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High-Pressure Investigations under CO/H_2 of Rhodium Complexes Containing Hemispherical Diphosphites

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Abstract: The two rhodium complexes $[Rh(acac)(\mathbf{L^R})]$ ($\mathbf{L^R}$ = (*S,S*)-5,11,17,23-tetra-*tert*-butyl-25,27-di(OR)-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene; **6**: R = benzyl, **7**: R = fluorenyl), each based on a hemispherical chelator forming a pocket about the metal centre upon chelation, are active in the hydroformylation of 1-octene and styrene. As expected for this family of diphosphanes, both complexes resulted in remarkably high selectivity towards the linear aldehyde in the hydroformylation of 1-octene (l/b ≈ 15 for both complexes). Linear aldehyde selectivity was also observed when using styrene, but surprisingly only **6** displayed a marked preference for the linear product (l/b = 12.4 (**6**) vs. 1.9 (**7**)). A detailed study of the structure of the complexes under CO or CO/H_2 in toluene was performed by high-pressure NMR (HP NMR) and FT-IR (HP-IR) spectroscopies. The spectroscopic data revealed that treatment of **6** with CO gave $[Rh(acac)(CO)(\eta^1\text{-}\mathbf{L^{benzyl}})]$ (**8**), in which the diphosphite behaves as a unidentate ligand. Subsequent addition of H_2 to the solution resulted in a well-defined chelate complex with the formula $[RhH(CO)_2(\mathbf{L^{benzyl}})]$ (**9**). Unlike **6**, treatment of complex **7** with CO only led to ligand dissociation and concomitant formation of $[Rh(acac)(CO)_2]$, but upon addition of H_2 a chelate complex analogous to **9** was formed quantitatively. In both $[RhH(CO)_2(\mathbf{L^R})]$ complexes the diphosphite adopts the bis-equatorial coordination mode, a structural feature known to favour the formation of linear aldehydes. As revealed by variable-temperature NMR spectroscopy, these complexes show the typical fluxionality of trigonal bipyramidal $[RhH(CO)_2(diphosphane)]$ complexes. The lower linear selectivity of **7** versus **6** in the hydroformylation of styrene was assigned to steric effects, due to the pocket in which the catalysis takes place being less adapted to accommodate CO or larger olefins and, therefore, possibly leading to facile ligand decoordination. This interpretation was corroborated by an X-ray structure determination carried out for **7**.

Keywords: calixarenes • confinement • NMR spectroscopy • hydroformylation • bite angle • rhodium

Introduction

Spatial confinement can strongly influence the catalytic properties of an organometallic species.[1–11] Embedding a catalytic centre in a molecular pocket, cleft or cage not only provides a way to efficiently protect the metal unit towards deactivation but also enables selective stabilisation of transition states that drive the reaction towards specific products.[12–14] When the pocket possesses receptor properties, it may also function as a substrate-selecting unit that leads to shape-selective catalysis.[15,16]

In recent work we have shown that calix-diphosphites **1**–**5**, which all have two bulky (*S,S*)-1,1′-binaphthalene-2,2′-dioxy moieties, form highly regioselective hydroformylation catalysts with $[Rh(acac)(CO)_2]$. The observed high linear aldehyde selectivities were attributed to a substantial metal confinement after complexation, which orientates the reac-

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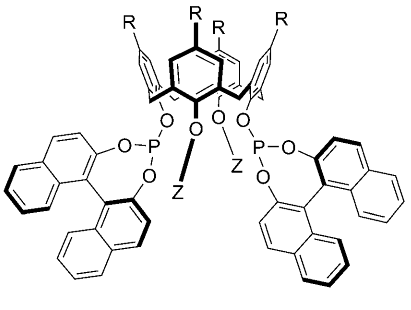
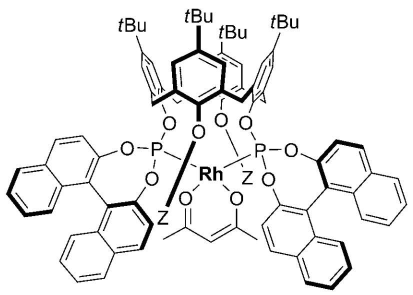
tion towards the formation of linear Rh–alkyl intermediates regardless of the olefin used.[17–20] Two geometrical features make the formation of a molecular pocket about the rhodium effective: 1) the large ligand bite angle, which induces a bending of two symmetrically-sited naphthyl fragments towards the complexed rhodium centre, and 2) the presence of two calixarene lower rim substituents that behave as a nonbonding pincer unit. From the pioneering studies of van Leeuwen et al. on large-bite-angle diphosphanes, it has become apparent that high selectivities towards linear aldehydes usually rely on the capacity of the bidentate ligand to form trigonal bipyramidal (TBP) hydrido carbonyl intermediates in which both phosphorus atoms occupy equatorial positions. In these complexes, the metal site becomes most effective and consequently favours the formation of a linear Rh(*n*-alkyl) complex rather than the corresponding branched analogue.[21–23] However, prediction of the relative disposition of the P atoms in the catalytic TBP intermediates is not easy, and it has also been shown that bis-equatorial coordination is not compulsory for high selectivity.[24] The stereochemistry of the hydrido carbonyl species formed under hydroformylation conditions with the above hemispherical diphosphites is not known to date, nor is the ease with which the key intermediates are formed. In an attempt to understand the origin of efficiency of rhodium complexes derived from such ligands, we have examined the behaviour of complexes **6** and **7** under H_2/CO by using combined high-pressure NMR/FT-IR spectroscopic techniques for this purpose. We anticipated that metal confinement would be more efficient with the ligand containing the O-benzyl substituents than with that bearing the less flexible O-fluorenyl groups. The relevance of high-pressure NMR and IR studies for the understanding of regioselectivity in hydroformylation has been emphasised recently by several authors.[24–28]

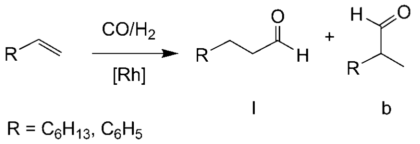


1 R = *t*Bu, Z = *n*Pr
2 R = *t*Bu, Z = CH_2Ph
3 R = *t*Bu, Z = CH_2-2-naphthyl
4 R = *t*Bu, Z = fluorenyl
5 R = H, Z = *n*Pr



6 Z = CH_2Ph
7 Z = fluorenyl

Results and Discussion



Scheme 1. Hydroformylation of α-olefins catalyzed by complexes **6** and **7**.

The following catalytic study was exclusively based on the use of complexes **6** and **7** in the hydroformylation reaction of 1-octene and styrene (Scheme 1). We began these investigations by assessing the two complexes in the hydroformylation of 1-octene. The catalytic runs were performed in toluene at 50 °C under a $p(CO/H_2)$ total pressure of 21 bar. Using a CO/H_2 ratio of 1:2 gave considerably higher turnover frequencies (TOFs) than with 1:1 or 2:1 mixtures, the regioselectivity remaining practically unchanged (Table 1, entries 1–3). This observation is unsurprising because for phosphites the rate-determining step is the addition of the olefin to the hydrido–rhodium–bis-carbonyl intermediate, a step that becomes more easy by reducing the relative carbon monoxide pressure.[29] Note, however, that the observed higher activities induced by the higher partial H_2 pressure cannot be explained by standard kinetics, which predict that a 30 % increase in the partial H_2 pressure would at most double the rate. A possible explanation for the observed abnormal activity increase is the existence of an equilibrium between the active hydrido carbonyl species and an inactive $[RhL(CO)_2]_2$ dimer, the proportion of which decreases on applying higher H_2 pressures. This interpretation has already been proposed (for other systems) by other authors.[30,31]

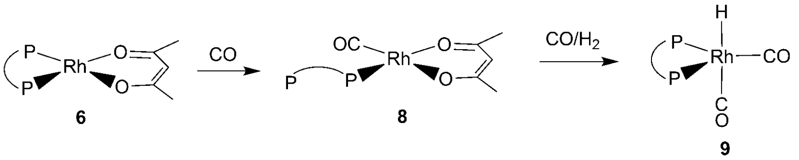
Table 1. Rhodium-catalyzed hydroformylation of 1-octene and styrene using complexes **6** and **7**.[a]

Entry	[Rh]	$p(CO)/p(H_2)$	Conv. [%]	TOF[b]	Isomer [%]	Aldehydes l [%]	b [%]	l/b
1-octene								
1	**6**	2:1	1.0	10	1.0	trace		–
2	**6**	1:1	6.8	70	1.2	94.4	5.6	16.8
3	**6**	1:2	38.8	390	4.6	93.5	6.5	14.5
4	**7**	1:2	18.1	180	1.1	93.1	6.9	13.5
styrene								
5	**6**	1:2	23.1	230	–	92.5	7.5	12.4
6	**7**	1:2	8.1	80	–	65.1	34.9	1.9

[a] General conditions: olefin (5 mmol), [Rh] (2 μmol), olefin/Rh = 2500, $p(CO/H_2)_{total} = 21$ bar, $T = 50$ °C, toluene/*n*-decane (15:0.5 mL), 2.5 h. The conversions were determined by GC by using decane as an internal standard. [b] TOFs were expressed in mol(converted olefin) $mol(Rh)^{-1} h^{-1}$.

The CO/H_2 ratio of 1:2 was then used for all further tests. Under these conditions **6** and **7** led to comparable linear/branched (l/b) aldehyde ratios of 14.5 and 13.5, respectively, with the catalyst activity being two times higher with the sterically less encumbered ligand **2** (Table 1, entry 3 vs. 4). When performing the runs with styrene, the linear aldehyde again turned out to be the major product with the benzyl-substituted complex **6**, but with **7** a significant drop in activity and selectivity was observed (Table 1, entries 5 and 6). The latter observation suggests that the expanded fluorenyl walls may strongly interact with bulkier olefins under catalytic conditions, thereby leading to catalytic intermediates different to those obtained with smaller olefins.

To get some insight into the structural peculiarities of **7**, we completed the above investigations by determining the solid-state structure of **7**•hexane•methyl-2-pentane. This study revealed that the unit cell contains two structurally very similar molecules. In both, the metal ion sits deeply inside the pocket delineated by two naphthyl units and the two fluorenyl groups (Figure 1). The distances between the rhodium atom and the closest neighbouring aromatic carbon atoms (which belong to naphthyl units) are remarkably short at around 3.5 Å. The high steric pressure exerted on the metal by the surrounding pocket is best seen in the non-zero dihedral angle between the acac plane and the PMP plane, 16.0° in molecule 1 and 20.5° in molecule 2. The averaged ligand bite angle is 102.7°. Interestingly, these geometrical features are similar to those found in the recently reported complex [Rh(acac)(**1**)] (PMP = 101.5°; acac/PMP tilt angle = 16.3°).[19] The fluorenyl planes of **7** adopt an orientation that is roughly parallel to the calixarene axis, thereby minimising the steric repulsion between these groups and the naphthyl units. As a result, the rhodium atom is sterically more confined than in [Rh(acac)(**1**)].



Scheme 2. Formation of complexes **8** and **9** starting from **6**.

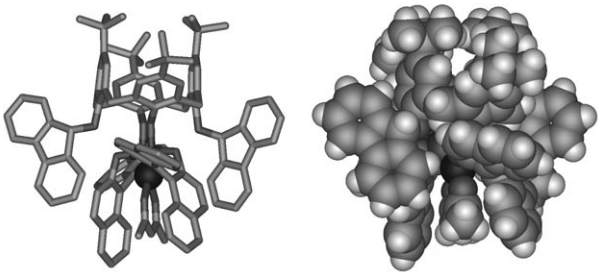


Figure 1. Solid-state structure of **7** showing the confinement of the rhodium atom (dark grey sphere). Only one of the two molecules present in the unit cell is shown. Hydrogen atoms have been omitted from the left view, but are shown in the CPK representation on the right. Selected bond lengths [Å] and angles [°]: Rh–O1 2.069(6), Rh–O2 2.071(6), Rh–P2 2.178(2), Rh1–P1 2.209(3); O1-Rh-O2 89.8(3), O1-Rh-P2 83.30(19), O2-Rh-P2 165.2(2), O1-Rh-P1 167.6(2), O2-Rh-P1 86.2 (2), P2-Rh-P1 103.11(9). Complex **7** crystallised with solvent molecules, which are not shown for clarity.

The above observations led us to investigate the nature of the species formed under catalytic conditions by using NMR spectroscopy. The following NMR experiments were performed in a sapphire tube under pressure. Applying a CO pressure of 7 bar to a solution of **6** in [D$_8$]toluene readily led to the formation of [Rh(acac)(CO)(η^1-**2**)] (**8**) (Scheme 2 and Figure 2). The unidentate nature of **2** in this complex was inferred from the corresponding ^{31}P{^{1}H} NMR spectrum, which showed a doublet centred at $\delta = 141.7$ ppm (^1J(Rh,P) = 297 Hz) and a singlet at $\delta = 123.3$ ppm assigned to the coordinated and the dangling phosphite arms, respectively. The formulation of **8** was further confirmed by the presence of a single strong CO stretching band at $\tilde{\nu} = 2010$ cm^{-1} in the IR spectrum (measured at 7 bar). The IR spectrum of **8** also revealed the presence of the coordinated acac ligand. Complex **8** was stable in the absence of CO because bubbling of nitrogen into a solution of the complex did not modify its ^{31}P NMR spectrum.

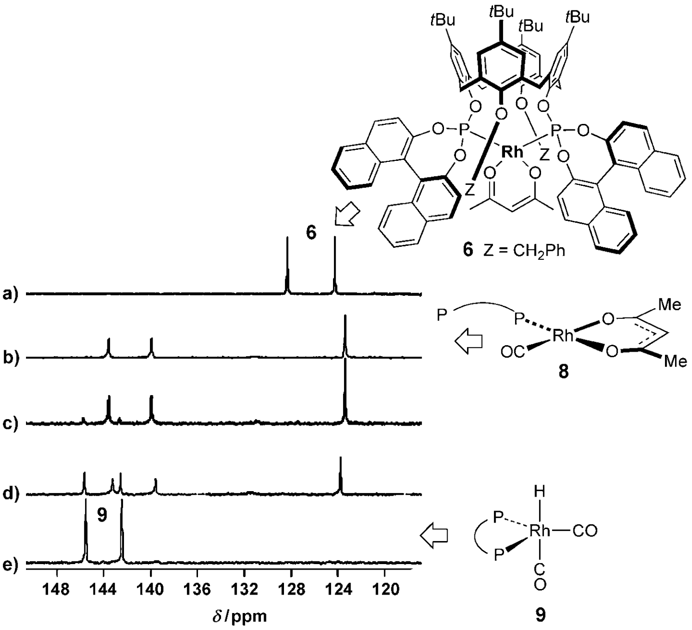


Figure 2. ^{31}P{^{1}H} NMR (sapphire tube, [D$_8$]toluene, 81.01 MHz) spectra of **6** under CO (7 bar) and CO/H$_2$ (1:2; 21 bar). a) Compound **6** only; b) **6** + CO; c) **6** + CO/H$_2$, RT; d) **6** + CO/H$_2$, 40 °C; e) **6** + CO/H$_2$, 50 °C.

On pressurizing the above sapphire tube with hydrogen at 14 bar to apply a p(CO)/p(H$_2$) ratio similar to the one that led to the highest TOFs in the catalytic tests, complex **9** slowly formed (Scheme 2 and Figure 2). Here, unlike in **8**, diphosphite **2** shows bidentate coordination, which could be inferred from the appearance of a doublet at $\delta = 144.1$ ppm (^1J(Rh,P) = 246 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Hydride formation was observed in the ^1H NMR spectrum, which exhibited a triplet centred at $\delta = -8.28$ ppm with a ^2J(P,H) coupling constant of 5.8 Hz (J(Rh,H) = 0 Hz). The small ^2J(P,H) coupling constant is in accord with a hydride *cis*-disposed with respect to the P atoms. Although complex **9** formally has C_1 symmetry, its ^{31}P NMR spectrum shows an A_2X instead of an ABX pattern. This is indicative of a fluxional process similar to that described by van Leeuwen et al. for related TBP complexes that contain flexible diphosphites (vide infra).[32] The IR spectrum of complex **9** showed two strong absorption bands at $\tilde{\nu} = 2063$ and 1965 cm^{-1}. The presence of two carbonyl ligands could be deduced from the room-temperature ^{31}P, ^{13}C, and ^1H NMR spectra of complex **9** measured after the latter had been synthesised in a separate experiment by using ^{13}C-enriched (99 %) carbon monoxide (Figure 3). Therefore, the above data are in agreement with the formation of a dynamic, trigonal bipyramidal complex with equatorially positioned phosphorus atoms and a hydride occupying an apical coordination site.[29,32–34] It is worth noting that the conversion of complex **8** into **9** occurred considerably faster in the HP-IR cell than in the NMR tube owing to more efficient stirring in the former apparatus. On heating the solution to 50 °C, full conversion of **8** into **9** occurred readily. Prolonged heating of a solution of **9** did not result in the formation of new species.

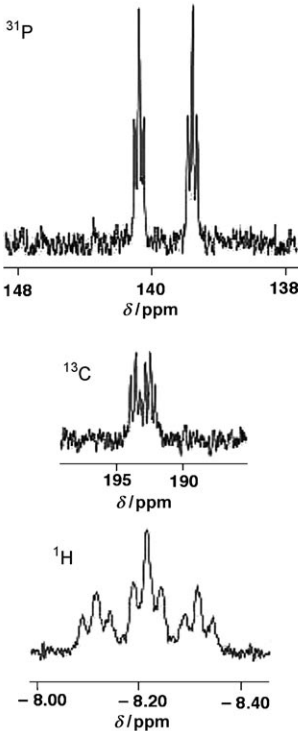


Figure 3. Room-temperature ^{31}P, ^{13}C and ^1H NMR (sapphire tube, [D$_8$]toluene, 81.01 MHz) spectra of **9** obtained under 99 % ^{13}CO. Important data inferred from these spectra: ^{31}P NMR: $\delta = 139.2$ ppm (dt, ^1J(Rh,P) = 249, ^2J(P,C) = 21 Hz); ^{13}C NMR: $\delta = 192.88$ ppm (dt, ^1J(Rh,C) = 60.4, ^2J(P,C) = 21.0 Hz); ^1H NMR: $\delta = -8.20$ ppm (tt, ^2J(C,H) = 18.2, ^2J(P,H) = 4.8 Hz).

To prove that complex **9** displays dynamic behaviour in solution, the NMR probe was gradually cooled to −80 °C. Upon cooling, the peak seen in the ^{31}P NMR spectrum at high temperature first broadened, then coalesced near −20 °C. At −80 °C, the $^{31}P\{^1H\}$ NMR spectrum (Figure 4) gave a well-resolved ABX spin system ($\delta_A = 143.5$ ppm, ^1J(Rh,P) = 238 Hz, ^2J(P,P) = 240 Hz; $\delta_B = 146.8$ ppm (^1J(Rh,P) = 241, ^2J(P,P) = 240 Hz), whereas the hydride region revealed a broad unresolved signal centred at $\delta = -7.85$ ppm (not shown). The observed ^2J(P,P) coupling constant is typical for phosphorus atoms occupying equatorial sites in a TBP species.

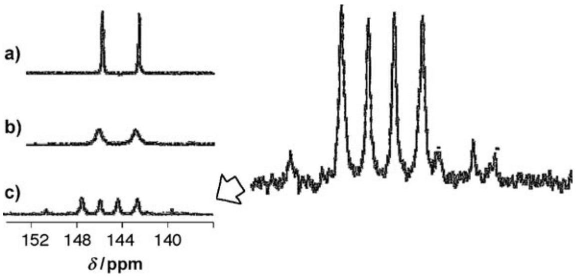
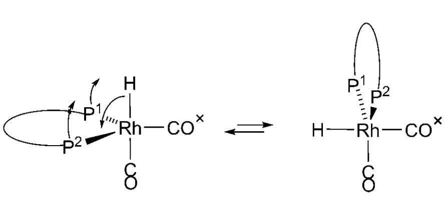


Figure 4. $^{31}P\{^1H\}$ NMR ([D$_8$]toluene) spectra of **9** at a) 25, b) −10, and c) −80 °C.

In addition, a low-temperature ^1H NMR spectrum was acquired in the presence of a 2:1 H_2/CO mixture that contained ^{13}C-enriched (99 %) CO. The hydride region showed a doublet of a broad signal, in accord with a hydrido ligand *trans* to a carbonyl ligand (^2J(H,C) = 40 Hz, see the Supporting Information). Overall, these findings indicate that the fluxionality of **9** can be frozen out at low temperatures and that the two exchanging species (which cannot be distinguished spectroscopically) have phosphorus atoms occupying exclusively equatorial coordination sites. These observations are consistent with the equatorial–equatorial phosphorus exchange proposed by van Leeuwen et al., which occurs in TBP [RhH(diphosphite)(CO)$_2$] complexes that contain diphosphites with a long P–P link (Scheme 3).[35] These results also corroborate earlier studies by Muetterties et al.[36,37] on the dynamics of five-coordinate TBP metal–



Scheme 3. Equatorial–equatorial phosphorus exchange in TBP [RhH(calix-diphosphite)(CO)$_2$] complexes that contain long P–P links. In these dynamics each CO ligand is alternately *cis* and *trans* bonded with respect to the hydrido ligand.

phosphane complexes. It is worth noting that in the proposed exchange mechanism each carbonyl ligand alternately occupies an apical and an equatorial position. Consistent with these dynamics, the ^{13}C NMR spectrum that was obtained under ^{13}C-enriched CO shows a symmetrical carbonyl signal at room temperature (actually a doublet of triplets with $^1J(\mathrm{Rh,C}) = 60.4$, $^2J(\mathrm{P,C}) = 21.0$ Hz). It is worth noting here that the proposed fluxionality is different from a hypothetical exchange mechanism restricted to a 180° rotation of the diphosphite about its intrinsic C_2 axis. In this case, in fact, two distinct carbonyl signals would appear in the room-temperature ^{13}C NMR spectrum.

To summarise, the above NMR spectroscopy studies demonstrate that, under catalytic conditions, hemispherical diphosphite **2** leads exclusively to a pentacoordinate [RhH(CO)$_2$(diphosphite)] intermediate that adopts a bis-equatorial P,P coordination mode.

The above reactions, which were carried out in an NMR tube with **6**, were repeated in the presence of 1-hexene (olefin/Rh = 145). The ^{31}P NMR spectrum acquired at 50 °C just after addition of CO revealed the exclusive formation of complex **8**. Subsequent addition of hydrogen gave **9**, with no other product being detected. After 1 h the solution was analysed by GC, which revealed the formation of a mixture of linear and branched aldehydes in a l/b ratio of 49. It is worth noting that when this reaction was repeated in an autoclave, similar regioselectivities were obtained.

A second series of experiments was run with fluorenyl complex **7**. The room-temperature ^{31}P NMR spectrum of this complex in [D$_8$]toluene showed a doublet at $\delta = 126.1$ ppm ($^1J(\mathrm{Rh,P}) = 327$ Hz). After pressurizing the solution with CO (7 bar), decoordination of diphosphite **4** with concomitant formation of [Rh(acac)(CO)$_2$] was observed (Scheme 4 and Figure 5). This latter complex, which did not form in the experiments performed with **6**, was unambiguously characterized by its IR spectrum, which showed two stretching bands at $\tilde{\nu} = 2082$ and 2011 cm^{-1}.[38] Here, ligand decoordination arises after formation of the intermediate [Rh(acac)(CO)(**4**)] (not seen), which probably cannot accommodate a double chelate structure owing to strong interactions between the CO ligand and the rigid fluorenyl moieties. Upon addition of hydrogen (14 bar, 25–50 °C), hydrido dicarbonyl complex **10** then slowly formed (Figure 5). Full conversion into **10** only occurred after heating the solution at 60 °C (Scheme 4 and Figure 5). At this temperature, the ^{31}P{^{1}H} NMR spectrum of compound **10** showed an unique doublet centred at $\delta = 144.1$ ppm ($^1J(\mathrm{Rh,P}) = 246$ Hz). The bis-equatorial coordination mode of the diphosphite ligand was again inferred from the ^{1}H NMR spectrum, which showed a broad hydride signal with a small $^2J(\mathrm{P,H})$ coupling constant (<2 Hz, unresolved signal). The dynamics of **10** are similar to those outlined above for **9**. Thus, as for **9**, the ^{31}P NMR spectrum of complex **10** measured at −50 °C displayed an ABX spin system, as expected for a C_1-symmetrical molecule undergoing slow exchange ($\delta_A = 147.2$ ppm; $\delta_B = 144.1$ ppm with $^1J(\mathrm{Rh,P_A}) = 247$, $^1J(\mathrm{Rh,P_B}) = 246$, and $^2J(\mathrm{A,B}) = 246$ Hz). When the activation of **7** with CO/H$_2$ was repeated in the presence of 1-hexene, the same rhodium carbonyl intermediates as those formed in the absence of olefin were observed. At the end of these experiments, aldehydes had formed with a l/b ratio of 3. Thus, the proportion of linear aldehyde here is considerably lower than that obtained with complex **6**. The relatively low linear selectivity observed here is in accord with the observation that unlike diphosphite **2**, ligand **4** shows a marked tendency to decoordinate, which would result in unsaturated and, therefore, unselective rhodium species.[39]

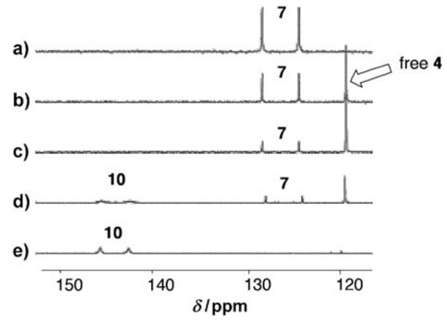
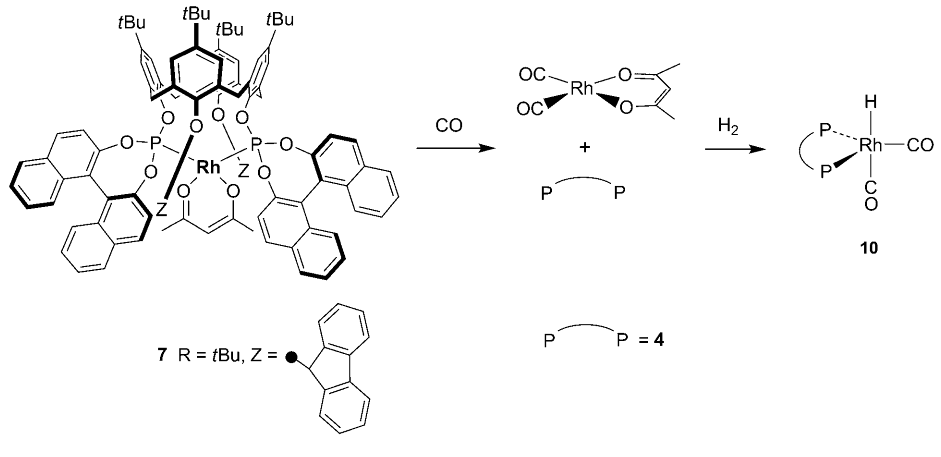


Figure 5. ^{31}P{^{1}H} NMR (sapphire tube, [D$_8$]toluene, 81.01 MHz) spectra of fluorenyl complex **7** under CO (7 bar) and CO/H$_2$ (1:2; 21 bar). a) Compound **7** only; b) **7**+CO; c) **7**+CO/H$_2$, RT; d) **7**+CO/H$_2$, 50 °C; e) **7**+CO/H$_2$, 60 °C.



Scheme 4. Activation of fluorenyl complex **7** with CO and H$_2$.

Conclusion

The Rh(acac) complex containing benzyl-substituted calix-diphosphite **2** exclusively forms the trigonal bipyramidal hydrido carbonyl complex [RhH(CO)$_2$(**2**)], in which both phosphorus atoms occupy equatorial coordination sites, under CO/H$_2$ at 50 °C. This particular configuration, which results in an effective confinement of the metal in a cleft formed by two symmetrical naphthyl units, certainly contributes to a large extent to the high linear aldehyde selectivity observed. However, this result does not allow one to quantify the contribution of the pocket effect arising from the presence of the calixarene Z substituents, which helps to create a tight envelope about the metal and favours linear aldehyde selectivity. An equatorial–equatorial configuration was also observed in complex **10**, which was formed under CO/H$_2$ from rhodium acac complex **7** based on ligand **4**, but the latter ligand turned out to be a poorer chelating ligand because temporary decoordination was observed when complex **7** was treated with CO. The latter observation may account for the weaker regioselectivity obtained with this ligand in styrene hydroformylation. Overall, this study gives a good understanding of the way hemispherical diphosphites may operate for controlling regioselectivity in the hydroformylation of olefins.

Experimental Section

All samples were prepared in dry solvents and under nitrogen. Ligands **2** and **4** and complexes **6** and **7** were obtained according to previously reported synthetic procedures.[18,19] HP NMR spectroscopic measurements were carried out by using a Bruker Avance II 200 spectrometer operating at 200.13 MHz (^{1}H NMR) or 81.01 MHz (^{31}P{^{1}H} NMR). For these experiments, a 10 mm o.d. sapphire tube (Saphikon, Milford, NH, USA) and a titanium high-pressure charging head (ICCOM-CNR, Sesto-Fiorentino, Italy) were used.[40] HP-IR experiments were performed in a high-pressure IR cell (ICCOM-CNR) consisting of a 75 mL autoclave equipped with ZnS windows (4 mm thickness, 8 mm diameter, optical path length 0.2 mm).[34] The catalytic solutions were analyzed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm).

X-ray crystallographic data for 7·hexane·methyl-2-pentane: Crystals of **7**·hexane·methyl-2-pentane were grown from a solution of the complex in dichloromethane/hexane/methyl-2-pentane. $C_{242}H_{226}O_{20}P_4Rh_2$; $M_r = 3787.96$; monoclinic; $P\bar{1}$; $a = 12.7031(4)$, $b = 27.156(1)$, $c = 32.506(1)$ Å; $\beta = 97.267(3)$; $V = 11123.4(6)$ Å^3; $Z = 2$; $\rho_{\text{calcd}} = 1.131$ mg m^{-3}; $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å; $\mu = 0.237$ cm^{-1}; $F(000) = 3984$; $T = 120$ K. Diffraction data were collected by using a NONIUS Kappa CCD diffractometer (graphite Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structure was solved by using SIR-97,[41] which revealed the non-hydrogen atoms of the molecule. The structure was refined with SHELXL97[42] using a riding model for hydrogen atoms; 2437 variables and 37181 observations with $I > 2.0\sigma(I)$. $R = 0.065$, $R_w = 0.155$ and $S_w = 0.784$, $\Delta\rho < 0.889$ e Å^{-3}. A major difficulty in structure determination arose from the tendency of the crystal to desolvate rapidly. The Alert level A revealed in the checkCIF is mainly due to the disordered hexane and methyl-2-pentane solvent molecules. The difficulty in locating the solvent molecules may explain the high value of parameter shift to su ratio and the large voids in the structure. CCDC-718244 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the hydroformylation experiments: The catalytic runs were carried out in a glass-lined, 100 mL stainless steel autoclave that contained a magnetic stirring bar. Typically, the autoclave was charged with a solution of [Rh(acac)L] (0.002 mmol) in toluene (15.0 mL), olefin (5 mmol, corresponding to ≈0.78 mL of 1-octene or 0.57 mL of styrene) and decane (0.50 mL) under nitrogen. Afterwards, the autoclave was flushed twice with syn-gas (CO/H$_2$, 1:1 v/v) and the pressurised with 21 bar of the desired CO/H$_2$ mixture before being heated at 50 °C. The reaction progress was monitored by using the gas consumption. Samples of the catalytic solution were taken regularly and analyzed by using GC.

General procedure for the HP NMR experiments: A solution of [Rh(acac)L] (**6** or **7**) (0.011 mmol) in [D$_8$]toluene (2 mL) was transferred under nitrogen into a 10 mm sapphire tube, which was then introduced into the NMR apparatus for acquisition of the ^{31}P{^{1}H} and ^{1}H NMR spectra at RT. Afterwards, the sapphire tube was removed from the NMR probe and charged with CO (7 bar) at RT, and new ^{31}P{^{1}H} and ^{1}H NMR spectra were acquired. The sapphire tube was again removed from the NMR probe and pressurised with hydrogen (14 bar) before new measurements were carried out at RT. Finally, the solution was gradually heated, first to 40 °C (full conversion was not observed at this temperature), then to 50 °C. At this latter temperature, the reaction progress was monitored until [RhH(CO)$_2$(L)] had quantitatively formed (complexes **9** and **10**). At the end of these experiments, the sapphire tube was gradually cooled to −80 °C to freeze out the dynamics of the hydrido carbonyl complex formed. Complexes **9** and **10** turned out to be stable at RT for several days, as verified by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. The above sequence of experiments was repeated in the presence of 1-hexene (200 μL, 1.59 mmol), including heating for 1 h at 50 °C. At the end of this experiment, the NMR probe was cooled to RT, the gas was vented from the sapphire tube and the solution was subjected to GC analysis.

General procedure for the HP-IR experiments: [Rh(acac)(L)] (**6** or **7**) (0.024 mmol) was dissolved in dichloromethane (26 mL) before being transferred to the high-pressure IR cell under nitrogen. The IR cell was pressurized at RT with CO (7 bar) and then introduced into the spectrometer. The spectrum was then run. After measurement, the IR cell was removed from the spectrometer, and charged with hydrogen (14 bar) at RT, then reintroduced into the spectrometer for a new measurement. The IR cell was then heated stepwise up to 50 °C (10 °C intervals) and maintained at this temperature for 1 h. At each temperature an IR spectrum was acquired. On reaching 50 °C, IR spectra were acquired at time intervals of 20 min.

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