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1,3,2-Oxazaphosphorinanes in rhodium(I) complexes

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Abstract

Acetylacetonate complexes of rhodium(I) with 1,3,2-oxazaphosphorinanes were obtained. The structure and features of the stereochemistry of these compounds were studied by X-ray crystallography, and ^{1}H and ^{31}P NMR spectroscopy. The places 1,3,2-oxazaphosphorinanes take in the spectrochemical series of organophosphorus ligands is discussed.

Introduction

1,3,2-Oxazaphosphorinanes are important examples of phosphornitrogen-containing heterocycles. Such cyclo-unsymmetrical six-membered systems incorporating one cyclic nitrogen atom offer much in terms of the broadening of the range of organophosphorus ligands and complexes and will help to establish general principles which determine the specific features of coordination of six-membered phosphoronitrogen containing heterocycles. It is hoped that studies of 1,3,2-oxazaphosphorinanes will fill the gaps which are still present in comparative characteristics of the cyclic and acyclic P–N bonds within one ligand. Finally, these heterocycles are of practical importance in routes to complex metal catalysts and medicinal preparations.

Okruszek and Verkade [1] were the first to report on the synthesis of platinum complexes with 1,3,2-oxazaphosphorinanes. We began our studies with corresponding rhodium(I) derivatives [2,3]. New results obtained in synthesis and structure studies of rhodium(I) complexes with 1,3,2-oxazaphosphorinanes are described herein.

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Results and discussion

X-Ray diffraction study of the acacRh(CO)[EtN(CH$_2$)$_3$OPNMe$_2$] complex (Fig. 1) confirmed the hypothetical plane-square coordination of the Rh atom with the chelate acac ligand (Rh–O(2) 2.095(2), Rh–O(3) 2.044(3) Å), the carbonyl ligand (Rh–CO 1.814(4) Å) and the phosphorus atom in the oxazaphosphorinane heterocycle. This type of structure is peculiar to acacRh(CO)L complexes [4,5]. The six-membered RhO(2)O(3) metal cycle is planar to within ±0.012 Å and the atoms in closest proximity to the Rh atom are coplanar to within ±0.06 Å. Such a metal cycle structure, and the equal lengths of the formally single and double C–C and the C–O bonds in the cycle testify to delocalization of electron density in the cycle and to certain pseudoaromaticity. The minor difference in the lengths of the Rh–O bonds (0.051(3) Å) is of note and can be attributed to a stronger *trans*-effect of the phosphorus-containing ligand compared with the carbonyl ligand [6].

The phosphorus atom in 1,3,2-oxazaphosphorinane has a distorted tetrahedral coordination (the valence angles at the P atom are 99.5(1)–117.0(1)°, the most strongly enlarged angles are those with an Rh ← P coordination bond. As in the case of a similar complex of rhodium with O(CH$_2$)$_3$OPNEt$_2$ [5], the Rh–P bond is axial with respect to the phosphorus-containing heterocycle and the P–N bond is equatorial. The six-membered phosphorinane cycle has the chair conformation with the P atom and the O(5) atom opposite it, being located on different sides of the plane comprising the four other atoms of the cycle (coplanar to within ±0.006 Å) at distances of −0.788(1) and 0.668(4) Å, respectively. The length of the Rh–P bond in the complex is 2.204(1) Å. This is lower than that in the triphenylphosphine complex acacRh(CO)PPh$_3$ [4] (2.444(2) Å) but exceeds that found in the complex with O(CH$_2$)$_3$OPNEt$_2$ 2.19 Å [5]. Strengthening of the Rh–P bonds in the series of

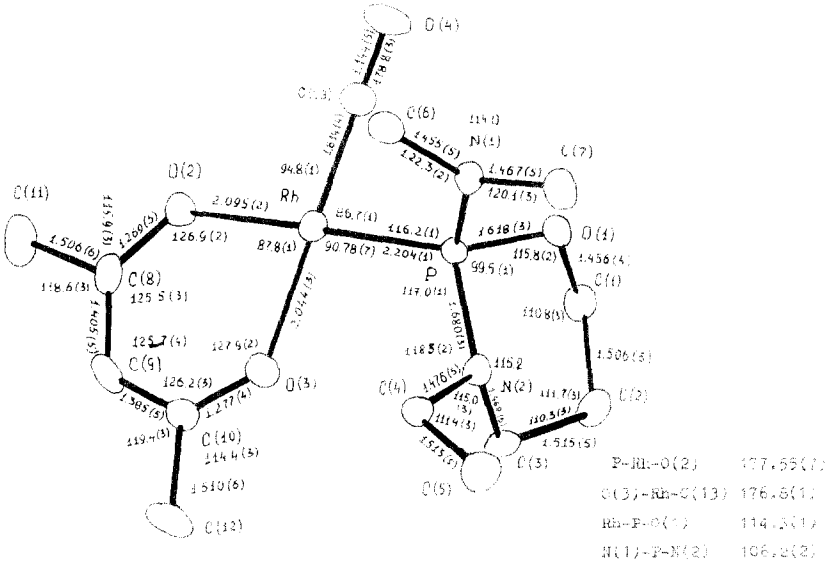

Fig. 1. The molecular structure of the acacRh(CO)[EtN(CH$_2$)$_3$OPNMe$_2$] complex.

rhodium compounds with PPh_3, $EtN(CH_2)_3OPNMe_2$, and $O(CH_2)_3OPNEt_2$ seems to be caused by enhancement of the electron-seeking properties of the substituents at the phosphorus atom, and by an increase in the effective positive charge at the Rh atom. It is noteworthy that enhancement of the electron-seeking properties of the substituents at the phosphorus atom in the series of compounds indicated above also manifests itself in the ^{31}P NMR spectra.

An interesting feature of the geometry of the 1,3,2-oxazaphosphorinane complex is the non-equivalence of the exo- and endocyclic P–N(2) bonds (bond lengths are 1.648(3) and 1.680(3) Å, respectively). The P–N(1) bond is similar to that found in the molecule of a dimethylamino derivative, $Me_2NP(OCH_2)_2CMe_2$ [7], and was found to be 1.642(5) Å; the authors believe that this testifies to the existence of π-interaction between the N and P atoms.

The shortening of the exocyclic P–N(1) bond relative to P–N(2) is due to a lower degree of pyramidality of the N(1) atom compared with the N(2) atom (the sum of the valence angles at the N atom are 356.4 and 346.7° and the heights of the pyramids are 0.168(3) and 0.301(3) Å, respectively). These findings corroborate the known dependence of P–N bond length on the degree of pyramidality of the nitrogen atom [8].

Other geometric parameters of the complex are regular and shortened intermolecular contacts are not present.

The X-ray crystallographic data are supplemented by an analysis of the ^{31}P NMR spectra of the complexes. The ^{31}P NMR spectra of the complexes contain doublet signals in the range 133.3–140.3 ppm . Doublet splitting, judging from the value of the spin–spin interaction constant (225.5–255.7 Hz), is determined by direct coordination of phosphorus at rhodium. A clear difference in the ^1J(Rh–P) values of the acacRh(CO)L complexes including the place isomer ligands: $EtN(CH_2)_3OPOEt$ (255.7 Hz) and $O(CH_2)_3OPNEt_2$ (241.7), suggests that the nitrogen atom in the 1,3,2-oxazaphorinane cycle has a higher electronegativity than that of the acyclic nitrogen. This difference seems to be associated with a higher degree of pyramidality of the cyclic nitrogen atom in 1,3,2-oxazaphosphorinane which is consistent with the results of an X-ray diffraction study. On the other hand, the non-equivalence of the cyclic and acyclic nitrogen atoms is not revealed in the ^1J(Rh–P) values of the acacRh(CO)L complexes with the following ligands: $EtN(CH_2)_3OPNEt_2$ (227.3 Hz) and $(Et_2N)_2POEt$ (227.5 Hz). This is probably because of the effect of the acyclic nirogen atoms of the $(Et_2N)_2POEt$ ligand on the Rh–P bond, is equivalent to the summed effects of the cyclic and acyclic nitrogen atoms in $EtN(CH_2)_3OP$-NEt_2; in other words, it seemes likely that there is a strong mutual influence of the nitrogen atoms in 2-dialkylamino-3-*R*-1,3,2-oxazaphosphorinanes and is directed via the phosphorus atom.

On the whole, the ^1J(Rh–P) value for rhodium derivatives of 2-dialkylamino-3-*R*-1,3,2-oxazaphosphoinanes lies between 225.5 and 233.6 Hz. Slight changes of ^1J(Rh–P) in this series of ligands ($\Delta\ ^1J$ 8.1 Hz) attest to almost identical configurations of the phosphorus atom in coordinated 1,3,2-oxazaphosphorinanes and stem primarily from the influence of the nature of the substituents at the phosphorus and nitrogen atoms in the ligands. Because rhodium complexes with 1,3,2-oxazaphosphorinanes have different stereochemical arrangements, greater variation in the ^1J(Rh–P) values is to be expected. Thus, $\Delta\ ^1J$(Rh–P) for similar complexes of rhodium with *cis*-, *trans*-$Et_2NP(OCH)(CH_3)(CH_2)_2O$ was 11.3 Hz [5] the sub-

Table 1

Spectral characteristics of acetylacetonate rhodium(I) complexes, acacRh(CO)[RN(CH$_2$)$_3$OPX]

Complex		IR (cm^{-1}, Nujol (toluene))		^{31}P NMR		
R	X	ν(CO)	ν(acac)	δ_P (ppm):	Coordination shift [b], $\Delta\delta_P$ (ppm)	^1J(Rh–P) (Hz)
i-Pr [a]	NEt_2	1982(1981)	1574,1514	135.9	1.0	233.6
i-Pr [a]	NMe_2	1981(1981)	1574,1515	135.8	2.6	233.2
i-Pr [a]	OEt	1995(1994)	1580,1513	133.6	−0.4	255.3
Bzl [a]	NEt_2	1980	1575,1508	140.3	−0.9	227.5
Bzl [a]	NMe_2	1982	1579,1510	139.1	1.6	230.7
Bzl [a]	Morph [c]	1980	1575,1508	137.0	−5.0	231.5
Me [a]	NEt_2	(1978)	(1578),(1505)	139.9	−4.2	225.5
Me [a]	NMe_2	(1978)	(1575),(1505)	138.8	−0.8	227.4
Et	NEt_2	1980	1576,1505	138.5	−0.2	227.3
Et	OEt	1990	1575,1510	133.3	−1.0	255.7
Et	NMe_2	1976	1572,1505	137.3	1.7	230.2
Et	Pip [d]	1979	1575,1505	135.5	0.6	228.0

[a] First described in [3], Bzl = CH_2–  . [b] $\Delta\delta = \delta$(complex) − δ(ligand). [c]  . [d]  .

stituents at the phosphorus atom in the ligands being identical. Such a characteristic change of the ^1J(Rh–P) value on going from complexes with *trans*-phosphorinanes to ones with *cis*-phosphorinanes can be related to a more pronounced basicity of the axial unshared electron pair of the phosphorus atom in the *cis*-isomer [9,10].

An analysis of the ^1J(Rh–P) values enabled as to place the relative strengths of the 1,3,2-oxazaphosphorinanes in the organophosphorus ligands series. The ^1J(M–P) value has already been used in drawing up spectrochemical series of organophosphorus ligands and at present is being considered as the reciprocal of the basicity of the P ligand [11–14].

In terms of the ^1J(Rh–P) value 1,3,2-oxazaphosphorinanes occupy an intermediate place between phosphines and phosphites and show definite electron-attracting behaviour. The ^1J(Rh–P) values (in Hz) for the acacRh(CO)L (L = PPh_3) complexes make up the following series (175.3) [5], RN(CH$_2$)$_3$OPX (225.5–256.6) (Table 1), O(CH$_2$)$_3$OPX (241.7–244.5) [5], $P(OBu)_3$ (262.6), $P(OEt)_3$ (267.3) [5], $P(OPh)_3$ (292.4) [15].

The conclusions about the electron-attracting character of 1,3,2-oxazaphosphorinanes and their intermediate location between phosphines and phosphites in the series of organophosphorus ligands agree well with the data on the correlation between ^1J(Rh–P) and δ_p of the oxidized form of the ligand (LO), (Fig. 2) (the correlation factor is 0.95). This kind of correlation was proposed by Darencsenji [14].

The ^{1}H NMR spectra of the complexes revealed certain differences in the chemical shifts of the annular protons at oxygen, nitrogen and C(5) on going from free ligand to ones coordinated at the rhodium atom (Tables 2, 3). The influence of the metal atom on the state of the hydrogen atoms located at the acyclic α-carbon is marked. Let us turn to the analysis of vicinal constants, ^3J(PNCH) and ^3J(POCH). On going from ligand to complex, their values change noticeably: e.g.

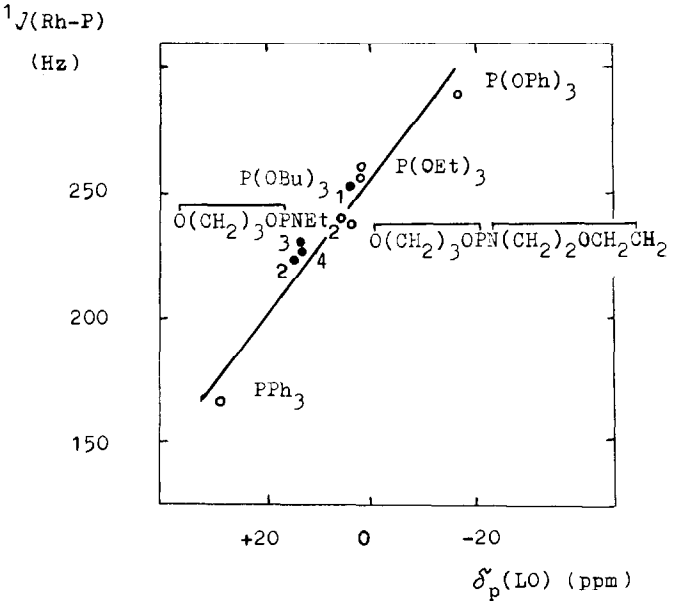

Fig. 2. The correlation between ^1J(Rh–P) of the acacRh(CO)L complexes and the chemical shift, δ_p, for oxides, LO. L: 1 – i-PrN(CH$_2$)$_3$OPOEt, 2 – EtN(CH$_2$)$_3$OPNEt$_2$, 3 – i-PrN(CH$_2$)$_3$OPNEt$_2$, 4 – i-PrN(CH$_2$)$_3$OPNMe$_2$.

i-PrN(CH$_2$)$_3$OPNEt$_2$ – ^3J(PNCH) is 2.3 and 1.0 Hz; i-PrN(CH$_2$)$_3$OPNMe$_2$ – ^3J(PNCH) is 2.2 and 1.3 Hz; Et N(CH$_2$)$_3$OPOEt – ^3J(PNCH) is 1.5 Hz, ^3J(POCH) is 3.0 Hz; EtN(CH$_2$)$_3$OPNMe$_2$ – ^3J(PNCH) is 2.5, 4.5 and 1.8 Hz (the first values in the ^3J series refer to protons at carbon atoms bound to the cyclic nitrogen atom and the second values to protons at the α-carbon of the acyclic substituent (Table 3). Such changes of the vicinal constants, ^3J(PNCH) and ^3J(POCH) are likely to have a denser packing of hydrogen atoms in the coordinated ligand. It is noteworthy that the most pronounced coordination shifts are observed in ^{1}H NMR data of alkyl substituents at the nitrogen atom located in the 1,3,2-oxazaphosphorinane cycle which seems to be caused by stronger configuration changes in the coordination of the cyclic nitrogen atom than in the coordination of the nitrogen atom, off the cycle.

Experimental

Infrared spectra were taken on a Specord 751R spectrometer in KBr. ^{31}P NMR spectra were recorded with a Varian FT-80 A instrument; chemical shifts were measured in C_6H_6 relative to 85% phosphoric acid as an external reference. ^{1}H NMR spectra were taken in C_6D_6 on a Bruker WH360 instrument with respect to hexamethyldisiloxane.

The X-ray diffraction study was carried out on an automatic Syntex $P2_1$ four-disk diffractometer (Mo-K_α radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta \leqslant 52°$) at -120 °C.

(*Continued on p. 244*)

Table 2

^{1}H NMR spectral data for free and coordinated 1,3,2-oxazaphosphorinanes

Ligand	Free phosphorinane							acacRh(CO)[RN(CH$_2$)$_3$OPX] complex						
	H_a^6	H_e^6	H_a^4	H_e^4	H_a^5	H_e^5	Other phosphorinane signals	H_a^6	H_e^6	H_a^4	H_e^4	H_a^5	H_e^5	Other signals of the complex
i-PrN(CH$_2$)$_3$OPNEt$_2$		3.71		2.67		1.41	NCH_2CH$_3$(m) 3.12, *J*(PNCH) 10.0 [b]; NCH$_2$CH_3(t) 1.09, *J*(HCCH) 7.5; (CH$_3$)$_2$CH(m) 3.39, *J*(PNCH) 10.7; (CH_3)$_2$CH(2d) 1.03, 1.09		3.90		2.79		1.29	NCH_2CH$_3$(2m) 3.47, 3.27, *J*(PNCH) 11.0; NCH$_2$CH_3(t) 1.09, *J*(HCCH) 7.5; (CH$_3$)$_2$CH(m) 4.50, *J*(PNCH) 13.0 (CH_3)$_2$CH(2d) 0.92, 1.13, *J*(HCCH) 6.6; C(CH_3)O(2s) 1.80, 1.94,
EtN(CH$_2$)$_3$OPOEt	3.99 [a]	3.57	2.96	2.43	1.41	1.18	*J*(PCCH) 6.6 OCH_2CH$_3$(2m) 3.72, 3.75 *J*(PCCH) 10.5; OCH$_2$CH_3(t) 1.18, *J*(PCCH) 7.5; NCH_2CH$_3$(2m) 2.91, 2.80	3.90	3.60	2.73	2.41	1.29	1.00	CCHC(s) 5.37 O(CH_2)CH$_3$(2m) 4.29, 3.96 *J*(POCH) 13.5; O(CH$_2$)CH_3(t) 1.20, *J*(POCH) 7.8; NCH_2CH$_3$(2m) 3.60, 3.37, *J*(PNCH) 15.0;

					J(PNCH) 13.5 14.2; NCH_2CH_3(t) 0.94						NCH_2CH_3(t) 1.05, J(HCCH) 7.0 $C(CH_3)O$(2s) 1.93, 1.82, $CCHC$(s) 5.37
	4.15		3.24		1.97	J(HCCH) 6.8	3.89		3.11		1.75	
i-Pr$\overline{N(CH_2)_3OP}NMe_2$		3.67		2.58		1.25	NCH_3(d) 2.53, J(PNCH) 9.5; $(CH_2)_3CH$(m) 3.40, J(PNCH) 10.3; $(CH_3)_2CH$(2d) 1.00, 1.07	3.68		2.55		0.92	$N(CH_3)$(d) 2.67, J(PNCH) 10.8; $(CH_3)_2CH$(m) 4.96, J(PNCH) 12.5; $(CH_3)_2CH$(d) 0.90, 1.08, J(HCCH) 6.6; $C(CH_3)O$(2s) 1.93, 1.79,
	4.11		3.07		1.64	J(HCCH) 6.6	3.95		2.74		1.48	$CCHC$ 5.36
Et$\overline{N(CH_2)_3OP}NMe_2$		3.67		2.56		1.37	$N(CH_3)$(d) 2.56, J(PNCH) 9.5; NCH_2(2m) 2.83 2.68		3.85		2.77		1.32	$N(CH_3)$(d) 2.75, J(PNCH) 11.3; NCH_2(2m) 3.18, 3.09, J(PNCH) 14.0;
						J(PNCH) 11.5 9.5;							NCH_2CH_3(t) 0.95, J(HCCH) 7.8;
	3.99		5.11		1.56	NCH_2CH_3(t) 0.99, J(HCCH) 7.5	4.14		2.77		1.32	$C(CH_3)O$(2s) 1.96, 1.78, $CCHC$ 5.38

[a] δ_P in ppm. [b] ^3J in Hz.

Table 3

Coordination shift of 1,3,2-oxazaphosphorinanes in the acacRh(CO)[RN$\overline{(CH_2)_3OPX}$] complexes

Ligand	i-PrN$\overline{(CH_2)_3OP}$ NEt_2	i-PrN$\overline{(CH_2)_3OP}$ NMe_2	EtN$\overline{(CH_2)_3OP}$ OEt	EtN$\overline{(CH_2)_3OP}$ NMe_2
H_a^6	−0.09	−0.16	−0.26	0.15
H_c^6	0.19	0.01	0.03	0.18
H_a^4	−0.23	−0.35	−0.13	−0.34
H_c^4	0.06	−0.03	−0.02	0.21
H_a^5	−0.12	−0.16	−0.22	−0.24
H_e^5	−0.12	−0.33	−0.18	−0.05
$\Delta\delta(NCH_2CH_3)$ [a]	0.35	–	0.68	0.35
	0.15		0.57	0.41
Δ^3J(PNCH) [b]	1.0	–	1.5	2.5
				4.5
$\Delta\delta(CH_2CH_3)$	0	–	0.11	−0.04
Δ^3J(HCHC)	0	–	0.2	0.03
$\Delta\delta((CH_3)_2CH)$	1.11	1.56	–	–
Δ^3J(PNCH)	2.3	2.2	–	–
$\Delta\delta((CH_3)_2CH)$	−0.11	−1.10	–	–
Δ^3J(HCCH)	0	0	–	–
$\Delta\delta(OCH_2CH_3)$	–	–	0.57	
			0.27	
Δ^3J(POCH)	–	–	3.0	
$\Delta\delta(OCH_2CH_3)$	–	–	0.02	–
Δ^3J(HCCH)	–	–	0.3	–
$\Delta\delta(NCH_3)$	–	0.14	–	0.19
Δ^3J(PNCH)	–	1.3	–	1.8

[a] $\Delta\delta = \delta$(complex) − δ(ligand) in ppm. [b] $\Delta^3J = {}^3J$(complex) − ^3J(ligand) in Hz.

Synthesis of 1,3,2-oxazaphosphorinanes

1,3,2-Oxazaphosphorinanes were prepared through interaction of benzene solutions of cyclic acid chlorides with suitable secondary amines or alcohols (HX), eq. 1.

$$R\overline{N(CH_2)_3OPCl} + HX \rightarrow R\overline{N(CH_2)_3OPX} \quad (1)$$

The reaction was run in an Ar atmosphere. The liberated hydrogen chloride was bound by an amine and in the form of a salt isolated from the reaction product. After solvent had been evaporated off, the phosphorinanes were distilled in vacuum. The physical and analytical data for products are listed in Table 4.

Synthesis of acacRh(CO)[RN$\overline{(CH_2)_3OPX}$] complexes

acacRh(CO)[RN$\overline{(CH_2)_3OPX}$] complexes were obtained by treating $acacRh(CO)_2$ [17,18] with the appropriate 1,3,2-oxazaphosphorinane in ether at 20 °C in an inert gas atmosphere, molar ratio P/Rh = 1, eq. 2. After the ether had been evaporated

$$acacRh(CO)_2 + R\overline{N(CH_2)_3OPX} \xrightarrow{-CO} acacRh(CO)\left[R\overline{N(CH_2)_3OPX}\right] \quad (2)$$

off at 25 °C (10 mmHg) and the products were crystallized from hexane [3]. The physicochemical characteristics of the complexes are presented in Tables 1–5.

The acacRh(CO)L complex ($L = (Et_2N)_2POEt$) was prepared similarly to that used in synthesis of phosphorinane complexes. The complex is a yellow solid. Yield

(Continued on p. 247)

Table 4

Physical and analytical data for 1,3,2-oxazaphosphorinanes

Phosphorinane $RN\overline{(CH_2)_3OPX}$		Yield (%)	B.p. (°C/mmHg)	n_D^{20}	δ(p) (ppm)
R	X				
i-Pr [a]	NEt_2	67	67/0.5	1.4810	134.9
i-Pr [a]	NMe_2	41	65/1	1.4830	133.2
i-Pr [a]	OEt	45	50/0.5	1.4605	134.0
Bzl [b]	NEt_2	34	125 [c]	1.5450	141.2
Bzl [b]	NMe_2	37	150 [c]	1.5483	137.5
Bzl [b]	Morph	46	130 [c]	1.5600	142.0
Me [b]	NEt_2	48	90/0.5	1.4818	144.1
Me [b]	NMe_2	52	53/1	1.4890	139.6
Et [d]	NEt_2	53	50/1	1.4840	138.7
Et [e]	OEt	41	39/1	1.4669	134.3
Et [f]	NMe_2	51	34/1	1.4841	135.6
Et [g]	Pip	37	87/1	1.5092	134.9

[a] First described in [16]. [b] [3]. [c] High-vacuum distillation. [d] Found: C, 52.9; H, 10.1; P, 15.2. $C_9H_{21}N_2OP$ calc: C 52.9, H 10.3, P 15.2%. [e] Found: C, 47.4; H, 9.0; P, 17.0. $C_7H_{16}NO_2P$ calc: C, 47.5; H, 9.0; P, 17.5%. [f] Found: C, 47.5; H, 9.6; P, 17.2. $C_7H_{17}N_2OP$ calc: C, 47.7; H, 9.7; P, 17.6%. [g] Found: C, 55.3; H, 10.1; P, 14.3. $C_{10}H_{21}N_2OP$ calc: C, 55.6; H, 9.7; P, 14.4%.

Table 5

Physical and analytical data for acetylacetonateRhodium(1) complexes, acacRh(CO)[$RN\overline{(CH_2)_3OPX}$]

Complex [a]		Yield (%)	M.p. (°C) (decomp.)	R_f [c]	Formula	Found (calc) (%)		
R	X					C	H	P
i-Pr [e]	NEt_2	88	(175–177) [b]	0.51	$C_{16}H_{30}N_2O_4PPh$	43.1 (42.9)	6.9 (6.7)	6.8 (6.9)
i-Pr [e]	NMe_2	82	95–97	0.47	$C_{14}H_{26}N_2O_4PRh$	40.5 (40.0)	6.4 (6.2)	7.1 (7.4)
i-Pr [e]	OEt	88	(136–138) [b]	0.42 [d]	$C_{14}H_{25}NO_5PRh$	40.1 (39.9)	6.2 (5.9)	7.3 (7.4)
Bzl [e]	NEt_2	84	158–160	0.73	$C_{20}H_{30}N_2O_4PRh$	48.2 (48.4)	6.4 (6.1)	6.0 (6.2)
Bzl [e]	NMe_2	88	102–104	0.64	$C_{18}H_{26}N_2O_4PRh$	46.6 (46.1)	5.4 (5.6)	6.3 (6.6)
Bzl [e]	Morph	82	103–105	0.41	$C_{20}H_{28}N_2O_5PRh$	46.8 (47.1)	5.0 (5.5)	5.9 (6.1)
Me [e]	NEt_2	84	(150–152) [b]	0.56 [d]	$C_{14}H_{26}N_2O_4PRh$	39.9 (40.0)	6.0 (6.2)	7.2 (7.4)
Me [e]	NMe_2	87	121–122	0.68 [d]	$C_{12}H_{22}N_2O_4PRh$	36.5 (36.7)	5.5 (5.6)	7.6 (7.9)
Et	NEt_2	87	(152–153)	0.53 [d]	$C_{15}H_{28}N_2O_4PRh$	41.0 (41.5)	6.9 (6.4)	7.8 (7.1)
Et	OEt	78	(135–136) [b]	0.71 [d]	$C_{13}H_{22}NO_5PRh$	39.0 (38.3)	5.1 (5.6)	7.2 (7.6)
Et	NMe_2	91	101–102	0.53	$C_{13}H_{24}N_2O_4PRh$	37.9 (38.4)	5.2 (5.9)	7.0 (7.6)
Et	Pip	89	126–128	0.43 [d]	$C_{16}H_{28}N_2O_4PRh$	42.7 (43.0)	6.6 (6.3)	7.3 (7.0)

[a] The colour of the complexes varies from light yellow to yellow. [b] Liquids. [c] Silufol UV-254, tetrahydrofuran/hexane, 1/3. [d] 1/5. [e] First described in [3].

Table 6

Hydrogen atomic coordinates ($\times 10^3$) and their isotropic temperature factors B ($Å^2$) in the acacRh(CO)[EtN(CH$_2$)$_3$OPNMe$_2$] structure

Atom	x	y	z	B
H(1.1)	26(5)	467(2)	123(2)	1.4(7)
H(2.1)	167(5)	329(3)	152(3)	2.1(9)
H(3.1)	410(5)	377(3)	247(3)	2.2(9)
H(4.1)	575(4)	596(2)	273(2)	2.0(6)
H(5.1)	823(5)	490(3)	318(2)	2.4(9)
H(5.3)	716(6)	403(3)	282(3)	5.0(1)
H(6.2)	513(5)	791(3)	109(2)	2.3(9)
H(7.1)	704(5)	614(2)	110(2)	1.8(7)
H(7.3)	620(6)	667(3)	37(3)	3.0(9)
H(11.1)	−359(8)	756(4)	366(4)	8(2)
H(11.3)	242(8)	772(4)	439(4)	7(2)
H(12.2)	267(6)	478(3)	455(3)	4(1)
Atom	x	y	z	B
H(1.2)	66(5)	428(3)	44(3)	2.6(9)
H(2.2)	334(5)	369(3)	114(2)	2.2(8)
H(3.2)	231(5)	429(3)	258(2)	1.3(8)
H(4.2)	526(5)	516(3)	328(2)	2.0(8)
H(5.2)	792(6)	489(3)	228(3)	3.0(1)
H(6.1)	416(5)	773(2)	183(2)	1.3(7)
H(6.3)	613(5)	748(3)	193(3)	2.6(9)
H(7.2)	565(6)	566(3)	57(3)	3.0(9)
H(9)	−28(6)	650(3)	470(3)	4.0(1)
H(11.2)	−226(7)	833(3)	386(4)	6(1)
H(12.1)	195(6)	533(3)	511(3)	5(1)
H(12.3)	366(7)	572(4)	485(3)	7(1)

Table 7

Non-hydrogen atomic coordinates ($\times 10^4$; for Rh $\times 10^5$) and their isotropic equivalent temperature factors, B_{eq}^{iso} ($Å^2$), in the acacRh(CO)[EtN(CH$_2$)$_3$OPNMe$_2$] structure

Atom	x	y	z	B_{eq}^{iso}
Rh	10611(4)	66188(2)	22529(2)	1.36(1)
P	3086(1)	5912(1)	1600(1)	1.09(2)
O(1)	2233(3)	5346(2)	782(1)	1.43(6)
O(2)	−899(3)	7235(2)	2890(1)	1.60(6)
O(3)	2038(3)	5946(2)	3324(2)	1.80(6)
O(4)	−114(4)	7602(2)	680(2)	3.02(8)
N(1)	4566(4)	6597(2)	1226(2)	1.47(7)
N(2)	4297(4)	5046(2)	2105(2)	1.30(7)
C(1)	1213(5)	4504(3)	923(2)	1.80(9)
C(2)	2412(5)	3795(3)	1412(2)	1.90(9)
C(3)	3269(5)	4191(2)	2234(2)	1.66(9)
C(4)	5715(5)	5295(3)	2790(2)	1.71(9)
C(5)	7404(5)	4707(3)	2778(3)	2.3(9)
C(6)	4995(5)	7532(3)	1550(2)	1.83(9)
C(7)	5969(5)	6189(5)	784(2)	2.14(9)
C(8)	−1063(5)	7130(3)	3647(2)	1.76(9)
C(9)	18(5)	6547(3)	4204(2)	2.03(9)
C(10)	1463(5)	6007(3)	4024(2)	1.71(9)
C(11)	−2566(6)	768(3)	3954(3)	2.97(8)
C(12)	2520(6)	5429(3)	4698(3)	2.91(9)
C(13)	322(5)	7219(3)	1289(2)	1.81(9)

67%, b.p. 144–146 °C, R_f 0.55 (Silufol UV-254, tetrahydrofuran/hexane, 1/3), δ_p 138.9 ppm, ^1J(Rh–P) 227.6 Hz. Found: C, 41.3; H, 7.5; P, 6.0. $C_{16}H_{32}N_2O_4PRh$ calc: C, 42.7; H, 7.1; P, 6.9%. The complex with L = $P(OBu)_3$ is a yellow liquid. Yield 83%, decomposition temperature 135–137 °C, R_f 0.52 (tetrahydrofuran/hexane, 1/5), δ_p 132.8 ppm, ^1J(Rh–P) 262.6 Hz. Found: C, 45.2; H, 7.2; P, 6.3. $C_{18}H_{34}O_6$ PRh calc: C, 45.0; H, 7.1; P, 6.5%.

X-Ray structure of acacRh(CO)[EtN(CH$_2$)$_3$OPNMe$_2$]

Crystals of the acacRh(CO)[EtN(CH$_2$)$_3$OPNMe$_2$] complex are monoclinic; at −120 °C: a 7.434(2), b 14.266(5), c 16.358(6) Å, β 97.68(3)°, d_{calc} 1.624 g/cm^3, Z 4, space group $P2_1/n$. From the total 3674 independent reflections 2744 with $[F] \geq 8\delta$ were used in calculations and refinements. The structure was determined by the heavy-atom method and refined in a block diagonal anisotropic approximation. Difference electron density synthesis located all hydrogen atoms; these atoms were included in the refinement to an isotropic approximation. The final R value was 2.50 ($R_w = 3.70$). All calculations were carried out on an Eclipse S/200 computer using the INEXTL complex programmes [19]. The coordinates and temperature factors of nonhydrogen and hydrogen atoms in the structure are given in Tables 6, 7.

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