\delta P_1 = 177.3$ ppm, $\delta P_2 = 175.4$ ppm, $^1J_{Rh-P1} = 238$ Hz, $^1J_{Rh-P2} = 232$ Hz, $^2J_{P-P} = 205$ Hz, T = 205 K). Two equal ^{13}C carbon monoxide absorptions suggest rapid pseudo-Berry rotations. The small $^2J_{P-H}$ coupling constants are the best indication for the predominance of structure **a**. Complex **5** (a typical example of the new ligands pioneered by Union Carbide[2]) has two chemically different phosphorus atoms but accidentally the chemical shifts in the complexes are often (nearly) identical. The ^1H hydride signal consists of a triplet caused by two equal phosphorus couplings or a virtual triplet due to a large mutual P–P coupling. The magnitude of the (average) $^2J_{P-H}$ coupling constants may point to rapid equilibria of isomers **a** and **b** as the latter should give rise to one large $^2J_{P-H}$ coupling constant. The ^{13}C spectra, however, show two non interacting carbon monoxide molecules (certain pseudo-Berry rotations may still take place) one of which is strongly coupled to two phosphorus atoms (average $^2J_{C(2)-P} = 43$ Hz) while the other one shows a strong coupling to the hydrogen atom ($^2J_{C(1)H} = 29$ Hz). These features support structure **a** for this complex as the dominant structure.

In conclusion, $RhH(diphosphite)(CO)_2$ are highly fluxional complexes. Subtle changes in the bridge determine whether equatorial-equatorial or axial-equatorial complexes are formed which is supported by molecular mechanics studies. The equatorial-equatorial conformation leads to the strongest interaction between ligand and hydro-carbyl group during catalytic processes, inducing the highest selectivity. These results will soon be published.

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[13] For other suitable structural types see ref. 10.

[14] a) Complexes **1–5** were prepared from stoichiometric amounts of P–P and $Rh(acac)(CO)_2$ under syngas (10–40 bar, 1–10 h, 300–340K). For **1**, **2** and **3** the *(R,R)*-enantiomers have been used.; b) Hydroformylation results on regioselectivity and enantioselectivity will be published elsewhere.

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