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Novel rhodium complexes with *N*-pyrrolylphosphines: attractive precursors of hydroformylation catalysts‡

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New rhodium(I) complexes with *N*-pyrrolylphosphine ligands of formula [Rh(acac)(CO){$P(NC_4H_4)_3$}] **1a**, [Rh(acac)(CO){$PPh(NC_4H_4)_2$}] **1b**, [Rh(acac)(CO){$PPh_2(NC_4H_4)$}] **1c**, [Rh(acac){$P(NC_4H_4)_3$}$_2$] **2a**, [Rh(acac){$PPh(NC_4H_4)_2$}$_2$] **2b** and [Rh(acac){$PPh_2(NC_4H_4)$}$_2$] **2c** (acac = acetylacetonate) have been found to be precursors of very active and selective hydroformylation catalysts as [RhH(CO){$P(NC_4H_4)_3$}$_3$] **3a**, [RhH(CO){$PPh(NC_4H_4)_2$}$_3$] **3b** and [RhH(CO){$PPh_2(NC_4H_4)$}$_3$] **3c** respectively, which at 60 °C and 10 atm H_2–CO produce 80–90% of aldehydes with *n*:*iso* 3–31:1.

Phosphorus(III) compounds of type PR_3 are frequently used as modifying ligands in homogeneous catalytic processes like hydroformylation, hydrogenation or isomerization of olefins.[1] Usually rhodium complexes with phosphorus ligands when applied to hydroformylation allow higher yields and selectivity for aldehydes compared with processes in which modifying ligands are not used. Another advantage of such modifying ligands is the mild reaction conditions under which a given reaction proceeds.[1]

Until now, the widest application has been for phosphines[2] (like PPh_3), diphosphines[3] $Ph_2P(CH_2)_xPPh_2$ as well as phosphites[4] [like $P(OPh)_3$] and diphosphites demonstrating high steric hindrance.[5] Trialkyl phosphites are not used because of low stability with respect to hydrolysis. Recently published results revealed a relation between the electronic and molecular structure of the phosphorus ligands and hydroformylation reaction selectivity. Higher selectivity (*n*:*iso*) is usually obtained in catalytic systems modified with phosphites,[6] which are stronger π-acceptor and weaker σ-donor ligands than corresponding phosphines. The lower basicity of phosphite ligands facilitates olefin insertion into the Rh–H bond in hydride complexes by an anti-Markownikoff mechanism which leads first to the formation of an alkyl complex with a straight-chain alkyl ligand and next to linear aldehydes as a final product of olefin hydroformylation. In the presence of more bulky phosphites not only a higher rate of hydroformylation but also a selectivity (*n*:*iso*) increase was found.[7]

According to our previous studies rhodium catalysts modified with such π-acceptor ligands as $P(OPh)_3$ are able to activate H_2 under very mild conditions (1 atm CO–H_2, room temperature).[8] Under such conditions, using H_2 or a H_2–CO mixture, [RhH{$P(OPh)_3$}$_4$] and [RhH(CO){$P(OPh)_3$}$_3$] complexes were synthesized, isolated and applied to hydroformylation of olefins and unsaturated esters.[9] The encouraging behaviour found for rhodium complexes with π-acceptor triphenyl phosphite ligands led us to investigations of a new class of π-acceptor ligands, *i.e.* *N*-pyrrolylphosphines of type $PPh_x(NC_4H_4)_{3-x}$ (x = 0–2). Recently published results[10] showing that their π-acceptor properties were stronger than those of $P(OPh)_3$ suggested at least comparable catalytic activity. An additional advantage of *N*-pyrrolylphosphines as modifying ligands is the high stability of the P–N bond (compared with P–O) in reaction with alcohols.[11] Thus higher chemical stability of the catalytic system is expected compared with that modified with $P(OPh)_3$ which undergoes hydrolysis over long times.

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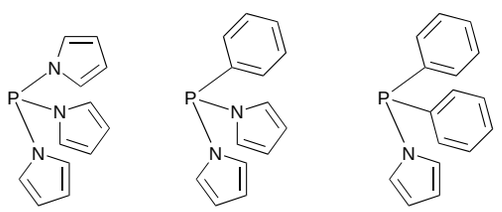
‡ *Non-Si unit employed*: atm = 101 325 Pa.



a **b** **c**

N-pyrrolylphosphines have not been applied until now in catalytic systems and therefore the present results are the first demonstration of their ability as modifying ligands in hydroformylation. The systems [Rh(acac)$(CO)_2$] (acac = acetylacetonate) and *N*-pyrrolylphosphines $P(NC_4H_4)_3$ **a**, $PPh(NC_4H_4)_2$ **b** and $PPh_2(NC_4H_4)$ **c** were studied.

Results and Discussion

Reactions of [Rh(acac)$(CO)_2$] with *N*-pyrrolylphosphines

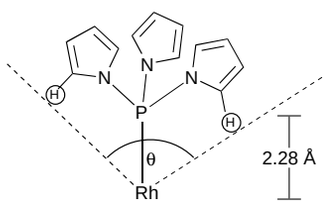
The *N*-pyrrolylphosphines $P(NC_4H_4)_3$ and $PPh(NC_4H_4)_2$ react with [Rh(acac)$(CO)_2$] in a similar way to that with $P(OPh)_3$.[12] Substitution of the first CO is much faster than that of the second and leads to the formation of [Rh(acac)(CO){$P(NC_4H_4)_3$}] **1a** and [Rh(acac)(CO){$PPh(NC_4H_4)_2$}] **1b** respectively, but at a higher excess of *N*-pyrrolylphosphine further CO substitution occurs and complexes of type [Rh(acac)L_2] are formed. Carbonyl stretching frequencies were found at high wavenumbers, 2012 and 2009 cm^{-1}, for **1a** and **1b** respectively. The shifts of ν_{CO} to higher frequencies confirm rather weak σ-donor and/or strong π-acceptor behaviour of the co-ordinated *N*-pyrrolylphosphines. In analogues rhodium phosphine (PPh_3) and phosphite [$P(OPh)_3$] complexes corresponding ν_{CO} frequencies are lower at 1975 and 2006 cm^{-1} respectively.[13]

The third *N*-pyrrolylphosphine, $PPh_2(NC_4H_4)$, in contrast, replaces only one CO group in [Rh(acac)$(CO)_2$]. The application of a three-fold excess of $PPh_2(NC_4H_4)$ per rhodium in [Rh(acac)(CO){$PPh_2(NC_4H_4)$}] **1c** even after 24 h did not produce any further products of substitution except the starting complex. In this respect it is similar to PPh_3, which in a similar reaction produces [Rh(acac)(CO)(PPh_3)] only.[14,15] The behaviour of $PPh_2(NC_4H_4)$ can be explained by its weaker π-acceptor and stronger σ-donor properties than the two other *N*-pyrrolylphosphines. The reactivity of PPh_3 was explained similarly.[16] The lack of steric influence on the substitution reaction was demonstrated by successful preparation of the complex

Table 1 Spectroscopic data for [Rh(acac)(CO)L] and [Rh(acac)L_2] complexes

Complex	^{1}H NMR (C_6D_6), δ: ^{1}H acac CH_3; CH	^{31}P [J(Rh–P)/Hz]	IR (KBr), $\tilde{\nu}_{CO}$/cm^{-1}	θ_1, θ_2 [a]/°
1a [Rh(acac)(CO){P(NC_4H_4)$_3$}]	1.62, 1.96; 5.4	102.5 [251]	2012	122, 141
1b [Rh(acac)(CO){PPh(NC_4H_4)$_2$}]	1.57, 1.98; 5.34	104.7 [218]	2009	116, 150
[Rh(acac)(CO){P(OPh)$_3$}][12]	1.52, 1.7; 5.11	212.1 [293]	2006	136 [b]
1c [Rh(acac)(CO){PPh$_2$(NC_4H_4)}]	1.6, 2.05; 5.4	90 [194]	2000	115, 154
[Rh(acac)(CO)(PPh$_3$)][13]	1.55, 2.04; 5.4	48.6 [179.7]	1975	118, 150; 145 [b]
2a [Rh(acac){P(NC_4H_4)$_3$}$_2$]	1.71; 5.41	107.6 [261]	—	
2b [Rh(acac){PPh(NC_4H_4)$_2$}$_2$]	1.63; 5.39	110.4 [229]	—	
2c [Rh(acac){PPh$_2$(NC_4H_4)}$_2$]	1.62; 5.43	94.4 [209]	—	

[a] Minimum (θ_1) and maximum (θ_2) cone angles calculated according to the Tolman procedure[19] (see text for details). [b] Tolman's cone angle.[19]



Scheme 1

[Rh(acac){PPh$_2$(NC_4H_4)}$_2$] **2c** from [Rh(acac)(C_8H_{14})$_2$] and [Rh(acac)(C_2H_4)$_2$]. A similar method was described for the synthesis of [Rh(acac)(PPh$_3$)$_2$].[17,18]

Steric properties of *N*-pyrrolylphosphines

To compare the steric parameters of the *N*-pyrrolylphosphines we calculated their cone angles according to the Tolman procedure[19] taking the metal–phosphorus distance and hydrogen atom radius as 2.28 Å and 0.3 Å respectively. Crystallographic data for P(NC_4H_4)$_3$ (in complex **1a**) and PPh$_3$ {in [Rh(acac)(CO)(PPh$_3$)][14]} have been used for calculations. In all cases the structural location of the *o*-hydrogen atoms in the phenyl or pyrrolyl rings determines the value of the H–M–H cone angle (Scheme 1). For each ligand, two extreme values of the cone angle (θ_1, θ_2) were calculated (Table 1). A smaller cone angle (θ_1) was obtained when the angles between the planes of the rings were taken from the crystallographic data. A bigger cone angle (θ_2) corresponds to the maximum H–M–H angle, obtained after rotation of one of the rings around the P–C (phenyl ring) or P–N (pyrrolyl ring) bond axis respectively. According to our calculations the maximum cone angle for PPh$_3$ is equal to 150° and is very similar to Tolman's value (145°).[19] We conclude that all other calculated values can be compared with Tolman's scale.

The cone angles of PPh(NC_4H_4)$_2$ and PPh$_2$(NC_4H_4) (Table 1) are slightly different and similar to the value for PPh$_3$ (145°), whereas that of P(NC_4H_4)$_3$ is a bit smaller (Table 1). According to Moloy's calculations the cone angles for PPh$_3$ and P(NC_4H_4)$_3$ are equal.[10]

Since all the considered *N*-pyrrolylphosphines are practically the same size, one may conclude that the steric effect cannot be the main factor determining their effectiveness as modifying ligands in rhodium complexes.

Electronic properties of *N*-pyrrolylphosphines

On the basis of the ν_{CO} band position for [Rh(acac)(CO)L] complexes (Table 1, L = different phosphorus ligands) the ligand L can be arranged in the following order of decreasing π-acceptor properties and increasing σ-donor properties respectively: P(NC_4H_4)$_3$ > PPh(NC_4H_4)$_2$ > P(OPh)$_3$ > PPh$_2$(NC_4H_4) > PPh$_3$. The compound PPh$_2$(NC_4H_4) is the strongest σ donor and the weakest π acceptor among the *N*-pyrrolylphosphines studied. A similar order of π-acceptor ligands has been obtained for [RhCl(CO)L_2] type complexes with the only difference being a reversed sequence of PPh(NC_4H_4)$_2$ and P(OPh)$_3$.[10]

Table 2 Spectroscopic (^{1}H and ^{31}P NMR) data for the system [Rh(acac)$(CO)_2$] + P(NC_4H_4)$_3$ at different concentration ratios

[P(NC_4H_4)$_3$]:[Rh]	NMR (C_6D_6), δ: ^{1}H acac CH_3	^{31}P [J(Rh–P)/Hz]	Compound
0.25:1	1.62, 1.96	102.5 [251]	**1a**
	1.77		**A**
0.4:1	1.62, 1.96	102.5 [251]	**1a**
	1.77		**A**
0.6:1	1.62, 1.96	102.5 [251]	**1a**
	1.77		**A**
1.0:1	1.62, 1.96	102.5 [205]	**1a**
	$\Delta\nu_{\frac{1}{2}}$ 25	$\Delta\nu_{\frac{1}{2}}$ 50	
1.2:1	1.79	100.0	**1a**
	$\Delta\nu_{\frac{1}{2}}$ 12	$\Delta\nu_{\frac{1}{2}}$ 440	
1.7:1	1.79	94.0 $\Delta\nu_{\frac{1}{2}}$ 780	**1a**
	1.71		**2a**
2.2:1	1.79	89.0 $\Delta\nu_{\frac{1}{2}}$ 580	**1a**
	1.71		**2a**

$\Delta\nu_{\frac{1}{2}}$ = Band width at half height in Hz; **A** = [Rh(acac)$(CO)_2$]

The differences in π-acceptor (and σ-donor) properties of *N*-pyrrolylphosphines are also reflected in ^{31}P NMR parameters. The J(Rh–P) coupling constants decrease with increasing σ-donor properties in the order of complexes **1a** to **1c** and **2a** to **2c**.

Chemical exchange of phosphines in [Rh(acac)(CO)L] type complexes [L = P(NC_4H_4)$_3$ or PPh(NC_4H_4)$_2$]

The ligand-exchange process was studied in the reaction of [Rh(acac)$(CO)_2$] + P(NC_4H_4)$_3$ (Table 2). At the ratio [P]:[Rh] < 1:1, ^{1}H and ^{31}P NMR spectroscopy detected only complex **1a**. At [P]:[Rh] > 1:1 one average line corresponding to the two CH_3 groups of the co-ordinated acac was detected by ^{1}H NMR (at δ 1.79) and only one broad line by ^{31}P NMR spectroscopy. Simultaneously, a low-intensity signal of the CH_3 (acac) group in complex **2a** (Table 2) appeared in the ^{1}H NMR spectra.

Removal of free CO from the reaction solution facilitates substitution of the second CO ligand in [Rh(acac)$(CO)_2$] and formation of complex **2a** (*i.e.* for the reaction mixture having [P(NC_4H_4)$_3$]:[Rh] = 1.7:1 the signals characteristic of **2a** increase and that of **1a** decrease in ^{1}H and ^{31}P NMR spectra).

Similar changes in NMR spectra were also observed for solutions containing complex **1a** and P(NC_4H_4)$_3$ as well as [Rh(acac)$(CO)_2$] and PPh(NC_4H_4)$_2$ indicating dynamic properties of the same type as those found for [Rh(β-diketonate)(CO)(PPh$_3$)] complexes in solutions containing an excess of unco-ordinated PPh$_3$.[13]

The substitution reaction of CO by pyrrolylphosphines in complexes **1a** and **1b** is distinctly slower than the analogous substitution with P(OPh)$_3$. Also slower is the ligand exchange

Table 3 Phosphorus-31 NMR data of [Rh(acac){$P(NC_4H_4)_3$}{$PPh_2(NC_4H_4)$}] and [Rh(acac){$PPh(NC_4H_4)_2$}{$PPh_2(NC_4H_4)$}] complexes in C_6D_6

	δ [*J*(Rh–P)/Hz]		
Compound	$P(NC_4H_4)_3$ or $PPh(NC_4H_4)_2$	$PPh_2(NC_4H_4)$	*J*(P–P)/Hz
[Rh(acac){$P(NC_4H_4)_3$}{$PPh_2(NC_4H_4)$}]	105.4 [273.9]	92.5 [198.6]	76.5
[Rh(acac){$PPh(NC_4H_4)_2$}{$PPh_2(NC_4H_4)$}]	107.3 [232.0]	94.2 [204.0]	69.9

in the system $[Rh(acac)(CO)_2]$ + $[Rh(acac)L_2]$. When L = $P(OPh)_3$, an equimolar mixture of these substrates immediately produces only one product, shown by IR and NMR spectroscopy to be [Rh(acac)(CO){$P(OPh)_3$}].[12] A similar experiment with $[Rh(acac)(CO)_2]$ and [Rh(acac){$P(NC_4H_4)_3$}$_2$] produces, according to ^{1}H and ^{31}P NMR measurements, only a small amount of complex **1a**.

Competition of *N*-pyrrolylphosphines in substitution reactions

Chemical exchange studies of $P(NC_4H_4)_3$ and $P(NC_4H_8)_3$ ligands in $[RhCl(CO)L_2]$ complexes led to the conclusion that under competition conditions, co-ordination of the stronger σ-donor ligand $P(NC_4H_8)_3$ to rhodium is preferred.[10] Within the present group of ligands, $PPh_2(NC_4H_4)$ is the strongest σ donor, whereas $P(NC_4H_4)_3$ is the weakest. To compare their co-ordination abilities the reactions of **1a** with $PPh_2(NC_4H_4)$ and **1c** with $P(NC_4H_4)_3$ have been studied. In the two cases the ^{31}P NMR spectra appeared to be identical and contained broadened lines at δ 80 and 65 manifesting dynamic processes involving contributions from two complexes identified as **1a** (ν_{CO} 2015 cm^{-1}) and **1c** (ν_{CO} 1994 cm^{-1}).

The above-described experiments, however, do not allow us to determine the specific influence of electronic or steric effects on the ligand-exchange course.

Chemical exchange of phosphines in [Rh(acac)L_2]-type complexes [L = $P(NC_4H_4)_3$, $PPh(NC_4H_4)_2$ or $PPh_2(NC_4H_4)$]

Complexes **2a**–**2c**, like [Rh(acac){$P(OPh)_3$}$_2$], do not show dynamics (on the NMR timescale) in solutions containing an excess of suitable unco-ordinated phosphorus compound [*N*-pyrrolylphosphine or $P(OPh)_3$,[20] respectively]. However, exchange of *N*-pyrrolylphosphines occurs as revealed by the presence of mixed-ligand complexes [Rh(acac){$P(NC_4H_4)_3$}{$PPh_2(NC_4H_4)$}] and [Rh(acac){$PPh(NC_4H_4)_2$}{$PPh_2(NC_4H_4)$}] as products obtained from the reaction of **2a** + 2 $PPh_2(NC_4H_4)$ and **2b** + 2 $PPh_2(NC_4H_4)$ respectively. Both these complexes are well characterized and their ^{31}P NMR parameters are collected in Table 3. For both the *J*(P–P) coupling constants are relatively small which suggests a *cis* arrangement of the phosphine ligands, whereas the *J*(Rh–P) coupling constants are similar to those in complexes **2a**–**2c** (Table 1).

Molecular structure of [Rh(acac)(CO){$P(NC_4H_4)_3$}] 1a and [Rh(acac){$P(NC_4H_4)_3$}$_2$] 2a

Complex **1a** has a square-planar structure (Fig. 1) with a slight deflection (0.011 Å) of the Rh atom from the plane comprising the four atoms bonded to it. The Rh–O bond distances are different, Rh–O(2) (*trans* to CO) 2.016(2), Rh–O(1) (*trans* to P) 2.054(2) Å, which may be explained by the *trans* effect of $P(NC_4H_4)_3$. However, the difference is smaller than that found for analogous complexes with PPh_3 in which corresponding bond lengths are 2.029(5) and 2.087(4) Å;[14] this points the *trans* effect of $P(NC_4H_4)_3$ being stronger than that of CO but weaker than that of PPh_3. The Rh–P bond distance [2.1657(7) Å] is similar to that in phosphite complexes *e.g.* [Rh(acac){$P(OPh)_3$}$_2$] 2.147(2), 2.156(2) Å,[21] but shorter than in phosphine complexes, *e.g.* [Rh(acac)(CO)(PPh_3)] 2.244(2) Å,[14] [Rh(quin)(CO)(PPh_3)] 2.261(2) Å (Hquin = 8-hydroxyquinoline),[22] and [Rh(trop)(CO)(PPh_3)] 2.232(2) Å [Htrop = tropolone (2-hydroxycyclohepta-2,4,6-trienone)].[23] Selected bond lengths and angles are given in Table 4.

Table 4 Selected bond lengths (Å) and angles (°) in [Rh(acac)(CO){$P(NC_4H_4)_3$}] **1a**

Rh–C(c)	1.826(3)	O(c)–C(c)	1.128(3)
Rh–O(2)	2.016(2)	N(11)–C(14)	1.388(4)
Rh–O(1)	2.054(2)	N(11)–C(11)	1.392(4)
Rh–P	2.166(1)	N(21)–C(21)	1.392(3)
P–N(21)	1.684(2)	N(21)–C(24)	1.392(3)
P–N(11)	1.687(2)	N(31)–C(34)	1.382(4)
P–N(31)	1.689(2)	N(31)–C(31)	1.385(4)
C(c)–Rh–O(2)	177.5(1)	C(14)–N(11)–P	128.6(2)
C(c)–Rh–O(1)	93.8(1)	C(14)–N(11)–C(11)	107.2(3)
O(2)–Rh–O(1)	88.6(1)	C(14)–N(11)–P	128.6(2)
C(c)–Rh–P	87.4(1)	C(11)–N(11)–P	124.2(2)
O(2)–Rh–P	90.2(1)	C(21)–N(21)–C(24)	107.1(2)
O(1)–Rh–P	178.7(1)	C(21)–N(21)–P	129.4(2)
N(21)–P–N(11)	104.5(1)	C(24)–N(21)–P	122.5(2)
N(21)–P–N(31)	100.6(1)	C(34)–N(31)–C(31)	107.2(3)
N(11)–P–N(31)	99.8(1)	C(34)–N(31)–P	125.0(2)
N(21)–P–Rh	114.6(1)	C(31)–N(31)–P	127.6(2)
N(11)–P–Rh	116.1(1)	O(c)–C(c)–Rh	177.8(2)
N(31)–P–Rh	118.8(1)		

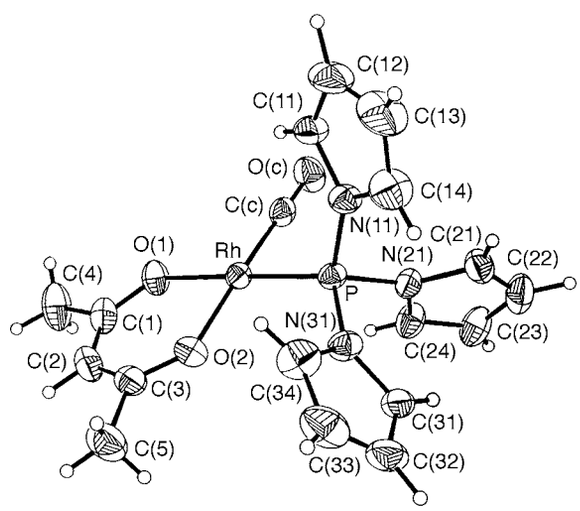


Fig. 1 Structure of [Rh(acac)(CO){$P(NC_4H_4)_3$}] **1a**

The Rh–O bond distances in complex **2a** are almost identical [2.034(4) and 2.054(4) Å], as expected for complexes of $[Rh(acac)L_2]$ type. The Rh–P bond lengths are also comparable [2.161(2) and 2.176(2) Å] but a bit longer than those in [Rh(acac){$P(OPh)_3$}$_2$].[21] Complex **2a** is almost square planar and the average deviation from the best plane is 0.05 Å (Fig. 2). Selected bond lengths and angles are given in Table 5. In both complexes **1a** and **2a** the co-ordination of the acac ligand is similar to that found in other rhodium complexes. The interatomic distances and angles are similar to those found, *e.g.* in [Rh(acac)(CO)(PPh_3)][13] and [Rh(acac){$P(OPh)_3$}$_2$].[21]

Both distances C_α-C_β and C_β-C_β in $P(NC_4H_4)_3$ in complexes **1a** and **2a** are similar to those found in complexes [RhCl(CO){$P(NC_4H_4)_3$}$_2$] and [$N(PPh_3)_2$][Rh(CO){$P(NC_4H_4)_3$}$_3$]·thf[10] (thf = tetrahydrofuran) and in the free phosphine.[24] These distances in **1a** are in the ranges 1.335(5)–1.354(5) and 1.375(6)–1.406(5) Å, whereas in **2a** they are 1.335(9)–1.361(8) and 1.388(11)–1.429(10) Å respectively.

Activation of H_2–CO in the system [Rh(acac)(CO)$_2$] + *N*-pyrrolylphosphine

Both types of rhodium complexes, **1a**–**1c** and **2a**–**2c** in the presence of an excess of *N*-pyrrolylphosphine react with a H_2–CO mixture under very mild conditions [room temperature, 1 atm pressure of H_2–CO (1:1)] producing hydridocarbonyl species [RhH(CO){P(NC$_4$H$_4$)$_3$}$_3$] **3a**, [RhH(CO){PPh(NC$_4$H$_4$)$_2$}$_3$] **3b** and [RhH(CO){PPh$_2$(NC$_4$H$_4$)}$_3$] **3c** respectively.

It is worth underlining that in rhodium chemistry there are very few examples of effective synthesis of monohydride complexes upon application of dihydrogen under 1 atm pressure.

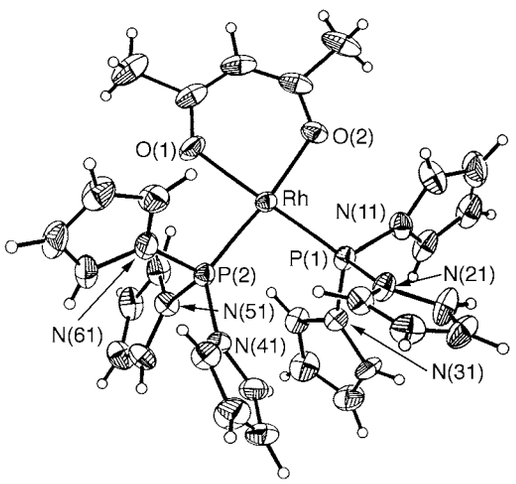


Fig. 2 Structure of [Rh(acac){P(NC$_4$H$_4$)$_3$}$_2$] **2a**

Table 5 Selected bond lengths (Å) and angles (°) for [Rh(acac){P(NC$_4$H$_4$)$_3$}$_2$] **2a**

Rh–O(2)	2.034(4)	N(11)–C(12)	1.378(8)
Rh–O(1)	2.054(4)	N(11)–C(15)	1.388(8)
Rh–P(1)	2.161(2)	N(21)–C(25)	1.369(7)
Rh–P(2)	2.176(2)	N(21)–C(22)	1.391(7)
P(1)–N(21)	1.691(4)	N(31)–C(35)	1.380(7)
P(1)–N(31)	1.699(5)	N(31)–C(32)	1.393(7)
P(1)–N(11)	1.707(5)	N(41)–C(45)	1.377(7)
P(2)–N(61)	1.691(5)	N(41)–C(42)	1.388(7)
P(2)–N(51)	1.693(5)	N(51)–C(52)	1.386(7)
P(2)–N(41)	1.710(4)	N(51)–C(55)	1.405(7)
		N(61)–C(65)	1.382(7)
		N(61)–C(62)	1.398(7)
O(2)–Rh–O(1)	88.4(2)	N(61)–P(2)–N(51)	102.8(2)
O(2)–Rh–P(1)	88.5(1)	N(61)–P(2)–N(41)	98.2(2)
O(1)–Rh–P(1)	173.7(1)	N(51)–P(2)–N(41)	98.3(2)
O(2)–Rh–P(2)	174.0(1)	N(61)–P(2)–Rh	111.0(2)
O(1)–Rh–P(2)	85.6(1)	N(51)–P(2)–Rh	114.2(2)
P(1)–Rh–P(2)	97.4(1)	N(41)–P(2)–Rh	128.6(2)
N(21)–P(1)–N(31)	103.0(2)	C(12)–N(11)–C(15)	107.3(6)
N(21)–P(1)–N(11)	98.2(2)	C(25)–N(21)–C(22)	107.4(5)
N(31)–P(1)–N(11)	98.8(2)	C(35)–N(31)–C(32)	107.2(5)
N(21)–P(1)–Rh	121.1(2)	C(45)–N(41)–C(42)	108.0(4)
N(31)–P(1)–Rh	115.4(2)	C(52)–N(51)–C(55)	107.4(5)
N(11)–P(1)–Rh	116.6(2)	C(65)–N(61)–C(62)	106.9(5)

Until now, under such mild conditions only [RhH{P(OPh)$_3$}$_4$] and [RhH(CO){P(OPh)$_3$}$_3$] were obtained from [Rh(acac)(CO)$_2$].[8] An analogous reaction occurs with PPh$_3$ only when both the temperature and pressure are elevated. We found that [Rh(acac)(CO)$_2$] and pyrrolylphosphines are able to split H_2 under relatively mild conditions. When the reaction is conducted in the presence of CO complexes of formula [RhH(CO)L$_3$] are formed.

Complexes **3a–3c** have a distorted trigonal-bipyramidal structure with three equivalent phosphorus ligands in equatorial position. The phosphine ligands give one signal in the ^{31}P NMR spectrum split into a doublet as a result of Rh–P coupling, whereas in ^{1}H NMR spectra, since *J*(P–H) is higher than *J*(Rh–H), a quartet of doublets is observed. In both complexes the phosphine ligands are equivalent, however the difference in ^{1}H NMR parameters indicates slightly different geometries of **3a–3c**. Their structures are also somewhat different from that of [RhH(CO){P(OPh)$_3$}$_3$] for which both coupling constants have similar values [*J*(Rh–H) = *J*(P–H) = 3 Hz].[8]

It is frequently accepted for rhodium hydride complexes that higher values of *J*(Rh–H) coupling constants correspond to tetrahedral structures, smaller values to trigonal-bipyramidal structures.[25] According to this, complex **3c** could have approximately trigonal-bipyramidal symmetry, similar to that of [RhH(CO)(PPh$_3$)$_3$].[26]

The ν_{CO} and ν(Rh–H) frequencies observed in the IR spectra of complexes **3** are shifted to lower values from **3a** to **3c** according to the increasing σ-donor and decreasing π-acceptor properties of the phosphines (Table 6).

Catalytic activity of [Rh(acac)(CO)$_2$] modified with *N*-pyrrolylphosphines

Three catalytic systems containing the catalyst precursor [Rh(acac)(CO)$_2$] and appropriate amounts of *N*-pyrrolylphosphine, P(NC$_4$H$_4$)$_3$ (system I), PPh(NC$_4$H$_4$)$_2$ (system II) and PPh$_2$(NC$_4$H$_4$) (system III), have been tested in the model reaction of hex-1-ene hydroformylation. In system I at a rather small excess of phosphine {[P(NC$_4$H$_4$)$_3$]:[Rh] = 2.8:1} at 60 °C and 10 atm H_2–CO (1:1) a total conversion of 600–4800 mol of hex-1-ene per mol of catalyst was attained in 90 min (Table 7). The concentration ratio of hex-1-ene to rhodium does not influence the reaction rate and selectivity. On increasing [P(NC$_4$H$_4$)$_3$]:[Rh] to 5–7:1 the hydroformylation selectivity factor, *n/iso*, increases to 18–31 (Table 8), achieving a six times higher value compared with the systems modified by PPh$_3$.[6] A similar selectivity *n/iso* can be obtained in the systems modified with P(OPh)$_3$ at 40 °C and 1 atm of H_2–CO but total conversion of olefin is achieved only after at least 5 h and the concentration of the isomerization reaction product, hex-2-ene, surpasses 30%.[27]

At lower P(NC$_4$H$_4$)$_3$ concentration 2-ethylpentanal, the product of hex-2-ene hydroformylation, was found in the products. Higher phosphine concentrations inhibit the above reactions, but do not affect the yield of isomerization of hex-1-ene to hex-2-ene, which remains constant (*ca.* 20%).

The effectiveness of system I in hydroformylation of hex-2-ene was confirmed in a separate experiment with pure hex-2-ene

Table 6 Spectroscopic (^{1}H and ^{31}P NMR, IR) data for [RhH(CO)L$_3$] complexes

	NMR (C$_6$D$_6$), δ		IR (KBr)
Complex	^{1}H [*J*(P–H), *J*(Rh–H)/Hz]	^{31}P [*J*(Rh–P)/Hz]	ν̃(Rh–H), ν̃$_{CO}$/cm^{-1}
3a [RhH(CO){P(NC$_4$H$_4$)$_3$}$_3$]	−9.1 [7.8, 2.7]	109 [211]	1992, 2079
3b [RhH(CO){PPh(NC$_4$H$_4$)$_2$}$_3$]	−9.0 [9.3, 1.8]	108.8 [187]	1976, 2051
3c [RhH(CO){PPh$_2$(NC$_4$H$_4$)}$_3$]	−8.9 [12.0, < 1]	88.1 [169]	1950, 2040
[RhH(CO){P(OPh)$_3$}$_3$]	−10.9 [3, 3]	141.2 [240]	2010, 2060
[RhH(CO)(PPh$_3$)$_3$]	−9.1 (m)	47.4 [132.5]	1920, 2040

Table 7 Composition of hex-1-ene hydroformylation products at different concentrations of [Rh(acac)(CO)$_2$] (system I)

		Reaction product (mol %)				
10^6 [Rh]/mol	[hex-1-ene]/[Rh]	Hex-2-ene	2-Ethylpentanal	2-Methylhexanal	Heptanal	*n*:*iso*
2.5	4800	20	—	11	68	6.1:1
4.1	2900	22	1.1	12.2	64.6	4.9:1
5.1	2300	17.7	2.5	15.1	64.8	3.7:1
6.7	1800	18	2.2	13.9	65.7	4.1:1
8.2	1500	15	2.4	14.5	68.2	4.0:1
19.0	632	14.4	2	14.6	68.5	4.1:1

Reaction conditions: [Rh(acac)(CO)$_2$], catalyst precursor, [P(NC$_4$H$_4$)$_3$]:[Rh] = 2.8:1; 1.2 × 10^{-2} mol hex-1-ene; 60 °C, 10 atm CO–H$_2$ (1:1), 90 min.

Table 8 Composition of hex-1-ene hydroformylation products at different [P(NC$_4$H$_4$)$_3$]:[Rh] ratios at 30–80 °C (system I)

		Reaction product (mol %)					
[P]:[Rh]	*T*/°C	Hex-1-ene	Hex-2-ene	2-Ethylpentanal	2-Methylhexanal	Heptanal	*n*:*iso*
1.8:1	60	—	18.7	3	16.9	61.4	3.1:1
2.8:1	60	—	14.4	2	14.6	68.5	4.1:1
4.1:1	30	46.5	7.6	—	1.6	44.3	27.7:1
	40	9.5	10.4	—	2.5	77.6	31.0:1
	60	—	22.7	—	7.1	70	9.9:1
	70	—	24.2	1.7	10.0	64	5.5:1
	80	—	20.2	2.4	13.5	63.9	4.0:1
5.4:1	60	—	25.2	—	3.6	71.2	19.8:1
7.1:1	60		20.5	—	2.5	74.8	29.9:1

Reaction conditions: [Rh(acac)(CO)$_2$], catalyst precursor, 1.9 × 10^{-5} mol; 1.2 × 10^{-2} mol hex-1-ene; 10 atm CO–H$_2$ (1:1), 90 min.

Table 9 Composition of hex-1-ene hydroformylation products at different [PPh(NC$_4$H$_4$)$_2$]:[Rh] ratios (system II)

	Reaction product (mol %)				
[P]:[Rh]	Hex-2-ene	2-Ethylpentanal	2-Methylhexanal	Heptanal	*n*:*iso*
1.7:1	14.7	1.6	17.8	65.9	3.4:1
2.6:1	9.5	3.5	21	65.9	2.1:1
4.7:1	12.4	1	11.3	75.3	6.1:1
6.0:1	9.5	—	7.2	83.3	11.5:1
8.0:1	9.2	—	5.7	85	14.8:1
13.0*:1	4.1	—	5.6	81	14.5:1

Reaction conditions: [Rh(acac)(CO)$_2$], catalyst precursor, 1.9 × 10^{-5} mol; 1.2 × 10^{-2} mol hex-1-ene; 60 °C, 10 atm CO–H$_2$ (1:1), 90 min. * 180 min, 9% of hex-1-ene unchanged.

as a substrate (6.5 × 10^{-3} mol). The reaction performed at [P(NC$_4$H$_4$)$_3$]:[Rh] = 2.8:1 and 60 °C gave after 90 min the following aldehydes: 2-ethylpentanal (28%), 2-methylhexanal (50%) and heptanal (12%). Studies of the temperature effect on the reaction course (Table 8) allowed us to conclude that at lower temperature (*i.e.* 40 °C) the selectivity of hydroformylation is higher mainly because of the decrease in rate of hex-1-ene to hex-2-ene isomerization. An increase in temperature leads to a decrease in the *n*:*iso* ratio caused by hex-2-ene hydroformylation, as is demonstrated by the presence of 2-ethylpentanal in the products.

In the reaction modified with PPh(NC$_4$H$_4$)$_2$ (system II) the selectivity factors *n*:*iso* are a bit smaller (Table 9) but still higher than those obtained for typical PPh$_3$-modified systems.[6] The advantage of system II *versus* I is the higher yield of aldehydes (90 *versus* 75%). A relatively high *n*:*iso* factor and low yield of hex-2-ene is obtained with a six-fold excess of free phosphine.

The third system (III), modified with PPh$_2$(NC$_4$H$_4$), is less attractive, mainly because of the low *n*:*iso* ratio. With this system, a relatively high yield of 2-methylhexanal, independent of phosphine concentration, is obtained (Table 10). An increase in phosphine concentration does not effect the *n*:*iso* ratio, but significantly decreases the rate of reaction.

Generally in all three systems the reaction rate decreases with increasing phosphine concentration, however in a different manner in each system. In system II modified with PPh(NC$_4$H$_4$)$_2$ the effect of phosphine concentration is the smallest

Table 10 Composition of hex-1-ene hydroformylation products at different [PPh$_2$(NC$_4$H$_4$)]:[Rh] ratios (system III)

	Reaction product (% mol)				
[P]:[Rh]	Hex-1-ene	Hex-2-ene	2-Methylhexanal	Heptanal	*n*:*iso*
2.3:1	11.1	2.7	21.6	64.6	6.0:1
4.7:1	7.6	2.1	19.5	70.7	3.6:1
6.4:1	5.5	2.1	19.4	73.1	3.8:1
9.2[a]:1	8.5	2.9	15.1	73.4	4.9:1
9.2[b]:1	7.2	2.6	15.5	74.8	4.8:1
13.6[c]:1	12.9	4.1	8.6	74.4	8.6:1

Reaction conditions: [Rh(acac)(CO)$_2$], catalyst precursor, 1.9 × 10^{-5} mol; 1.2 × 10^{-2} mol hex-1-ene; 60 °C, 10 atm CO–H$_2$ (1:1), 90 min. [a] 120 min. [b] 70 °C. [c] 190 min.

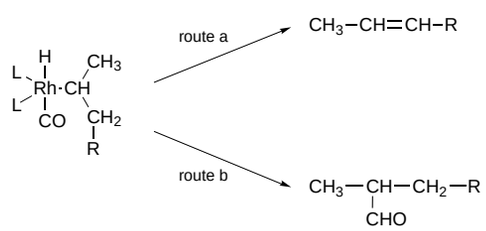
and the decrease in reaction rate was observed only at a 13-fold excess of free phosphine {[PPh(NC$_4$H$_4$)$_2$]:[Rh] = 13:1}. In system I [with P(NC$_4$H$_4$)$_3$] a small decrease in the reaction rate was observed at [PPh$_2$(NC$_4$H$_4$)]:[Rh] = 7.1:1. The best system seems to be II in which, at a relatively low concentration of free phosphine, both a high yield of aldehydes (*ca.* 90%) and high selectivity (*n*:*iso ca.* 10) are achieved. The high effectiveness of PPh(NC$_4$H$_4$)$_2$ as modifying ligand may be explained both by its electronic and steric properties, however similar cone angles of all the *N*-pyrrolylphosphines suggest that the steric effect is rather smaller.

The different selectivity of the systems can be explained according to the general hydroformylation reaction mechanism. In I and III comparable amounts of intermediate rhodium–alkyl (branched) complex are formed as is manifested by the similar total yield of hex-2-ene and 2-methylhexanal (*ca*. 25%). The insertion of CO into the rhodium–carbon bond in the branched alkyl complex leads to the branched aldehyde (route b, Scheme 2), whereas β-hydrogen elimination from the methyl group produces hex-2-ene (route a, Scheme 2).

β-elimination is preferred in system I, although at a lower concentration of phosphine both processes occur with similar probability. The relatively high yield of hex-2-ene (route a) is characteristic for this system. In system III insertion of CO into the Rh–C bond (route b) is dominant which causes a higher yield of 2-methylhexanal than of hex-2-ene. The low yield of branched alkyl complex in system II is favourable for good selectivity.

Experimental

Rhodium complexes were obtained according to literature method: $[Rh(acac)(CO)_2]$,[28] $[Rh(acac)(C_8H_{14})_2]$ and $[Rh(acac)(C_2H_4)_2]$.[29] The compounds $P(NC_4H_4)_3$, $PPh(NC_4H_4)_2$ and $PPh_2(NC_4H_4)$ have been obtained as described[10] and characterized by ^1H, ^{31}P NMR (C_6D_6) and mass spectrometry. $P(NC_4H_4)_3$: ^1H NMR δ 6.35 (pseudo t, 6 H) and 6.71 (d of pseudo t, 6 H); ^{31}P NMR δ 79.1; *m/z* 229 (78), 163 (100), 136 (50), 118 (14), 96 (23), 70 (33) and 69 (32%). $PPh(NC_4H_4)_2$: ^1H NMR δ 6.37 (m, 4 H), 6.93 (m, 4 H) and 7.0 (d, 5 H); ^{31}P NMR δ 70.2; *m/z* 240 (67), 174 (100), 172 (27), 147 (20), 145 (13), 107 (23), 36 (16) and 77 (12%). $PPh_2(NC_4H_4)$: ^1H NMR δ 6.5 (t, 2 H), 7.02 (pseudo qnt, 2 H), 7.12 (m, 6 H) and 7.33 (m, 4 H); ^{31}P NMR δ 47.8; *m/z* 251 (79), 185 (64), 183 (100), 174 (11), 152 (14) and 107 (18%).



Scheme 2

Preparation of complexes

Complexes 1a–1c. These were obtained by a similar procedure given in detail for **1a**. To $[Rh(acac)(CO)_2]$ (0.09 g, 3.5×10^{-4} mol) in thf was added $P(NC_4H_4)_3$ (0.085 g, 3.7×10^{-4} mol). Evolution of CO was observed and the mixture was stirred for 5 min. The solution was condensed *in vacuo* and heptane was added resulting in the formation of a light yellow precipitate. Crystals for X-ray analysis were obtained by the same method (Found: C, 47.05; H, 4.3; N, 9.1. Calc. for $C_{18}H_{19}N_3O_3PRh$ **1a**: C, 47.05; H, 4.15; N, 9.15. Found: C, 50.45; H, 4.3; N, 6.41. Calc. for $C_{20}H_{20}N_2O_3PRh$ **1b**: C, 51.1; H, 4.3; N, 5.95. Found: C, 54.15; H, 4.05; N, 2.95. Calc. for $C_{22}H_{21}NO_3PRh$ **1c**: C, 54.9; H, 4.4; N, 2.9%).

Complexes **2a** and **2b** were obtained by a similar procedure given in detail for **2a**. To $[Rh(acac)(CO)_2]$ (0.052 g, 2×10^{-4} mol) in thf was added $P(NC_4H_4)_3$ (0.1 g, 4.4×10^{-4} mol). Dinitrogen was bubbled through the solution for 15 min to remove CO completely. Addition of heptane resulted in the precipitation of a yellow product. Crystals for X-ray analysis were obtained by the same method (Found: C, 52.0; H, 4.8; N, 12.45. Calc. for $C_{29}H_{31}N_6O_2P_2Rh$ **2a**: C, 52.75; H, 4.7; N, 12.7. Found: C, 57.25; H, 4.3; N, 9.1. Calc. for $C_{33}H_{33}N_4O_2P_2Rh$ **2b**: C, 58.1; H, 4.75; N, 8.2%).

Complex 2c. To a solution of $[Rh(acac)(C_2H_4)_2]$ (0.06 g) in diethyl ether was added $PPh_2(NC_4H_4)$ (0.2 g). During stirring an orange product precipitated (Found: C, 65.4; H, 4.9; N, 3.45. Calc. for $C_{37}H_{35}N_2O_2PRh$: C, 66.0; H, 5.25; N, 4.15%).

Complexes 3a–3c. These were obtained by a similar procedure given in detail for complex **3a**. A Schlenk flask was charged with $[Rh(acac)(CO)_2]$ (0.026 g, 1×10^{-4} mol), toluene (2 cm^3) and $P(NC_4H_4)_3$ (0.08 g, 3.5×10^{-4} mol). The flask was evacuated, the solution was placed under 1 atm H_2–CO (1:1) and stirred overnight at room temperature. Most of the solvent was removed under vacuum and ethanol was added to precipi-

Table 11 Crystal data and structure refinement parameters for complexes **1a** and **2a***

	1a	**2a**
Empirical formula	$C_{18}H_{19}N_3O_3PRh$	$C_{29}H_{31}N_6O_2P_2Rh$
M	459.24	660.45
T/K	296(2)	294(2)
Space group	$P2_1/n$	$P2_1/c$
a/Å	8.381(2)	17.211(3)
b/Å	16.339(3)	11.998(2)
c/Å	14.726(3)	15.312(3)
β/°	102.60(3)	106.74(3)
U/Å^3	1968.0(7)	3027.9(9)
D_c/g cm^{-3}	1.550	1.449
D_m/g cm^{-3}	1.55	1.45
Cell measurement, θ range/°	21.5–38.9	23.4–38.7
Crystal size/mm	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.25
μ/cm^{-1}	9.71	7.06
F(000)	928	1352
2θ Range/°	5–56	4–50
Range of *h*, *k*, *l*	0–11, 0–21, −19 to 18	0–20, 0–14, −18 to 16
Reflections collected	4905	5360
Independent reflections	4782 (R_{int} = 0.0091)	5360
No. parameters varied	311	363
Goodness of fit on F^2	1.099	1.131
Reflections observed [$I > 3.5\sigma(I)$]	3382	2773
Final *R*1, *wR*2 [$I > 3.5\sigma(I)$]	0.0224, 0.0586	0.0298, 0.0729
Minimum, maximum difference peak/e Å^{-3}	−0.385, 0.381	−0.265, 0.694

* Details in common: monoclinic: $Z = 4$; ω–2θ scans; three standard reflections every 100: $w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.7249P]$ where $P = (F_o^2 + 2F_c^2)/3$.

tate the white complex (Found: C, 54.15; H, 4.1; N, 15.25. Calc. for $C_{37}H_{37}N_9OP_3Rh$ **3a**: C, 54.2; H, 4.55; N, 15.4. Found: C, 60.1; H, 4.35; N, 9.35. Calc. for $C_{43}H_{40}N_6OP_3Rh$ **3b**: C, 60.55; H, 4.75; N, 9.85. Found: C, 66.75; H, 4.3; N, 4.2. Calc. for $C_{49}H_{43}N_3OP_3Rh$ **3c**: C, 66.45; H, 4.9; N, 4.54%).

Chemical exchange studies

The following solutions have been analysed by IR, ^1H and ^{31}P NMR spectroscopy: 1, $[Rh(acac)(CO)_2]$ (0.05 mmol) and $P(NC_4H_4)_3$ (0.05 mmol) mixed in C_6D_6 and $PPh_2(NC_4H_4)$ (0.055 mmol) added after 5 min; 2, $[Rh(acac)(CO)_2]$ (0.054 mmol) and $PPh_2(NC_4H_4)$ (0.057 mmol) mixed in C_6D_6 and $P(NC_4H_4)_3$ (0.047 mmol) added after 5 min; 3, complex **1c** (0.057 mmol) + $P(NC_4H_4)_3$ (0.011 mmol); 4, **1a** (0.055 mmol) + $PPh_2(NC_4H_4)$ (0.146 mmol).

Hydroformylation experiments

Hydroformylation reactions were carried out in a steel autoclave (40 cm^3) under 10 atm of H_2–CO (1:1) starting pressure. In a typical experiment $[Rh(acac)(CO)_2]$ (2×10^{-5} mol, 0.0052 g) and a corresponding amount of phosphine were weighed in small Teflon vessels and introduced into the autoclave under a dinitrogen atmosphere. Benzene (1.5 cm^3) containing *p*-xylene (0.73 mol, internal standard) and hex-1-ene (1.5 cm^3, 1.2×10^{-2} mol) were added. The autoclave was closed, purged with dihydrogen and filled with 5 atm of H_2 and 5 atm of CO. The reaction mixture was stirred magnetically and heated at 60 °C. After 90 min the autoclave was cooled. The products were separated by vacuum distillation and analysed by GC (or GC–mass spectrometry). The *n*:*iso* values were calculated from the peak area ratios in the chromatogram.

Crystallography

All measurements were made on a Kuma MK-4 computer-controlled κ-axis diffractometer with graphite-monochromated Mo-Kα radiation. Experimental details are given in Table 11. The structures were solved by direct methods with SHELXL 86[30] and refined by full-matrix least-squares methods using SHELXL 93.[31] The hydrogen atoms in complex **1a** were found by Fourier difference synthesis and refined isotropically. All positions of the hydrogen atoms in **2a** were calculated based on the geometry of the molecule and with the isotropic thermal parameter fixed at 1.2 U_{eq} of their parent atoms and refined isotropically. Non-hydrogen atoms in **1a** and **2a** were refined anisotropically.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/471.

Instruments

The following instruments were used: Fourier-transform, Nicolet Impact 400; GC–mass spectrometry, Hewlett-Packard 5890 II; NMR, Bruker 300 MHz (121.5 MHz for ^{31}P).

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