Rhodium-Catalyzed Hydroformylation and Deuterioformylation with Pyrrolyl-Based Phosphorus Amidite Ligands: Influence of Electronic Ligand Properties

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The influence of electronic ligand properties on the catalyst performance in the rhodium-catalyzed hydroformylation of alkenes has been investigated. Two bidentate phosphorus amidite and phosphinite ligands have been synthesized: 1,1′-biphenyl-2,2′-diyl-bis(dipyrrolylphosphoramidite) (**3**) and 1,1′-biphenyl-2,2′-diyloxy-bis(diphenylphosphinite) (**4**). Their monodentate analogues have also been studied: phenyldipyrrolylphosphoramidite (**1**) and phenyl diphenylphosphinite (**2**). These two sets of ligands have very similar steric properties but the amidites are much stronger π-acceptor ligands. Spectroscopic studies showed that under hydroformylation reaction conditions the monodentate ligands **1** and **2** form mixtures of $HRhL_2(CO)_2$ and $HRhL_3(CO)$ complexes depending on the ligand and rhodium concentrations and the carbon monoxide pressure. Depending on the reaction conditions, the bidentate ligands **3** and **4** form mixtures of $HRh(L\cap L)(CO)_2$ and $HRh(L\cap L)(L\cap L')(CO)$, where L∩L′ functions as a monodentate. All ligands have been tested in the hydroformylation reaction of oct-1-ene. A high π-acidity of the ligand resulted in a high rate of hydroformylation. The monodentate ligands **1** and **2** showed moderate selectivity for the linear aldehyde. The catalyst formed with the bidentate phosphorus amidite ligand **3** revealed high regioselectivity for the linear aldehyde (ratio l/b = ∼100) at a high rate together with a moderate selectivity for isomerization (∼7%). Deuterioformylation experiments of 1-hexene showed that the hydride (deuteride) migration is reversible in the hydroformylation system formed by **3**. Surprisingly, both the linear rhodium−alkyl and the branched rhodium−alkyl complex undergo β-hydride elimination. Furthermore, the 2-hexylrhodium intermediate regenerates more often monodeuterated 1-hexene than 2-hexene. The rhodium hydride species formed this way reacts relatively slowly with the excess of D_2 and as a result large amounts of monodeuterated heptanal (40% D_1 vs 60% D_2) and monodeuterated 1-hexene are formed. At higher conversions the latter gives trisdeuterated heptanal as well as bisdeuterated heptanal.

Introduction

One of the key issues in hydroformylation research is the development of new ligands to obtain highly active and selective catalysts.[1−5] Attention has been devoted to the steric and electronic ligand properties and, for bidentate ligands, the bite angle of the ligands.[6−12] Many examples of modified phosphine ligands are known in the literature.[1,8,10] These ligands sometimes form very selective catalysts although the activity in the hydroformylation reaction is often moderate. Many examples of phosphite ligands are known that form active hydroformylation catalysts,[1] but these ligands

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(1) See for references about phosphorus ligand modified hydroformylation the following books and reviews and references herein: (a) van Leeuwen, P. W. N. M.; Casey, C. P.; Whiteker, G. T. *Rhodium Catalysed Hydroformylation*; van Leeuwen, P. W. N. M., Claver, C., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000; Chapter 4. (b) Agbossou, F.; Carpentier, J. F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485. (c) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17.

(2) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 63.

(3) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A., Jr.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.

(4) van der Veen, L. A.; Boele, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616.

(5) (a) van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1983**, *258*, 343. (b) Jongsma, T.; Challa, G.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1991**, *421*, 121. (c) Van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; Van den Aardweg, F.; Van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1096. (d) Van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34. (e) Magee, M. P.; Luo, W.; Hersh, W. H. *Organometallics* **2002**, *21*, 362. (f) Breit, B.; Winde, R.; Mackewitz, T.; Paciello, R.; Harms, K. *Chem. Eur. J.* **2001**, *7*, 3106. (g) Jackstell, R.; Klein, H.; Beller, M.; Wiese, K.-D.; Rottger, D. *Eur. J. Org. Chem.* **2001**, *20*, 3871. (h) Breit, B. *Chem. Commun.* **1996**, 2071.

(6) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19.

(7) Moser, W. R.; Papile, C. J.; Brannon, D. A.; Duwell, R. A. *J. Mol. Catal.* **1987**, *41*, 271.

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introduce less steric hindrance close to the rhodium center compared to phosphines, which can lead to moderate selectivity for the linear aldehyde. Low selectivity but extremely high rates can be obtained by using bulky monophosphite ligands.[5a−d] In recent years especially ligands that are good electron acceptors have been found to be effective ligands.[5e−g] Bulky bidentate phosphites can give high selectivity to linear aldehydes, but these catalysts are less active than bulky monophosphites.[13] Phosphorus amide ligands introduce more steric bulk close to the phosphorus atom compared to the electron-withdrawing phosphites because of the high degree of substitution of nitrogen compared to oxygen. For dialkylamido phosphorus ligands the χ-values are typically low, but when suitably substituted the χ-values[14] of phosphorus amidites can be in the same high range as those of phosphites.[5,15] Therefore, a suitable combination of steric and electronic properties will result in crowded, electron-poor catalysts, which might increase both the activity and selectivity of the hydroformylation catalyst. In recent years a few examples of π-acidic phosphorus amides as ligands in the hydroformylation reaction have been published.[5,16−20] The results obtained with these ligands showed improved activity compared to phosphine systems and improved selectivity compared to phosphite systems. Moloy and co-workers found that pyrrolyl substituents on the phosphorus atom lead to highly π-acidic phosphorus ligands.[15] Ziólkowski and Beller and co-workers investigated the rhodium-catalyzed hydroformylation reaction using several monodentate *N*-pyrrolylphosphine ligands.[5g,17] Here we report on novel monodentate and bidentate phosphorus amidite ligands that contain two pyrrolyl substituents (**1**, **3**). The performance of the hydroformylation catalyst based on these ligands will be compared to that of similar diphenyl-substituted phosphinite ligands (**2**, **4**). Substitution of the phenyl substituent for a pyrrolyl substituent has a large influence on the π-acidity of the ligand. By using these ligands (**1**−**4**), the electronic effect on the catalyst performance can be investigated with a minimal change in steric influences. The electronic properties of the ligands have been determined by comparison of the IR stretching frequency of the carbonyl ligand in *trans*-RhCl(CO)L_2 (L = **1**, **2**). The solution structures of the rhodium complexes formed under hydroformylation conditions were studied and these complexes were tested in the hydroformylation reaction of alkenes. The reaction mechanism was studied with use of ligand **3** in the deuterioformylation of 1-hexene.

Scheme 1. Monodentate and Bidentate Phosphorus Amidite and Phosphinite Ligand Structures

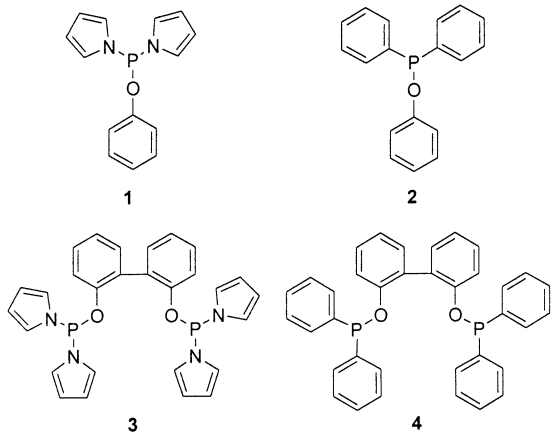


Table 1. IR Frequencies of the Carbonyl Ligands of Various RhCl(CO)L_2

ligand	ν_{CO} (cm^{-1})[a]
PPh_3	1978[b]
$Ph_2P(OPh)$ (**2**)	1991
$(pyrrolyl)_2PPh$	2007[c]
$P(OPh)_3$	2016[b]
$(pyrrolyl)_2POPh$ (**1**)	2019
$P(pyrrolyl)_3$	2024[c]

[a] Measured in CH_2Cl_2. [b] See refs 26 and 27. [c] See ref 16.

Results and Discussion

Synthesis and Determination of the Electronic Ligand Properties. Phosphorus ligands (**1**−**4**) were prepared by the reaction of either chlorodipyrrolylphosphine or chlorodiphenylphosphine and the corresponding alcohol in the presence of a base. The ligands were purified by crystallization, washing, or column chromatography and stored under an inert atmosphere, although they are relatively stable toward water and oxygen. To investigate the electronic properties of these phosphorus amidite and phosphinite ligands, *trans*-RhCl(CO)(**1**)$_2$ (**5**) and *trans*-RhCl(CO)(**2**)$_2$ (**6**) were synthesized. The carbonyl frequency in the IR spectrum is a measure of the π-acidity of ligands **1**−**4**.[15,23] The IR frequencies of the carbonyl ligands of the *trans*-RhCl(CO)L_2 (L = **1**, **2**) complexes are presented in Table 1. The position of the carbonyl frequency of *trans*-RhCl(CO)(**1**)$_2$ (**5**) in the IR spectrum shows that the electronic character of ligand **1** is similar to that of triphenyl phosphite. Comparison of the carbonyl frequency of *trans*-RhCl(CO)(**2**)$_2$ (**6**) with that of the *trans*-RhCl(CO)-

(8) van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1999**, *18*, 4765.
(9) Cuny, G. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 11616.
(10) Wink, D. J.; Kwok, T. J.; Yee, A. *Inorg. Chem.* **1990**, *29*, 5006.
(11) Billig, E.; Abatjoglou A. G.; Bryant, D. R., U.S. Patent 4,668,-651; European Patent. Application 213,639, 1987 (to Union Carbide); *Chem. Abstr.* **1987**, *107*, 7392.
(12) Billig, E.; Abatjoglou, A. G.; Bryant, D. R.; Murray, R. E.; Maher, J. M., U.S. Patent 4,599,206, 1986 (to Union Carbide); *Chem. Abstr.* **1988**, *109*, 233177.
(13) (a) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, F.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835. (b) Billig, E.; Abatjoglou, A. G.; Bryant, D. R.; Murray, R. E.; Maher, J. M., U.S. Patent 4,599,206, 1986 (to Union Carbide); *Chem. Abstr.* **1988**, *109*, 233177.
(14) Moasser, B.; Gladfelter, W. L.; Roe, D. C. *Organometallics* **1995**, *14*, 3832.
(15) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953
(16) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696
(17) van der Slot, S. C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Fraanje, J.; Goubitz, K.; Lutz, M.; Spek, A. L. *Organometallics* **2000**, *19*, 2504.
(18) van Leeuwen, P. W. N. M.; Roobeek, C. F. *Tetrahedron* **1981**, *37*, 1973.
(19) Franció, G.; Faraone, F.; Leitner, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1428.
(20) Clarke, M. L.; Cole-Hamilton, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Chem. Commun.* **2000**, 2065.
(21) Li Wu, M.; Desmond, M. J.; Drago, R. S. *Inorg. Chem.* **1979**, *18*, 679.
(22) Trzeciak, A. M.; Glowiak, T.; Grybek, R.; Ziólkowski, J. *J. Chem. Soc., Dalton Trans.* **1997**, 1831.
(23) Naili, S.; Mortreux, A.; Agbossou, F. *Tetrahedron Asymmetry* **1998**, 3421.

Table 2. Spectroscopic Data of Several $HRh(L)_x(CO)_{4-x}$ Complexes ($x = 2, 3$)

complex	$\delta(^1H)$ (ppm)[a]	$\delta(^{31}P)$ (ppm)[a]	J_{HP} (Hz)	J_{HRh} (Hz)	J_{RhP} (Hz)	ν_{CO} (cm^{-1})[b]
$HRh(\mathbf{1})_2(CO)_2$	−10.1 (br)	137	n.d.	n.d.	219	2076, 2024
$HRh(\mathbf{2})_2(CO)_2$	−9.5 (br)	145	n.d.	n.d.	165	2045, 1970
$HRh(PPh_3)_2(CO)_2$[c]		37			139	2042, 1981
$HRh(P(OPh)_3)_2(CO)_2$[c]						2070, 2018
$HRh(\mathbf{1})_3(CO)$	−9.8 (dq)	134	7	3	217	2063
$HRh(\mathbf{2})_3(CO)$	−9.4 (dq)	142	13	3	169	1943
$HRh(PPh_3)_3(CO)$[d]	−9.1 (m)	47	n.d.	n.d.	133	2040[e]
$HRh(P(pyrrolyl)_3)_3(CO)$[d]	−9.1 (dq)	109	8	3	211	2079[e]
$HRh(P(OPh)_3)_3(CO)$[d]	−10.9 (dq)	141	3	3	240	2060[e]

[a] Measured in toluene-d_8 or benzene-d_6, dq = double quartet. [b] Measured in cyclohexane. [c] See ref 29. [d] See ref 21. [e] Measured in KBr.

$(PPh_3)_2$ complex shows that the electron-donating character of ligand **2** is in the same range as that of triphenylphosphine. Comparison of the carbonyl frequencies of *trans*-RhCl(CO)(**1**)$_2$ (**5**) and *trans*-RhCl(CO)-(**2**)$_2$ (**6**) shows that ligand **1** is a stronger π-acid than ligand **2**, whereas ligands **1** and **2** will have comparable steric ligand properties, **1** being slightly smaller than **2**. The electronic properties of the bidentate ligands **3** and **4** are very similar to those of ligands **1** and **2**, respectively, because of the similarity of the substituents used.

Catalyst Characterization Studies. The structures of the complexes formed under hydroformylation conditions were studied with high-pressure (HP) NMR and IR spectroscopy. The catalyst was formed by using Rh(acac)$(CO)_2$ in the presence of various ligand concentrations at 20 bar of CO/H_2 (1/1). The spectroscopic data of the hydride complexes observed are presented in Table 2. The monodentate ligands gave two different complexes under syn-gas pressure: $HRhL_2(CO)_2$ and $HRhL_3(CO)$. The ratio between these two complexes depends on the concentrations of rhodium, ligand, and carbon monoxide. Higher rhodium and ligand concentrations resulted in a larger proportion of $HRhL_3(CO)$. The presence of two complexes is not unusual for these relatively small monodentate ligands; similar results have been obtained for triphenylphosphine and triphenyl phosphite.[24,25]

Rhodium complexes of the form $HRhL_x(CO)_{4-x}$ (x = 1, 2, 3) generally have a (distorted) trigonal bipyramidal structure. Detailed NMR and IR studies have shown that the hydride ligand coordinates at an apical position of the bipyramid. The phosphorus atoms can coordinate at either the equatorial positions or the remaining apical position. The coordination mode of the phosphorus ligands can be derived from the magnitude of the J_{PH} NMR coupling constant as has been shown in many catalyst characterization studies.[3,4,31]

The hydride resonances observed for the complexes containing two monodentate ligands ($HRhL_2(CO)_2$, L = **1**, **2**) are broad (see Table 2). The resonance remained broad when the sample was cooled to −70 °C. Therefore the structure of these complexes could not be determined by using the J_{PH} and J_{RhH} coupling constants. The IR spectra of these complexes showed two (terminal) carbonyl frequencies, indicating that only one isomer is present (either **ee** or **ea**). While by NMR spectroscopy often fast equilibration between **ee** and **ea** isomers cannot be halted, two sets of two carbonyl frequencies are observed in the IR spectrum when two isomers are present.[8] The positions of the carbonyl frequencies of $HRh(\mathbf{1})_2(CO)_2$ are similar to those observed for the **ee**-coordinated rhodium−bis-triphenyl phosphite complex and the positions of the carbonyl frequencies of $HRh(\mathbf{2})_2(CO)_2$ are comparable to those of the **ee**-coordinated rhodium−bis-triphenylphosphine complex (see Table 2).[25] The J_{RhP} coupling constant of $HRh(\mathbf{1})_2(CO)_2$ was in the same range as those found for similar phosphite ligands in equatorial positions (219 Hz), while the J_{RhP} coupling constant of $HRh(\mathbf{2})_2(CO)_2$ was comparable to those in complexes having arylphosphines in equatorial positions (165 Hz).

Depending on the ligand concentration, a significant amount of $HRhL_3(CO)$ (L = **1**, **2**) was formed under the conditions used for the spectroscopic studies. These hydride complexes have relatively large J_{PH} coupling constants for a pure cis coordination (7 and 13 Hz respectively), indicating a slight distortion of the geometry of the trigonal bipyramidal structure.[26,27] Again, the J_{RhH} coupling constant (3 Hz) and the J_{RhP} coupling constants observed for the rhodium−hydride complexes are in the same range as those found for similar phosphine- or phosphite-containing hydride complexes (Table 2).[21] The positions of carbonyl frequencies observed in the high-pressure IR spectra are consistent with the π-acidity of the ligands.

Analogous to the results observed for the monodentate ligands **1** and **2**, mixtures of two different hydride complexes were found for the bidentate ligands **3** and **4** depending on the ligand and rhodium concentrations and the carbon monoxide pressure. In the NMR experiments ([Rh] = 10 mM), a ligand-to-rhodium ratio of 1 is sufficient to obtain complete conversion to the hydride complex. For the high-pressure IR experiments, lower rhodium concentrations are used and therefore higher ligand concentrations are a prerequisite to obtain complete conversion to the rhodium−hydride complex. With use of ligand **3** in these experiments, a ligand-to-rhodium ratio of 1.5 is enough, but for ligand **4** a ligand-to-rhodium ratio of 3 is necessary for complete conversion of the rhodium precursor (Rh(acac)$(CO)_2$) to the

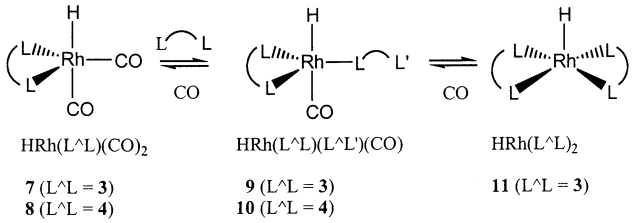
(24) Breit, B. *J. Mol. Catal.* **1999**, *143*, 143.
(25) Pottier, Y.; Mortreux, A.; Petit, F. *J. Organomet. Chem.* **1989**, *370*, 333.
(26) Haar, C. M.; Huang, J.; Nolan, S. P.; Petersen, J. L. *Organometallics* **1998**, *17*, 5018.
(27) Li Wu, M.; Desmond, M. J.; Drago, R. S. *Inorg. Chem.* **1979**, *18*, 679.
(28) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133.
(29) Diéguez, M.; Claver, C.; Masdeu-Bultó, A. M.; Ruiz, A.; van Leeuwen, P. W. N. M.; Schoemaker, G. C. *Organometallics* **1999**, *18*, 2107.
(30) Buisman, G. J. H.; Vos, E. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1995**, 409.
(31) Nettekoven, U.; Kamer, P. C. J.; Wildhalm, M.; van Leeuwen, P. W. N. M. *Organometallics* **2000**, *19*, 4596.

Table 3. Spectroscopic Data of $HRh(L)_x(CO)_{4-x}$ Complexes (x = 2, 3, and 4)

Complex	$\delta(^1H)$ (ppm)[a]	$\delta(^{31}P)$ (ppm)[a]	J_{HP} (Hz)	J_{HRh} (Hz)	J_{RhP} (Hz)	ν_{CO} (cm^{-1})[b]
HRh(**3**)$(CO)_2$ (**7**)	−10.7 (br)	138	n.d.	n.d.	218	2078, 2026
DRh(**3**)$(CO)_2$						2067, 2020
HRh(**4**)$(CO)_2$ (**8**)	−9.2 (dt)	149	5	4	166	2055, 1996
HRh(**3**)$_2$(CO) (**9**)	−10.5 (br q)[c]	135 (m) 111 (s)[d]	6	≤3	n.d.[e]	2069
DRh(**3**)$_2$(CO)						2041
HRh(**4**)$_2$(CO) (**10**)	−9.6 (dq)[c]	153 (m) 115 (s)[d]	13	3	n.d.[e]	2036
HRh(**3**)$_2$ (**11**)	−10.9 (dqui)	129	36	6	203	
	−10.3 (dqui)	130	36	6	203	

[a] Measured in toluene-d_8 or benzene-d_6. [b] Measured in cyclohexane. [c] All phosphorus atoms have similar J_{HP} coupling constants. q = quartet, qui = quintet. [d] This chemical shift belongs to the noncoordinated phosphorus atom of (L∩L′). [e] Not determined.

Scheme 2. Geometry of the Hydride Complexes Formed with the Bidentate Ligands



hydride complex.The spectroscopic data of the observed hydride complexes with **3** and **4** are presented in Table 3. The hydride resonance of HRh(**3**)$(CO)_2$ was broad and remained broad after cooling to −60 °C and the values of the J_{RhH} and J_{PH} coupling constants remained unresolved. The NMR data do not lead to detailed information about the trigonal bipyramidal structure. The IR spectrum obtained from the NMR sample of HRh(**3**)$(CO)_2$ showed two absorption bands for the carbonyl ligands at 2078 and 2026 cm^{-1}. In view of the number and position of the carbonyl frequencies, we conclude that only the **ee** isomer is present.[4] The hydride resonance of HRh(**4**)$(CO)_2$ was sharp and all J_{XH} coupling constants (X = ^{103}Rh or ^{31}P) were assigned after selective decoupling of the phosphorus resonance of the hydride complex. The J_{RhH} and J_{PH} coupling constants of 4 and 5 Hz, respectively, are indicative of coordination of both phosphorus atoms in the equatorial plane of the trigonal bipyramid. The presence of two carbonyl absorption bands in the IR spectrum obtained from the NMR sample of HRh(**4**)$(CO)_2$ indicates that the **ee** isomer is the only isomer present. The positions of the phosphorus resonances and J_{RhP} coupling constants of HRh(**3**)$(CO)_2$ and HRh(**4**)$(CO)_2$ are similar to those found for the monodentate ligands. As mentioned above, for both ligands **3** and **4** ligand-to-rhodium ratios higher than one are required to reach complete conversion to the rhodium−hydride complexes in the (high-pressure) IR experiments performed under hydroformylation reaction conditions ([**3**] = ∼1−12 mM). The high-pressure IR spectra with L/Rh ≥ 1.5 showed a third carbonyl frequency in the terminal CO region. When the high-pressure NMR experiments were performed with L/Rh ≥ 1.5, additional hydride resonances were observed. The multiplicity of these hydride resonances (double quartets) indicates that three phosphorus atoms are coordinated to the rhodium center. The ^{31}P NMR spectra showed complex multiplets in the region where coordinated phosphorus atoms resonate together with an additional singlet, close to the resonance of the free phosphorus ligand. From these results we conclude that in the presence of more than 1 equiv of ligand per rhodium some of the rhodium−hydride complexes HRh(L∩L)$(CO)_2$ are converted to hydride complexes of the form HRh(L∩L)(L∩L′)(CO). One of the bidentate ligands, denoted L∩L′, coordinates in a monodentate fashion.[32] The geometry of this type of rhodium−hydride complexes is depicted in Scheme 2. High-pressure IR studies showed that the concentrations of HRh(L∩L)(L∩L′)(CO) and HRh(L∩L)$(CO)_2$ present in solution depend on the ligand and rhodium concentrations and the carbon monoxide pressure. HRh(L∩L)$(CO)_2$ and HRh(L∩L)(L∩L′)(CO) were always observed together, except when only 1 equiv of L∩L was used, which led to formation of the former complex only. Both HRh(**3**)$_2$(CO) (**9**) and HRh(**4**)$_2$(CO) (**10**) have relatively large J_{HP} coupling constants (6 and 13 Hz, respectively), indicating a distortion of the trigonal bipyramidal structure.[13,30] The complex multiplet observed for the phosphorus resonances of these complexes indicates that the phosphorus atoms are inequivalent on the NMR time scale.

We synthesized HRh(**3**)$_2$ (**11**) by the reaction of Rh(acac)$(CO)_2$ and 2 equiv of ligand **3** under hydrogen pressure. The spectroscopic data of this complex are depicted in Table 3. Two hydride resonances, double quintets, were observed in the ^{1}H NMR spectrum, and two doublets were observed in the ^{31}P NMR spectrum having identical J_{RhH}, J_{PH}, and J_{RhP} coupling constants, indicating that two isomers of **11** are present in solution. The quintet structures indicate fast movement of the hydride atom with respect to the phosphorus atoms. The two isomers are probably two diastereomers resulting from the atropisomerism of the diphenol backbone. Addition of carbon monoxide (1 bar) to a solution of **11** results in complete conversion to **10**. From this we conclude that under hydroformylation reaction conditions complex **11** is totally absent.

When we used a L/Rh ≥ 2 for ligand **4** a third hydride resonance (multiplet) at −9.7 ppm was observed in the ^{1}H NMR spectrum. In the ^{31}P NMR spectrum additional resonances appeared in the region of the coordinated phosphorus ligand. Selective decoupling of the phosphorus resonance at 153 ppm showed a doublet in the hydride region, having a J_{RhH} coupling constant of 3 Hz. The IR spectrum did not show any additional terminal or bridging carbonyl bands. These results suggest that the structure of the additional hydride complex might be formulated as HRh(**4**)$_2$, similar to HRh(**3**)$_2$ (vide supra, **11**). The ratio between HRh(**4**)$_2$(CO) (**10**) and this

(32) Hughes, R. O.; Young, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 6636.

Table 4. Results of the Hydroformylation of 1-Octene with Ligands 1, and 2[a]

ligand	L/Rh	time (h)	conversion (%)	l/b	TOF[b]	linear (%)	2-octenes (%)
1	5	0.084	35	3.1	10×10^3	61	18
	10	0.074	32	3.7	12×10^3	68	14
	50	0.26	30	3.5	4×10^3	66	16
2	5	5.1	3	2.3	15	50	27
	5[c]	2.8	32	2.6	n.d.[d]	56	22
	50[c]	2.0	35	2.3	219	68	2

[a] Conditions used: $T = 80$ °C, [Rh] = 0.2 mM, $p_{CO} = p_{H_2} = 10$ bar, [1-octene] = 0.64 M in toluene. [b] Initial TOF in mol aldehyde (mol Rh·h)$^{-1}$. [c] [Rh] = 0.5 mM. [d] The TOF could not be determined because of incomplete catalyst formation.

Table 5. Results of the Hydroformylation of 1-Octene with Ligands 3 and 4[a]

ligand	L/Rh	tim (h)	conversion (%)	l/b	TOF[b]	linear (%)	2-octenes (%)
3	1.5	0.10	33	107	10×10^3	86	11
	3	0.054	20	110	10×10^3	92	7
	10	0.27	46	98	5×10^3	86	13
	50	0.55	23	104	1×10^3	85	15
4[c]	3	1.5	24	5	424	80	5
	5	2.5	20	9	246	85	5
	50	3.0	21	6	240	83	3

[a] Conditions used: $T = 80$ °C, [Rh] = 0.2 mM, $p_{CO} = p_{H_2} = 10$ bar, [1-octene] = 0.64 M in toluene. [b] Initial TOF in mol aldehyde (mol Rh·h)$^{-1}$. [c] 3 h instead of 1 h catalyst formation time was used.

additional hydride complex remained constant (1:1) upon increasing the ligand concentration and removing carbon monoxide. Attempts to isolate HRh(**4**)$_2$ were unsuccessful.

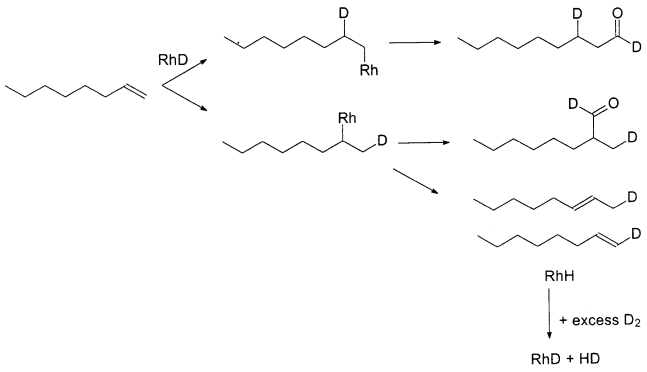
Hydroformylation of Alkenes. Ligands **1**−**4** were applied in the rhodium-catalyzed hydroformylation of 1-octene. The catalysts were prepared in situ from Rh(acac)(CO)$_2$, the required amount of ligand, CO, and H_2 at 80 °C. As already mentioned in the previous section, several rhodium−hydride complexes can be formed under hydroformylation reaction conditions depending on the ligand and rhodium concentrations and the carbon monoxide pressure. The ligand and rhodium concentrations used in catalysis are much lower than those used in the NMR spectroscopic experiments. Therefore, the proportion of HRhL$_x$(CO)$_2$ ($x = 2$ for L = **1**, **2** and $x = 1$ for L = **3**, **4**) in the reaction mixture used in catalysis is significantly higher than that used in the spectroscopic experiments. The hydroformylation reaction has been performed with several ligand-to-rhodium ratios to investigate the effect of the ligand concentration on the catalyst activity and selectivity.

The results of the hydroformylation reaction of 1-octene for systems based on **1** and **2** are presented in Table 4. The activity and selectivity obtained with ligand **1** are in the range of those observed with bulky phosphite ligands.[5] At the rhodium concentration used, the ligand-to-rhodium ratio of 5 is the minimum amount of ligand needed; the use of lower L/Rh ratios resulted in a large amount of 2-octene and we observed that the catalyst activity increased during the reaction. These results point to incomplete catalyst formation with L/Rh < 5. Increasing the ligand-to-rhodium ratio from 10 to 50 results in a large decrease of the activity. This negative dependency of the reaction rate on ligand concentration can be explained by the formation of less reactive complexes.[29,33−35]

Ligand **2** was tested in the hydroformylation reaction by using the same reaction conditions as ligand **1**. With use of these low ligand and rhodium concentrations, the catalyst based on **2** was hardly active and a high percentage of 2-octenes was formed (Table 4). The large amount of 2-octenes indicates that by using low phosphinite ligand concentrations small amounts of Rh(acac)(CO)$_2$ are present in solution that can be converted to HRh(CO)$_4$, which is a good isomerization catalyst. To ensure complete catalyst formation, we increased the rhodium and ligand concentrations 2.5-fold ([Rh] = 0.5 mM). In this instance the catalyst did not show any activity during the first 2.5 h. After 2.5 h, the reaction started, indicating that the catalyst formation time of 1 h was not enough to obtain complete conversion of the rhodium precursor. Again, a high percentage of 2-octenes was found with use of these higher concentrations. When we used a catalyst formation time of 3 h instead of 1 h, the catalyst activity decreased, indicating premature decomposition of the catalyst. By increasing the ligand-to-rhodium ratio to 50 and using 1-h catalyst formation time, the catalyst activity did not change during the run and 2-octene formation was low, thus catalyst formation is complete with high ligand and rhodium concentrations.The hydroformylation reaction of 1-octene with the bidentate ligands **3** and **4** was also performed at various ligand-to-rhodium ratios. The results obtained are depicted in Table 5. A ligand-to-rhodium ratio of 1.5 was the minimum value for ligand **3** with this low rhodium concentration (0.2 mM). Use of smaller amounts of ligand resulted in a high percentage of 2-octenes and low hydroformylation activity, indicating incomplete catalyst formation. The catalyst formed with pyrrolyl-based ligand **3** was highly active in the hydroformylation reaction and a very high regioselectivity for the linear aldehyde was observed, linear/branched ratios typically being on the order of 100. The percentage of 2-octenes formed during the reaction (±11%) is rather high, which results in a moderate overall catalyst selectivity (±85%). The catalyst is inactive for the hydroformylaton of 2-octene and thus the linearity remains very high even at prolonged reaction times. The combination of both high hydroformylation and isomerization activity is reminiscent of the results observed for bulky (bidentate) phosphite ligands.[13] This similarity can be explained by the electron-withdrawing character of these phosphorus amidite ligands. Generally, electron-withdrawing phosphorus ligands show an increase of the reaction rate as a result of the facile carbon monoxide dissociation and stronger alkene coordination.[4,7,36] The linearity observed with this bidentate phosphorus amidite ligand (**3**) is much higher than that observed for bidentate phosphite ligands having similar backbones.[13] A decrease of the hydroformylation activity together with a constant selectivity was observed when the concentration of ligand **3** was increased. The decrease in hydroformylation activity is probably caused by coordination of

(33) Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 2753.
(34) Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660.
(35) Hjortkjaer, J.; Toromanova-Petrova, P. *J. Mol. Catal.* **1982**, *14*, 19.
(36) Jongsma, T.; Challa, G.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1991**, *421*, 121.

Scheme 3. Deuterioformylation Involving Isomerization and Fast Exchange of RhH and Excess D_2



additional ligand resulting in an increasing amount of hydride complex **9** as was shown in the spectroscopic experiments.

When ligand **4** is used in the hydroformylation reaction of 1-octene, at least 3 equiv of ligand and 3 h of catalyst formation time are required to obtain complete conversion of the rhodium precursor to the rhodium−hydride complex. A longer catalyst formation time (5 h) led to a decrease of the activity, indicating some catalyst decomposition. The use of higher rhodium and ligand concentrations did not have any effect. The activity and selectivity observed with ligand **4** were moderate and comparable to that observed for phosphine ligands having similar electron-donating properties.[4,37] Comparison of the hydroformylation results of ligands **3** and **4** shows that increasing the electron-withdrawing capacity of the ligand, with only a small change in steric hindrance, results in improved activity and selectivity.

The combination of high activity and high regioselectivity obtained for 1-octene with HRh(**3**)$(CO)_2$ prompted us to test this catalyst also in the hydroformylation reaction of styrene. In this experiment the optimal ligand-to-rhodium ratio is 1.5 (at [Rh] = 0.2 mM). With styrene as the substrate at 80 °C, the selectivity for the linear aldehyde found amounted to 46% (l/b = 0.84), which is relatively high for styrene. The turnover frequency of 2800 mol aldehyde (mol Rh·h)$^{-1}$ is high as well, specially when compared to phosphine-based systems (Xantphos: 724 m·m^{-1}·h^{-1}, l/b = 0.88).[4,13]

Deuterioformylation with Ligand 3. The results of the hydroformylation with ligand **3** showed a high selectivity to nonanal (l/b ratio ∼100) and approximately 10% isomerization of 1-octene to 2-octene. The latter is formed via reversible insertion and deinsertion of a 2-octylrhodium species. The question arose whether the formation of linear aldehyde also involved reversible insertion of alkene into the rhodium hydride bond. Deuterioformylation experiments can give detailed information about the reversibility of the first steps in the hydroformylation reaction.[38,39] Casey has shown[38] that the linear aldehyde formed with BISBI under mild conditions of deuterioformylation contains two deuterium labels, one at the aldehyde carbon atom and the other at the β-carbon atom (Scheme 3), which indicates that insertion of 1-alkenes to give 1-alkylrhodium is irreversible.[45] Reversible formation of 2-alkylrhodium species may result in 1-deuterio-2-alkene (or a 1-deuterio-1-alkene) and a rhodium hydride.[39] Thus, after a moderate preference for the linear alkyl in the alkene insertion step, the backward reaction of the 2-alkylrhodium species to alkenes may lead to an overall selectivity for linear aldehyde. In these systems the formation of 2-alkenes is indicative of this type of kinetics, implying a lower intrinsic preference for 1-alkyl formation than the l/b ratio might suggest.

The rhodium hydride formed may either react with a new molecule of 1-alkene, thus giving a monodeuterated aldehyde, or undergo a fast exchange with the excess of D_2 present in the system, regenerating a rhodium deuteride. This situation is outlined in Scheme 3. However, Casey has shown that in the BISBI system insertion to 2-alkylrhodium is indeed reversible, giving 1-deuterio-1-alkene for 75% at 33 °C and 5−6 bar (the remainder forms branched, bisdeuterated aldehyde). The present system contains a ligand that is much more electron poor and the reaction was studied at higher temperatures. Lazzaroni[39] has found that hydroformylation at room temperature is characterized by an irreversible insertion, but he reported that at 100 °C incorporation of deuterium in 1-hexene was observed.

The deuterioformylation with ligand **3** was performed under the same conditions as the hydroformylation experiments of 1-octene (T = 80 °C, [Rh] = 0.2 mM, L/Rh = 1.5, [1-hexene] = 0.81 M, $p_{CO} = p_{D_2}$ = 10 bar). 1-Hexene was used for the deuterioformylation studies to facilitate comparison with literature data of the ^{1}H and ^{2}H NMR spectra.[38] The rate of reaction for the hydroformylation of 1-hexene and the percentage of 2-hexenes formed were similar to those observed for 1-octene. The initial linear-to-branched ratio was very high for 1-hexene, viz. 161. The side product 2-hexene has an extremely low activity for hydroformylation under these conditions and thus the linearity remained high. The aldehyde production was monitored by gas chromatography. The number of deuterium atoms incorporated into 1-hexene, 2-hexene, and heptanal was monitored by gas chromatography/mass spectroscopy. After complete conversion of 1-hexene the deuterium contents at each position in heptanal were determined by ^{2}H NMR spectroscopy. The activity and selectivity for the deuterioformylation of 1-hexene were the same as those of the hydroformylation of 1-octene. The data of the deuterium distribution observed with gas chromatography/mass spectroscopy have been collected in Table 6. The table gives the composition of the system,

(37) Hughes, R. O.; Unruh, J. D. *J. Mol. Catal.* **1981**, *14*, 71.

(38) Casey, P. C.; Petrovich, L. M. *J. Am. Chem. Soc.* **1995**, *117*, 6007.

(39) Lazzaroni, R.; Uccello-Barretta, G.; Benetti, M. *Organometallics* **1989**, *8*, 2323.

(40) The absorption band of C(O)H should be at 1733 cm^{-1} (cyclohexane).

(41) van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 336.

(42) Elsevier, C. J. *J. Mol. Catal.* **1994**, *92*, 285.

(43) Atherton, M. J.; Fawcett, J.; Hill, A. P.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Saunders, G. C.; Stead, R. M. J. *J. Chem. Soc., Dalton Trans.* **1997**, 1137.

(44) Keim, W.; Maas, H. *J. Organomet. Chem.* **1996**, *514*, 271.

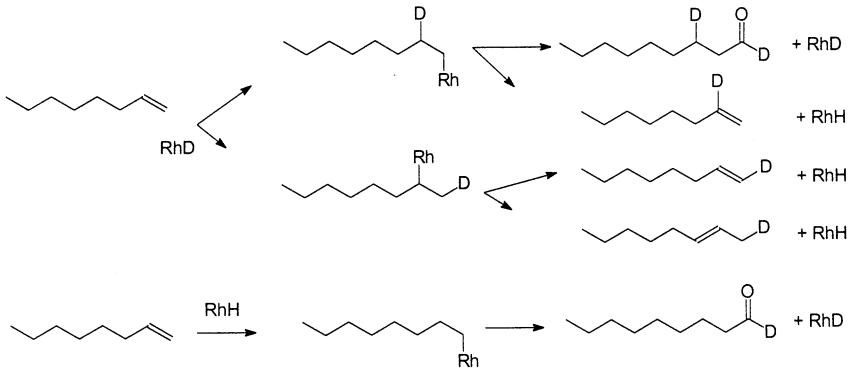
(45) Reversible insertion without alkene−rhodium dissociation would also lead to formation of D_2 aldehydes, but as yet there is no evidence for an irreversible alkene coordination. In fact this latter would mean that alkene complexation is rate determining, but not necessarily regioselectivity determining; kinetic measurements cannot distinguish between these two possibilities.[1a]

Table 6. Deuterium Distribution Observed in the Deuterioformylation of 1-Hexene[a]

sample (conversion, %)	time (s)	l/b ratio	total % 1-hexene	total % heptanal	no. of deuterium atoms, *n*	% 1-hexene D_n	% 2-hexene D_n	% heptanal D_n
1 (10)	85		90	9	0	84	0.5	0.2
					1	5.3	0.4	3.6
					2	1	0.1	5.2
					3	0	0	0
2 (21)	172	161	79	20	0	73	0.6	1.6
					1	5	0.7	7.3
					2	1	0.1	10.0
					3	0	0	1.2
3 (30)	253	132	70	28	0	62.6	0.9	2.6
					1	6.0	0.8	9.6
					2	1.0	0.1	13.7
					3	0.2	0	2.1
					4	0.2	0	0
4 (35)	326	133	65	33	0	54.3	0.9	3.7
					1	9.1	0.9	11.4
					2	1.4	0.2	15.3
					3	0.13	0	2.6
					4	0.07	0	0
5 (42)	409	128	58	40	0	46.7	1.1	3.9
					1	9.3	1.1	13.3
					2	1.5	0.22	19.3
					3	0.6	0	3.8
					4	0	0	0
6 (100)	7,200	78	0	90	0	0	1.9	6.4
					1	0	2.4	24.2
					2	0	2.8	34.8
					3	0	2.0	17.2
					4	0	0.9	7.3

[a] Conditions used: $T = 80$ °C, [Rh] = 0.2 mM, $p_{CO} = p_{D_2} = 10$ bar, [1-hexene] = 0.81 M, in benzene. Conversion is that of 1-hexene. Data are calibrated for a total of 100% for 1-hexenes, 2-hexenes, and heptanal.

Scheme 4. Deuterioformylation Involving Isomerization and Slow Exchange of RhH and Excess D_2



educt, and products at a range of conversion levels, normalized to mole percent to demonstrate the amount of incorporated deuterium in each component at the respective conversion of 1-hexene. The amounts of the compounds found were corrected for the natural abundance of ^{13}C.

Sample 1, taken after 10% conversion of 1-hexene, shows that 60% of the heptanal formed contains two deuterium atoms (5.2 mol % in Table 6) as one would expect for a deuteriohydroformylation, but 40% contains only one deuterium atom (3.5%). Monodeuterated aldehyde is formed, we propose, by a cycle that starts with rhodium hydride, because in the initial period of the experiment the final step involving D_2 will always deliver one deuterium atom to heptanal. Rhodium hydride is formed via reversible insertion−deinsertion of hexenes as is evidenced by the deuterium-enriched hexenes that were observed. The hydroformylation cycle, started by rhodium hydride and completed by reaction of the acylrhodium species with D_2, thus leads to monodeuterated product. Usually, it is tacitly assumed that the intermediary rhodium-hydride reacts rapidly with the excess of D_2 to regenerate a rhodium−deuteride species (and HD). At low conversion this would have given rise to D_2 aldehydes only. Since this is not the case, the rate of hydroformylation must be higher than (or at least approximately equal to) the rate of H−D exchange between D_2 and RhH. To confirm this surprising outcome, we decided to measure this rate independently. Indeed, at the initial 1-hexene concentration, hydroformylation (and insertion−deinsertion) is about 10 times faster than H−D exchange (vide infra, in separate section) with this catalyst. At 10% conversion of 1-hexene (to heptanal and 2-hexene, sample 1) we see indeed incorporation of deuterium in hexenes. The commonly accepted mechanism would suggest that deuterated 2-hexene would be produced. The amount of deuterium "lacking" in heptanal (3.5 mol, normalized to 100) was not recovered as D_1-2-hexene, wich contained only 0.7 equiv of deuterium, but it was recovered in 1-hexene (5.3 mol %). Thus, reversible formation of 1-hexene is the main pathway for the deinsertion

(Scheme 4). Interestingly, for BISBI the observation was the same qualitatively, but little attention was paid to this, because the absolute numbers were so much smaller.[38]

Also in samples 2−5 it is seen that the proportion of D_1-heptanal is much higher than that of D_1-2-hexene and that more deuterated 1-hexene is formed. Monodeuterated 1-hexene can form from reversible insertion via 1-hexylrhodium and reversible insertion via 2-hexylrhodium. Reversible insertion via 1-hexylrhodium, which is peculiar in that usually 1-alkylrhodium formation is regarded as irreversible, leads eventually to an extra deuterium in the β-position of heptanal formed. Reversible insertion of 1-hexene via 2-hexylrhodium leads, after hydroformylation, eventually to heptanal containing deuterium in the α-position. Reversible insertion of 1-hexene via 2-hexylrhodium is also peculiar, since usually the intermediate 2-hexylrhodium is thought to lead to 2-hexene, the isomerization product.[1a] Since we have not established the position of deuterium in D_1-1-hexene, at this point we can only conclude that a high proportion of deuterated 1-hexene is formed via reversible insertion, either route being unexpected under these conditions. Scheme 4 outlines the routes. At least 40% of the insertion is reversible. Note that rhodium hydride will also participate in nonproductive reversible insertion−deinsertion reactions.

At higher conversions D_3-heptanal is formed from D_1-1-hexenes. The ratios D_1:D_2:D_3 for the increments of heptanal formed from the isotopic mixture of hexenes present closely follow the preference of 40:60 as found in sample 1, expressing the ratio of the rates and concentrations of rhodium−hydride and rhodium−deuteride.

The proportion of D_0-heptanal in samples 2−6 is somewhat high in view of the small amount of HD that has been formed, which requires further discussion. After 2 h complete conversion was reached and sample 6 was analyzed. From the total deuterium balance we see that, on average, two deuterium atoms have been built into heptanal, as is to be expected more or less since the exchange of rhodium−hydride and D_2 is slow! The residual 2-hexene also contains on average two deuterium atoms, indicating that hexene has participated in more than one reaction sequence. Since we started with approximately 70 mmol of D_2 and 16 mmol of 1-hexene, the resulting 2-hexene contains 3.2 mmol of deuterium and from this we calculate that the final ratio of HD:D_2 is roughly 1:20. At high conversions of 1-hexene the rate of hydroformylation drops and the rate of the RhH/D_2 exchange becomes more important. A large isotope effect, as we have observed before in the deuterioformylation of cyclohexene,[36] may cause a much faster reaction for HD than D_2, which leads to a high proportion of D_0-heptanal.

Hydroformylation of 2-hexene has not been taken into account, as it was shown in separate experiments that the rate of hydroformylation of internal alkenes (2-octene) is several orders of magnitude lower for this catalyst. Thus in the present experiment the formation of 2-hexene should be considered as irreversible as far as heptanal formation is concerned. The enrichment observed for the resulting 2-hexene means that either 1-hexene goes back and forth a couple of times enriching

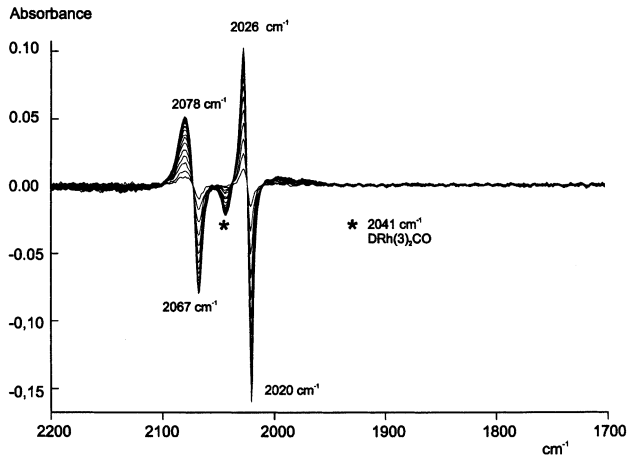


Figure 1. Difference IR spectrum obtained after addition of H_2 to a solution of Rh(**3**)$(CO)_2$ and Rh(**3**)$_2$(CO) under carbon monoxide pressure at 80 °C.

1-hexene before forming 2-hexene or 2-hexene does insert into the RhH and RhD bonds but never manages to carry out a migratory insertion of carbon monoxide.

From sample 6 heptanal was separated from the reaction mixture by distillation. The deuterium content at the aldehyde carbon, α- and β-positions, was determined with ^{2}H NMR spectroscopy. The ^{2}H NMR spectrum of the linear aldehyde showed deuterium at the α-carbon atoms (12−15%), β-carbon atoms (90−92%), and the aldehyde carbon (95−97%). The ^{1}H NMR spectrum of sample 6 showed 3−5% heptanal having a proton at the aldehyde carbon atom. D_3-Heptanal is formed via hydroformylation of deuterium-enriched 1-hexene. D_2-Heptanal is formed both by hydroformylation of D_0-hexene via the rhodium−deuteride complex (Scheme 4; for the sake simplicity not shown) and hydroformylation of D_1-hexene via the rhodium−hydride complex.

In the IR spectrum we only observed the C(O)D absorption band (1722 cm^{-1} in pentane) and not the absorption of C(O)H.[36,40] This shows that D_1-heptanal contains its deuterium atom predominantly (> 95%) at the aldehyde carbon atom. It is formed from nondeuterated 1-hexene and rhodium−hydride. In the final product we observe 18% of D_3-heptanal and 7.8% of D_4-heptanal; as a relative percentage of heptanals this amounts to 27.4% of the heptanals formed. The deuterium content at the α-carbon is 12−15%, which stems from reversible formation of 2-hexylrhodium from rhodium−deuteride and 1-hexene. This accounts for only half of the heptanal containing more than two deuterium atoms. Thus, the remainder of the extra deuterium atoms reside on the β-carbon atoms. This can only form via reversible 1-hexylrhodium formation from 1-hexene and rhodium−deuteride. Thus, the linear alkyl formation must also be partly reversible for this catalyst system.

Exchange between RhD and H_2. We studied the H/D exchange rate in the absence of substrate using IR spectroscopy. The IR absorptions of the carbonyl ligands of a rhodium−deuteride and a rhodium−hydride complex differ significantly for rhodium complexes containing two phosphorus ligands in the equatorial plane (Table 3). For the investigation of the H/D exchange rate, we synthesized DRh(**3**)$(CO)_2$ in situ from Rh(acac)-

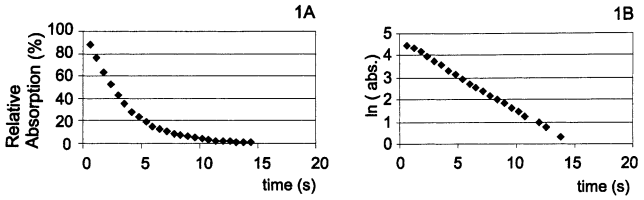


Figure 2. Kinetic data for the H/D exchange. (A) Exponential decay of ν_{CO} at 2020 cm^{-1} vs time. (B) Logarithmic plot of the decay of the relative absorption at 2020 cm^{-1} vs time.

$(CO)_2$ and 1.5 equiv of ligand **3** under 20 bar of CO/D_2 (1/1). Besides DRh(**3**)$(CO)_2$, a small amount of DRh(**3**)$_2$(CO) (**9**) was formed in the reaction mixture. After complete conversion to the deuteride complex, the D_2 gas was removed by flushing several times with 5 bar of carbon monoxide. The H/D exchange was initiated by adding 10 bar of hydrogen to DRh(**3**)$(CO)_2$ under 10 bar of carbon monoxide. The exchange process was monitored by using rapid scan high-pressure IR spectroscopy at 80 °C (1.3 spectra·s^{-1}). The difference IR spectrum presented in Figure 1 shows that the rhodium−deuteride complexes DRh(**3**)$(CO)_2$ and DRh(**3**)$_2$(CO) (negative peaks at ν_{CO} = 2067, 2041, and 2020 cm^{-1}) are quantitatively converted into the rhodium−hydride complex HRh(**3**)$(CO)_2$ (positive peaks at ν_{CO} = 2078 and 2026 cm^{-1}). The presence of small amounts of HRh(**3**)$_2$(CO) (**9**) could not be determined because of overlap with one of the absorptions of the deuteride complex.

The exponential decay of the strongest carbonyl absorption is presented in Figure 2a (ν_{CO} = 2020 cm^{-1}). The maximum absorbance of this frequency was taken as 100%. The natural logarithm of the relative absorption of the carbonyl frequency at 2020 cm^{-1} versus time is presented in Figure 2b. The decay of the carbonyl frequency of the deuteride complex shows first-order kinetics in the rhodium concentration and the pressure of H_2. The calculated slope of the line through the data depicted in Figure 2b is the negative of the H/D exchange rate. On the basis of these results, a H/D exchange rate of 1140 h^{-1} was calculated. The r^2 coefficient of the least-squares fit of the line is 0.999. Although the H/D exchange reaction is very fast indeed, the initial rate of hydroformylation of 10×10^3 mol aldehyde (mol Rh·h)$^{-1}$ is still an order of magnitude higher. Therefore, we conclude that up to 70% conversion H/D exchange is not significant and rhodium−hydride will react with the next moleule of alkene before rhodium−deuteride is formed. At high conversion the rate of hydroformylation is lower, because of the first-order dependence in the alkene concentration, and therefore some H/D exchange will occur and small amounts of heptanal having a proton at the aldehyde carbon will be formed.

Summarizing the results observed in the deuterioformylation experiments, we conclude that the linear and branched rhodium−alkyl complexes undergo β-hydride elimination and that the hydride migration is in part a reversible step under the conditions studied. On the basis of the large amount of deuterium in 1-hexene originating from both linear and branched alkyl complexes, we conclude that carbon monoxide insertion is slower than alkene coordination and dissociation, hydride migration, and β-hydride elimination. Probably the carbon monoxide insertion is controlling the reaction rate under the conditions studied and thereby inducing the high linear-to-branched ratio observed for this catalyst.

Hydroformylation Reaction of Internal Alkenes. The hydroformylation catalyst formed with ligand **3** showed high isomerization rates together with a high preference for the linear aldehyde. The deuterioformylation experiments showed that the rate of the carbon monoxide insertion for branched rhodium−alkyl complex is slow compared to that of the linear alkyl complex. This combination of catalyst properties might be ideal for the hydroformylation of internal alkenes to linear aldehydes. The reaction conditions for the hydroformylation of internal alkenes are different from the conditions used for 1-alkenes. Often high temperatures are used to enhance the isomerization reaction, together with low syn-gas pressures to facilitate the carbon monoxide dissociation and alkene coordination.[41] The hydroformylation of 2-octene was performed at 120 °C, [Rh] = 1.0 mM, Rh/L = 1/1.5, [2-octene] = 0.64 M, $p_{CO} = p_{H_2}$ = 2.5 bar. After 15 h 3% conversion of 2-octene to aldehydes was observed, showing a linear-to-branched ratio of only 1. The rate of hydroformylation remained very low. Thus, the selectivities are comparable with those of Jackstell et al.,[5g] using monodentate pyrrolyl phosphorus ligands, but the rates are lower.

Conclusions

Introduction of the electron-withdrawing pyrrolyl substituents resulted in a very active catalyst for the hydroformylation of 1-octene. Especially the bidentate pyrrolyl-containing ligand formed a catalyst that showed high activity together with a high regioselectivity for the linear aldehyde and moderate amount of 2-octenes.

Investigation of the deuterioformylation reaction mechanism with use of the pyrrolyl-based bidentate ligand **3** showed that the hydride migration is a reversible step under the conditions studied for both linear and branched alkylrhodium species. Branched rhodium−alkyl complexes prefer exclusively β-hydride elimination to carbon monoxide insertion resulting in high l/b ratios, and formation of 2-alkenes and, surprisingly, regeneration of deuterated 1-alkenes. All linear rhodium−alkyl species eventually undergo carbon monoxide insertion leading to highly linear aldehydes.

Experimental Section

General Information. All preparations were carried out under an atmosphere of argon with standard Schlenk techniques. Solvents were distilled from sodium/benzophenone. All glassware was dried by heating under vacuum. Column chromatography was performed with silica gel 60 230−400 mesh obtained from Merck or activated neutral alumina 50−200 μm obtained from Acros Organics. All chemicals were azeotropically dried before use. The alkene was filtered over neutral alumina to remove peroxides. The routine NMR spectra were recorded on a Varian Mercury-VX (300 MHz) spectrometer (^1H, ^{31}P, ^{13}C). The high-pressure NMR experiments were recorded on a Bruker DRX (300 MHz) spectrometer. Chemical shifts are given in ppm referenced to TMS or H_3PO_4 (external). IR spectra were recorded on a Nicolet 510 FT-IR spectrometer.

High-pressure NMR experiments were performed in a 10 mm (o.d.) sapphire NMR tube described by Elsevier et al.[42] In

a typical experiment 5 mg (0.019 mmol) of Rh(acac)$(CO)_2$ and 1, 1.5, 2, or 5 equiv of ligand were dissolved in 1.5 mL of toluene-d_8 or benzene-d_6. The solution was brought into the argon-flushed tube. The tube was flushed with syn-gas ($CO/H_2 = 1/1$) and put under a pressure of 20 bar. The tube was heated in the NMR machine to 80 °C and the complex formation was monitored in time.

High-pressure IR experiments were performed in a 50-mL autoclave (SS 316) equipped with IRTRAN windows (ZnS, transparent up to 700 cm^{-1}, i.d. 10 mm, optical path length = 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure transducer. In a typical experiment 5 mg of Rh(acac)$(CO)_2$ and 1.5, 3, 5, or 10 equiv of ligand were dissolved in 15 mL of cyclohexane under argon. The solution was brought into the autoclave and the autoclave was pressurized with 15 bar of CO/H_2 (1/1). The autoclave was placed in the infrared spectrometer and heated to 80 °C. IR spectra were recorded while the sample was stirred.

Hydroformylation experiments were performed in a stainless steel (SS 316) autoclave (196 mL). The autoclave was stirred mechanically and equipped with a substrate reservoir, a pressure transducer, a thermocouple, and a sampling device. As shown before[5d] no mass transfer limitations occur. In a typical experiment Rh(acac)$(CO)_2$ and the ligand were dissolved in 15 mL of toluene and brought into the autoclave. After flushing the autoclave with CO/H_2 (1/1), the autoclave was put under a pressure of 15 bar. The autoclave was heated at 80 °C, and after 1 h the substrate solution (2 mL of 1-octene, 1 mL of decane, and 2 mL of toluene) was charged into the reservoir and added to the reaction mixture by overpressure. The alkene was filtered over neutral alumina to remove peroxides. During the reaction several samples were taken at approximately 0.5 bar pressure drops corresponding with ~15% increments of conversion and immediately quenched by adding an excess of P(O-*n*-Bu)$_3$, to deactivate hydroformylation or isomerization active rhodium species. The total pressure drop never exceeded 2 bar. The samples were analyzed by GC with decane as internal standard.

The concentrations used in the deuterioformylation experiment were similar to those used in the hydroformylation experiments. Instead of toluene, benzene was used as solvent to facilitate the separation of aldehyde and solvent. The autoclave was charged with 1 mg of Rh(acac)$(CO)_2$ and 3 mg of **3** in 15 mL of benzene and pressurized with 15 bar of CO/D_2 (1/2). The autoclave was heated to 80 °C and after 1 h 2 mL (16 mmol) of 1-hexene in 2 mL of benzene and 1 mL of decane were charged into the reservoir and added to the reaction mixture by overpressure of carbon monoxide. The autoclave was pressurized up to 20 bar with carbon monoxide. During the reaction several samples were taken and quenched immediately by adding an excess of P(O-*n*-Bu)$_3$, to deactivate hydroformylation- or isomerization-active rhodium species. The samples were analyzed by GC. The deuterium contents in the substrate and products during the reaction were determined by using gas chromatography/mass spectrometry. After 2 h, complete conversion was reached and the aldehydes were distilled. ^1H and ^2H NMR spectroscopic data of the linear aldehydes were identical with those obtained by Casey et al.[38]

Chlorodipyrrolylphosphine and the monodentate and bidentate phosphinite ligands **2** and **4** were synthesized according to literature procedures.[16,43,44] The syntheses are given below, because no detailed information about the synthesis, purification, and characterization of these compounds was given in the literature. The *trans*-RhCl$(CO)L_2$ complexes were prepared according literature procedures.[26]

Chlorodipyrrolylphosphine. A solution of 13.9 mL (0.2 mol) of pyrrole and 100 mL of triethylamine (excess) in 50 mL of THF was added dropwise to a solution of 8.7 mL (0.1 mol) of phosphorus trichloride in 200 mL of THF at 0 °C. Triethylamine·HCl precipitated directly upon addition. The reaction mixture was stirred overnight at room temperature. The suspension was diluted with 100 mL of THF and the salts were filtered off. The product was obtained as a colorless oil after vacuum distillation (bp 88 °C, 2.7 mmHg). Yield 51%; ^1H NMR ($CDCl_3$) δ 6.5 ppm (m, 4 H, C*H*CHNP), 7.2 ppm (m, 4 H, CHC*H*NP); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 104.8 ppm; ^{13}C NMR ($CDCl_3$) δ 122.9 ppm (d, $^2J_{PC} = 17$ Hz, CH*C*HNP), 114.0 ppm (d, $^3J_{PC} = 5$ Hz, *C*HCHNP).

Phenyldipyrrolylphosphorusamidite (1). A solution of 1.58 g (17 mmol) of phenol dissolved in 10 mL of toluene was added dropwise to a solution of 3.34 g (17 mmol) of chlorodipyrollylphosphine and 10 mL of triethylamine (excess) dissolved in 50 mL of toluene at room temperature. The triethylamine·HCl salt was filtered off after 1 h of stirring at room temperature. The solvent was removed in a vacuum. The product was dissolved in toluene and filtered over neutral alumina and crystallized from pentane at −30 °C. At room temperature the product was obtained as a colorless oil. Yield 3.49 g (80%); ^1H NMR ($CDCl_3$) δ 6.5 (m, 4 H, C*H*CHNP), 7.0 (m, 3 H, *o, p*-PhOP), 7.2 (m, 4 H, CHC*H*NP), 7.4 ppm (m, 2 H, *m*-PhOP); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 108.4 ppm; ^{13}C NMR ($CDCl_3$) δ 113 (d, $^3J_{PC} = 5$ Hz, *C*HCHNP), 120 (d, $^2J_{PC} = 9$ Hz, CH*C*HNP), 122.0 (d, $^3J_{PC} = 5$ Hz, *o*-PhOP), 125 (s, *p*-PhOP), 131 (s, *m*-PhOP), 154 ppm (d, $^2J_{PC} = 11$ Hz, *ipso*-PhP); FAB/MS *m/e* 256.08, Anal. Calcd for $C_{14}H_{13}N_2OP$: C, 65.62; H, 5.11; N, 10.93. Found: C, 65.27; H, 4.94; N, 10.90.

Phenyl Diphenylphosphinite (2). A solution of 1.41 g (15 mmol) of phenol dissolved in 20 mL of toluene was added dropwise to a solution of 2.69 mL (15 mmol) of chlorodiphenylphosphine and 10 mL of triethylamine (excess) dissolved in 100 mL of toluene at room temperature. The triethylamine·HCl salt was filtered off after 1 h of stirring at room temperature. The solvent was removed in a vacuum. The product was obtained as colorless oil. Yield 3.62 g (87%); ^1H NMR ($CDCl_3$) δ 7.2 (m, 1 H, *p*-PhOP), 7.3 (m, 2 H, *o*-PhOP), 7.4 (m, 2 H, *m*-PhOP), 7.5 (m, 6 H, *o, p*-PhP), 7.8 ppm (m, 4 H, *m*-PhP); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 111.8 ppm; ^{13}C NMR ($CDCl_3$) δ 119 (d, $^2J_{PC} = 11$ Hz, *o*-PhP), 123 (s, *p*-PhOP), 129 (d, $^3J_{PC} = 6$ Hz, *m*-PhP), 130.8 (s, *p*-PhP), 131.1 (s, *m*-PhP), 141 (d, $^1J_{PC} = 17$ Hz, *ipso*-PhP), 158 ppm (d, $^2J_{PC} = 10$ Hz, *ipso*-PhOP); FAB/MS *m/e* 278.09.

1,1′-Biphenyl-2,2′-diyl-bis(dipyrrolylphosphoramidite) (3). A solution of 2.8 g (15 mmol) of 2,2′-dihydroxy-1,1′-biphenyl in 10 mL of THF was added dropwise to a solution of 6.0 g (30 mmol) of chlorodipyrrolylphosphine and 10 mL of triethylamine (excess) in 50 mL of THF at room temperature. The triethylamine·HCl salts were filtered off after 1 h of stirring at room temperature and the solvent was removed under vacuum. The white solid was dissolved in toluene and filtered over neutral alumina ($R_f = 1$). The product precipitated when the toluene was concentrated. Yield 68%; mp 95 °C, ^1H NMR ($CDCl_3$) δ 6.2 (m, 8 H, C*H*CHNP), 6.7 (m, 8 H, CHC*H*NP), 6.9 (d, 2H, $^3J_{HH} = 7$ Hz, *o*-Ph), 7.2 (d, 2H, $^3J_{HH} = 7$ Hz, *m*-Ph-Ph), 7.3 ppm (m, 4H, *m,p*-Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 109.4 ppm; ^{13}C NMR ($CDCl_3$) δ 112.5 (d, $^2J_{PC} = 4$ Hz, CH*C*HNP), 119.5 (d, $^3J_{PC} = 12$ Hz, *o*-Ph), 121.6 (d, $^3J_{PC} = 5$ Hz, *C*HCHNP), 124.7 (s, *p*-Ph), 129.7 and 132.0 (s, *m*-Ph), 130.2 (d, $^3J_{PC} = 4$ Hz, *o*-Ph-Ph), 151.1 (d, $^2J_{PC} = 10$ Hz, *ipso*-Ph); FAB/MS *m/e* 511. Anal. Calcd for $C_{28}H_{24}N_4O_2P_2$: C, 65.88; H, 4.74; N, 10.98. Found: C, 65.91; H, 4.66; N, 10.85.

1,1′-biphenyl-2,2′-diyloxy-bis(diphenylphosphinite) (4). A solution of 1.8 g (10 mmol) of 2,2′-dihydroxy-1,1′-biphenyl in 7 mL of THF was added dropwise to a solution of 4.4 g (20 mmol) of chlorodiphenylphosphine and 7 mL of triethylamine (excess) in 35 mL of THF at room temperature. The triethylamine·HCl salts were filtered off after 1 h of stirring at room temperature and the solvent was removed under vacuum. The white solid was dissolved in toluene and washed with water. Yield 4.0 g (73%); mp 77 °C; ^1H NMR ($CDCl_3$) δ 7.3−7.1 ppm (all aromatic H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 111.9 ppm; ^{13}C NMR ($CDCl_3$) δ 118 (d, $^2J_{PC} = 16$ Hz, *o*-PhP), 123 (s, *p*-PhOP), 128 (d, $^3J_{PC} = 7$ Hz, *m*-PhP), 129 (s, *m*-PhOP), 129.5 (s, *p*-PhP),

130 (d, $^3J_{PC}$ = 22 Hz, *o*-PhOP), 131 (d, $^3J_{PC}$ = 4 Hz, *o*-PhOP), 132 (s, *m*-PhOP), 141 (d, $^1J_{PC}$ = 17 Hz, *ipso*-PhP), 155 ppm (d, $^2J_{PC}$ = 7 Hz, *ipso*-PhOP); FAB/MS *m/e* 554.16.

***trans*-RhCl(CO)(1)$_2$ (5).** A solution of 0.1 g (0.4 mmol) of ligand **1** dissolved in 3 mL of dichloromethane was added dropwise to a solution of 38 mg (0.1 mmol) of $[RhCl(CO)_2]_2$ dissolved in 5 mL of dichloromethane. Carbon monoxide evolved immediately upon addition of the ligand. The yellow solution was stirred for 1 h at room temperature. The solvent was reduced to 1 mL. The product precipitated immediately when 10 mL of pentane was added. Yield 50 mg (37%); mp 133 °C dec; ^{1}H NMR ($CDCl_3$) δ 6.4 (m, 8 H, C*H*CHNP), 7.0 (m, 6 H, *o, p*-PhOP), 7.1 (m, 8 H, CHC*H*NP), 7.3 ppm (m, 4 H, *m*-PhOP); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 111.4 ppm (J_{RhP} = 190 Hz); ^{13}C NMR ($CDCl_3$) ^{13}C NMR ($CDCl_3$) δ 113 (*C*HCHNP), 122 (CH*C*HNP), 124 (*o*-PhOP), 126 (s, *p*-PhOP), 131 (s, *m*-PhOP), 152 (*ipso*-PhOP), 180 ppm (m, Rh(*CO*)); IR (CH_2Cl_2) $\nu_{Rh(CO)}$ = 2018 cm^{-1}. Anal. Calcd for $C_{29}H_{26}ClN_4O_3P_2Rh$: C, 51.31; H, 3.86; N, 8.25. Found: C, 50.82; H, 4.21; N, 8.16.

***trans*-RhCl(CO)(2)$_2$ (6).** A solution of 0.1 g (0.4 mmol) of ligand **2** dissolved in 3 mL of dichloromethane was added dropwise to a solution of 38 mg (0.1 mmol) of $[RhCl(CO)_2]_2$ dissolved in 5 mL of dichloromethane. Carbon monoxide evolved immediately upon addition of the ligand. The yellow solution was stirred for 1 h at room temperature. The solvent was reduced to 1 mL. The product precipitated as a yellow oil. Yield 112 mg (78%); ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 2 H, *p*-PhOP), 7.2 (m, 8 H, *o,m*-PhOP), 7.4 (m, 12 H, *o,p*-PhP), 7.8 ppm (m, 8 H, *m*-PhP); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 123 ppm (J_{RhP} = 143 Hz); ^{13}C NMR ($CDCl_3$) δ 121 (s, *o*-PhP), 124 (s, *p*-PhP), 128−133 (*m,p*-PhP, *o,m*-PhOP), 136 (dt, J_{CP} = 26 Hz, J_{RhC} = 3 Hz, *ipso*-PhP) 155 ppm (s, *ipso*- PhOP), the carbonyl carbon atom was not observed; IR (CH_2Cl_2) $\nu_{Rh(CO)}$ = 1991 cm^{-1}; FAB/MS *m/e* [RhCl(**2**)$_2$ − CO] 694.1.

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