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Rhodium(I) complexes containing 4-pyridylmethylene-4'-alkoxyanilines as ligands: formation of rhodium containing liquid crystals by coordination of non-mesogenic organic ligands

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Abstract

The complexes $[\text{RhCl}(\text{COD})\text{L}]$ (COD = cyclocta-1,5-diene; $\text{L} = \text{NC}_3\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$) have been prepared by reaction of the corresponding L ($n = 8, 14$) ligands with $[\text{RhCl}(\text{COD})]_2$. They react with CO to give *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$ ($n = 2, 4, 6-10, 12, 14$). Reaction of *cis*-dicarbonyl compounds with L in the presence of Me_3NO gives *trans*- $[\text{RhCl}(\text{CO})\text{L}_2]$ ($n = 4, 8$). Monocarbonyl compounds of formulae $[\text{RhCl}(\text{CO})\text{L}(\text{P}(\text{OMe})_3)]$ ($n = 6, 8, 14$) have been made by reaction of *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$ with $\text{P}(\text{OMe})_3$ in dichloromethane. The mesogenic properties of the compounds $[\text{RhCl}(\text{CO})_2\text{L}]$ ($n = 8-10, 12, 14$) are described.

Introduction

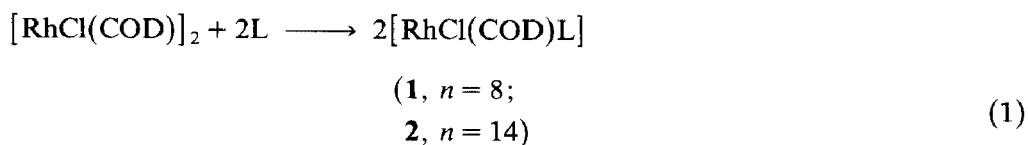
The chemistry of platinum group metal compounds with mesogenic ligands has received a great deal of attention [1–8]. Much of this interest has been stimulated by the potential applications of liquid crystals which contain metals [9,10]. For example, the choice of an appropriate metal ion can introduce colour or paramagnetism into the new material, and possibly give rise to other unusual optical or electric properties [11].

The number of rhodium complexes with liquid crystal properties remains small. Maitlis et al. have reported that mesogenic nitriles react with $[\text{RhCl}(\text{CO})_2]_2$ to cleave the chloride bridges and give the complexes *cis*- $[\text{RhCl}(\text{CO})_2\text{L}]$, which are mesogenic. However, these complexes show a nematic range of only 2°C before they decompose on clearing [3,4]. Mesogenic rhodium complexes with metal–metal bonds and carboxylate ligands have been described by Marchon et al. [5].

Recently we described the preparation of the first family of iridium-containing liquid crystals, *cis*-[IrCl(CO)L] (L = NC₅H₄CH=NC₆H₄OC_nH_{2n+1}). For *n* = 6 or 7 the complexes show monotropic transitions, whereas enantiotropic nematic and smectic phases are exhibited by the higher members of the series. These compounds were formed by complexation of the non-mesomorphic organic ligand to the metal [12]. In continuation of our work in this field, we now report the synthesis of new rhodium(I) complexes with the same ligands. These complexes are the first rhodium-containing liquid crystals formed by interaction of non-mesomorphic organic ligands with an organometallic rhodium fragment.

Results and discussion

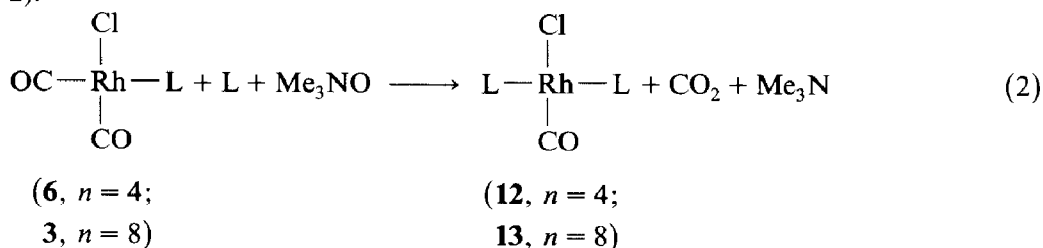
The dimeric complex [RhCl(COD)]₂ reacts with the ligands L = NC₅H₄CH=NC₆H₄OC_nH_{2n+1}, *n* = 8 and *n* = 14 in 1/2 molar ratio to form the square-planar complexes of general formula [RhCl(COD)L], according to eq. 1:



The IR (Nujol) spectra of these diolefinic complexes show the absorptions due to the pyridine ligands along with a single Rh–Cl stretching mode at 270 (1) or 265 (2) cm⁻¹, characteristic of a rhodium–chloro terminal bond *trans* to a C=C double bond [13]. The NMR spectra show the resonances expected for the ligands L and the CH₂ groups of the diene, the downfield displacement (ca. 0.2 ppm) of the α-pyridinic protons resonances of the ligand L in the complex relative to free ligand confirming that the pyridinic nitrogen is linked to the rhodium atom. At room temperature, only a single vinylic resonance is observed for the diolefin ligand, which suggests the existence of a rapid exchange process, such as was observed for some other similar systems [14,15].

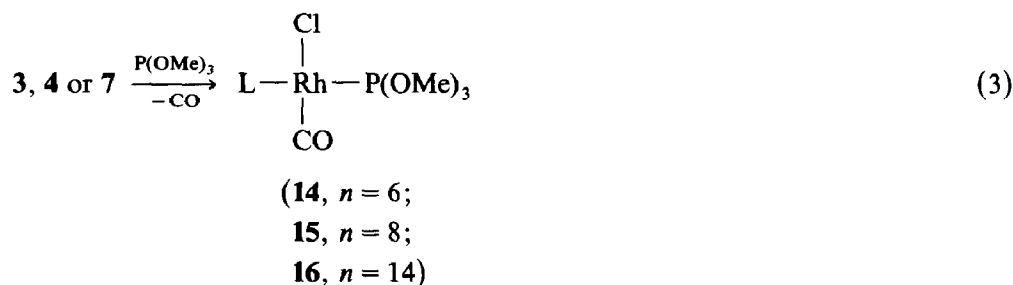
Bubbling of CO through a dichloromethane solution of 1 or 2 results in displacement of the coordinated olefin and formation of *cis*-[RhCl(CO)₂L] (*n* = 8 (3), 14 (4)). The analogous compounds 5–11 (*n* = 2 (5), 4 (6), 6 (7), 7 (8), 9 (9), 10 (10), 12 (11)) can be made by reaction of CO with the solution formed by addition of L to [RhCl(COD)]₂ in dichloromethane. These *cis*-dicarbonyl derivatives have been isolated as yellow air-stable microcrystalline solids in good yield (60–80%). The IR spectra in Nujol show a band at c.a. 320 cm⁻¹ attributable to a Rh–Cl terminal bond, while in dichloromethane solution there are two strong ν(CO) bands at 2085 and 2010 cm⁻¹, consistent with the *cis* geometry.

Monocarbonyl compounds of formulae [RhCl(CO)L₂] (*n* = 4 (12), 8 (13)) have been obtained by reaction of *cis*-[RhCl(CO)₂L] with L in presence of Me₃NO (eq. 2).



The spectroscopic data for **12** and **13** are in good agreement with the structures proposed. IR (Nujol) spectra have the $\nu(\text{CO})$ band at 1960 (**12**) or 1970 (**13**) cm^{-1} , along with a $\nu(\text{Rh}-\text{Cl})$ band at 285 (**12**) or 275 (**13**) cm^{-1} . The ^1H NMR spectra confirm that the ligands L are equivalent.

The dicarbonyl complexes also react with $\text{P}(\text{OMe})_3$. Addition of a one molar proportion of $\text{P}(\text{OMe})_3$ to **3**, **4** or **7** results in displacement of only one CO ligand and formation of the derivatives $[\text{RhCl}(\text{CO})\text{L}(\text{P}(\text{OMe})_3)]$ ($n = 6$ (**14**), 8 (**15**), 14 (**16**)) (eq. 3).



For the compounds **14**–**16** the NMR and IR spectra strongly support the structure shown in eq. 3. The ^{13}C NMR spectrum of **16** shows a signal at 183.6 ppm (CO) as a doublet of doublets, with Rh–C and P–C coupling constants of 80 and 21 Hz, respectively. The IR spectra in dichloromethane have a $\nu(\text{CO})$ band at 1995 cm^{-1} . Furthermore in the IR spectra in Nujol the $\nu(\text{Rh}-\text{Cl})$ bands appear at ca. 290 cm^{-1} . These spectroscopic data are in good agreement with those observed for other rhodium carbonyl complexes with similar structures [16].

Table 1
IR and $^{31}\text{P}\{^1\text{H}\}$ NMR data for the complexes **1**–**16** at 25 °C ^a

Complex	IR		^{31}P	
	$\nu(\text{CO})$	$\nu(\text{Rh}-\text{Cl})$	δ	$J(\text{Rh}-\text{P})$
1	–	270	–	–
2	–	265	–	–
3	2095,2005,1993,1983 (2085,2010) ^b	320	–	–
4	2095,2005,1992,1985 (2085,2010) ^b	315	–	–
5	2090,2070,2010 (2083,2010) ^b	324	–	–
6	2085,2070,2005, 1978 (2085,2010) ^b	315	–	–
7	2088,2000,1980 (2085,2010) ^b	325	–	–
8	2090,2000,1990,1983 (2085,2010) ^b	312	–	–
9	2092,2002,1990,1983 (2085,2010) ^b	315	–	–
10	2095,2010,1993,1985 (2085,2010) ^b	315	–	–
11	2095,2008,1993,1983 (2085,2010) ^b	315	–	–
12	1960(1965) ^b	285	–	–
13	1970(1965) ^b	275	–	–
14	1995(1992) ^b	285	135.2(d)	239
15	1998(1995) ^b	285	134.9(d)	240
16	1993(1995) ^b	300	135.2(d)	239

^a IR in Nujol, ν in cm^{-1} . ^{31}P in CDCl_3 , δ in ppm, J in Hz, standard 85% H_3PO_4 ext. ^b In CH_2Cl_2 . d = doublet.

Table 2

¹H NMR chemical shifts (ppm) and coupling constants (Hz) for complexes 1-4, 6, 12-16 (in CDCl₃)

Complex			CH=N	H ^a , H ^b ^a	OCH ₂	(CH ₂) _n	CH ₃	COD	P(OCH ₃) ₃	
	H ^α	H ^β ^a								H ^a , H ^b ^a
1	8.82	7.73	8.43(s)	7.27,6.92	3.97(t)	1.8-1.3	0.88(m)	4.1(br)	2.5(br), 1.8(br)	-
	<i>J</i> _{αβ} 6.5			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.5					
2	8.82	7.74	8.44(s)	7.28,6.93	3.98(t)	1.8-1.3	0.87(m)	4.2(br)	2.5(br), 1.8(br)	-
	<i>J</i> _{αβ} 6.5			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.5					
3	8.79	7.90	8.51(s)	7.43,6.95	3.99(t)	1.8-1.3	0.89(m)	-	-	-
	<i>J</i> _{αβ} 6.5			<i>J</i> _{ab} 8.8	<i>J</i> (HH) 6.5					
4	8.79	7.89	8.51(s)	7.33,6.95	3.99(t)	1.8-1.3	0.87(m)	-	-	-
	<i>J</i> _{αβ} 6.5			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.5					
6	8.79	7.90	8.51(s)	7.34,6.96	4.01(t)	1.7-1.5	0.99(m)	-	-	-
	<i>J</i> _{αβ} 6.5			<i>J</i> _{ab} 8.8	<i>J</i> (HH) 6.5					
12	9.05	7.71	8.46(s)	7.32,6.95	4.00(t)	1.7-1.5	0.99(m)	-	-	-
	<i>J</i> _{αβ} 6.5			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.5					
13	9.05	7.71	8.46(s)	7.31,6.94	3.99(t)	1.8-1.3	0.90(m)	-	-	-
	<i>J</i> _{αβ} 5.8			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.5					
14	8.95	7.83	8.49(s)	7.31,6.94	3.98(t)	1.8-1.3	0.90(m)	-	-	3.86(d)
	<i>J</i> _{αβ} 5.8			<i>J</i> _{ab} 8.8	<i>J</i> (HH) 6.5					<i>J</i> (PH) 12
15	8.94	7.82	8.48(s)	7.31,6.94	3.98(t)	1.8-1.3	0.88(m)	-	-	3.86(d)
	<i>J</i> _{αβ} 6.3			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.6					<i>J</i> (PH) 12
16	8.94	7.83	8.49(s)	7.32,6.94	3.99(t)	1.7-1.3	0.88(m)	-	-	3.86(d)
	<i>J</i> _{αβ} 5.8			<i>J</i> _{ab} 8.9	<i>J</i> (HH) 6.5					<i>J</i> (PH) 12

^a AA'XX' system. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet.

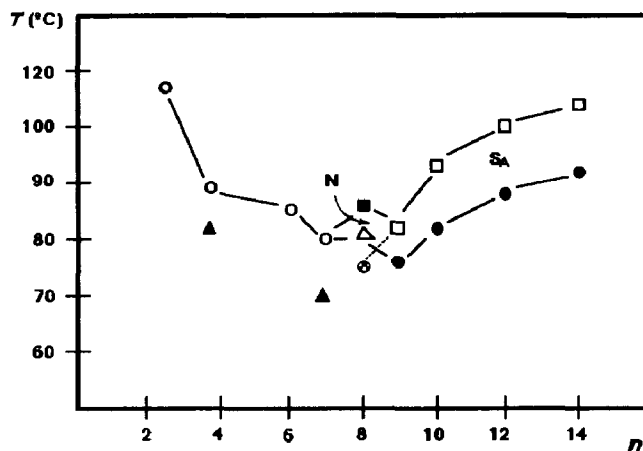


Fig. 1. Temperature transition data for *cis*-dicarbonyl derivatives 3, 4, 9–11.

The IR and NMR spectral data for the complexes 1–16 are listed in Tables 1 and 2. The assignment of the protons H^{α} and H^{β} of the pyridine ring is based on recent studies carried out on rhodium(I) and irridium(I) compounds with pyrazolyl alkanes as ligands [17,18].

Mesogenic properties

The *cis*-dicarbonyl derivatives 3, 4, 9–11 show mesogenic properties. The temperature and enthalpy data are shown in Fig. 1 and Table 3. For the higher members of the series only smectic A phases were observed, but compound 3 ($n = 8$) exhibits an enantiotropic nematic phase along with a monotropic S_A phase.

Table 3

Transition temperatures and enthalpy data for $[\text{RhCl}(\text{CO})_2\text{L}]$ complexes

Complex	n	Transition ^a	Temperature (°C)	ΔH (kJ mol ⁻¹)
$\text{RhCl}(\text{CO})_2\text{L}$	2	C–I	108.0	25.5
$\text{RhCl}(\text{CO})_2\text{L}$	4	C–C'	82.7	18.0
		C'–I	88.8	10.8
$\text{RhCl}(\text{CO})_2\text{L}$	6	C–I	85.1	23.0
$\text{RhCl}(\text{CO})_2\text{L}$	7	C–C'	70.5	
		C'–I	81.7	23.5 ^c
$\text{RhCl}(\text{CO})_2\text{L}$	8	C–N	78.8	19.5
		N–I	86.5	0.3
		N– S_A ^b	76.5	0.4
$\text{RhCl}(\text{CO})_2\text{L}$	9	C– S_A	76.3	32.6
		S_A –I	82.5	1.2
$\text{RhCl}(\text{CO})_2\text{L}$	10	C– S_A	82.8	36.1
		S_A –I	92.3	0.8
$\text{RhCl}(\text{CO})_2\text{L}$	12	C– S_A	87.6	45.3
		S_A –I	99.8	1.8
$\text{RhCl}(\text{CO})_2\text{L}$	14	C– S_A	92.9	48.7
		S_A –I	104.5	1.9

^a C: crystal, N: nematic, S_A : smectic A, I: isotropic. ^b Monotropic transition. ^c Combined enthalpies.

For all these compounds, the best textures were observed on cooling of the isotropic liquid. The textures obtained in this way are generally better for mesophase identification.

The nematic texture exhibited by **3** was identified by the appearance of nematic droplets at the clearing point on cooling from the isotropic phase, which form a typical nematic Schlieren texture. This texture displays dark brushes with irregular conical shapes and correspond to extinction positions of the nematic liquid. It is possible at some points to observe two or four dark brushes meeting [19].

The smectic A phases were identified by the appearance of batonnets in the clearing points. These batonnets collapse to give a focal conic fan texture. The fan-shaped texture contains optical discontinuities, and the usual focal conic-pair was clearly observed [20]. Under mechanical stress this texture gave way to a melinic one, with large areas of homeotropic texture.

None of the complexes **12–16** obtained showed mesogenic behaviour. The complexes $[\text{RhCl}(\text{CO})\text{L}_2]$ have a rod-like shape which should be very favourable for mesophase formation. In fact these compounds exhibit very high melting points (decomposition above 300 °C). These observations suggest that there are strong intermolecular interactions in the solid due to a favourable molecular geometry, and as a result mesophases can not be observed.

$[\text{RhCl}(\text{CO})\text{L}(\text{P}(\text{OMe})_3)]$ complexes have lower melting points than the $[\text{RhCl}(\text{CO})_2\text{L}]$ analogues; however the bigger size of $\text{P}(\text{OMe})_3$ group in relation to carbonyl prevents regular ordering on melting, and so the complexes do not exhibit mesogenic behaviour. Similarly the diolefinic complexes **1** and **2** do not exhibit mesogenic properties.

To the best of our knowledge, the mesogenic complexes previously described contained a liquid crystal ligand or, alternatively involved significant structural changes upon coordination of the organic ligand. Our results show that the new liquid crystals can be obtained by direct coordination to an organometallic fragment of a single molecule of a non mesogenic ligand. These materials represent further examples of mesomorphic complexes derived from non-mesogenic ligands.

Experimental

All reactions were carried out under nitrogen by Schlenk techniques. Starting materials L ($n = 2, 4, 6-10, 12, 14$) [21] and $[\text{RhCl}(\text{COD})]_2$ [22] were prepared by published methods. C, H, N, analysis were determined with a Perkin Elmer 240B microanalyzer. IR spectra were recorded on a Perkin Elmer spectrometer. ^1H , ^{31}P and ^{13}C NMR spectra were carried out in CDCl_3 solution at room temperature on a Varian XL 200 spectrometer. The melting points, transition temperatures, and enthalpies were determined with a Perkin Elmer DSC-2 differential scanning calorimeter. The optical observations were made with a Reichert-Termovar HT1B11 polarizing microscope equipped with a heating stage.

*Preparation of $[\text{RhCl}(\text{COD})\text{L}]$ (**1**, $n = 8$).* A solution of $[\text{RhCl}(\text{COD})]_2$ (25.0 mg; 0.05 mmol) in 10 ml of dichloromethane was treated with L ($n = 8$) (31.5 mg; 0.1 mmol) and the mixture was stirred for 30 min at room temperature. The solution was then concentrated under reduced pressure to ca. 0.5 ml. Slow addition of hexane led to precipitation of a yellow solid, which was filtered off, washed with hexane, and dried in vacuo. Yield 40 mg (70%). Anal. Found: C, 60.17; H, 6.68; N,

5.14. $C_{28}H_{38}N_2OClRh$ calcd.: C, 60.38; H, 6.87; N, 5.02%. Melting point $137.8^\circ C$; ΔH $28.35 \text{ kJ mol}^{-1}$.

Preparation of $[RhCl(COD)L]$ (2, $n = 14$). The procedure described for **1**, but starting from 50.0 mg (0.10 mmol) of $[RhCl(COD)]_2$ and 80.0 mg (0.20 mmol) of L ($n = 14$), gave a yellow microcrystalline solid. Yield 105 mg (81%). Anal. Found: C, 63.63; H, 8.25; N, 4.42. $C_{34}H_{50}N_2OClRh$ calcd.: C, 63.69; H, 7.86; N, 4.37%. Melting point $124.0^\circ C$.

Preparation of $cis-[RhCl(CO)_2L]$ (3, $n = 8$). A solution of **1** (226.0 mg; 0.40 mmol) in 20 ml of dichloromethane was stirred at room temperature under CO for 30 min. The solution was concentrated under reduced pressure and hexane added to give a yellow precipitate, which was filtered off, washed with hexane, and dried in vacuo. Yield 180 mg (88%). Anal. Found: C, 52.17; H, 5.41; N, 5.84. $C_{22}H_{26}N_2O_3ClRh$ calcd.: C, 52.34; H, 5.19; N, 5.54%.

Preparation of $cis-[RhCl(CO)_2L]$ (4, $n = 14$). The procedure described for **3**, but starting from 260.0 mg (0.40 mmol) of **2**, gave a yellow microcrystalline solid. Yield 200 mg (85%). Anal. Found: C, 57.70; H, 6.84; N, 4.90. $C_{28}H_{38}N_2O_3ClRh$ calcd.: C, 57.10; H, 6.50; N, 4.75%.

Preparation of $cis-[RhCl(CO)_2L]$ (5, $n = 2$). A solution of $[RhCl(COD)]_2$ (100.0 mg; 0.20 mmol) in 20 ml of dichloromethane was treated with L ($n = 2$) (91.8 mg; 0.4 mmol) and the mixture then stirred for 30 min under a CO atmosphere. The solution was concentrated under reduced pressure and hexane added to give an orange precipitate, which was filtered off, washed with hexane, and dried in vacuo. Yield 108 mg (63%). Anal. Found: C, 46.34; H, 3.78; N, 6.66. $C_{16}H_{14}N_2O_3ClRh$ calcd.: C, 45.68; H, 3.35; N, 6.65%.

Preparation of $cis-[RhCl(CO)_2L]$ (6, $n = 4$, 7, $n = 6$; 8, $n = 7$; 9, $n = 9$, 10, $n = 10$; 11, $n = 12$). The complexes **6–11** were prepared by the procedure described for **5**. Details of the analytical data, yields, and colours of these compounds are given in Table 4.

Preparation of $trans-[RhCl(CO)L_2]$ (12, $n = 4$). A solution of **6** (70 mg; 0.15 mmol) in 10 ml of acetone was treated with L ($n = 4$) (39.7 mg; 0.15 mmol) and Me_3NO (11.3 mg; 0.15 mmol) and the mixture stirred for 3 h at room temperature.

Table 4

Colour, microanalyses and yields for the complexes **6–11**

Complex	Colour	Analysis (Found (calcd) (%))			Yield (%)
		C	H	N	
6	orange	47.90 (48.18)	4.21 (4.04)	6.44 (6.24)	75
7	yellow	50.04 (50.38)	4.97 (4.65)	6.09 (5.87)	75
8	yellow	51.17 (51.39)	5.10 (4.92)	5.45 (5.70)	75
9	yellow	53.21 (53.24)	5.65 (5.44)	5.27 (5.40)	81
10	yellow	54.01 (54.09)	5.65 (5.67)	5.69 (5.25)	65
11	yellow	56.16 (55.67)	6.42 (6.10)	5.05 (4.99)	56

The orange precipitate was filtered off, washed with acetone, and dried in vacuo. Yield 31 mg (30%) Anal. Found: C, 58.47; H, 5.45; N, 8.14. $C_{33}H_{36}N_4O_3ClRh$ calcd.: C, 58.72; H, 5.37; N, 4.89%.

Preparation of trans-[RhCl(CO)L₂] (13, n = 8). The procedure described for **12**, but starting from 100.0 mg (0.20 mmol) of **3** and 61.0 (0.20 mmol) of L (n = 8) and 15.0 (0.20 mmol) of Me₃NO, gave an orange microcrystalline solid. Yield 48 mg (31%). Anal. Found: C, 62.44; H, 7.02; N, 6.99. $C_{41}H_{52}N_4O_3ClRh$ calcd.: C, 62.55; H, 6.65; N, 7.11%.

Preparation of [RhCl(CO)L(P(OMe)₃)] (14, n = 6). A solution of **7** (144.0 mg; 0.30 mmol) in 10 ml of dichloromethane was treated with P(OMe)₃ (35 μl; 0.30 mmol) and the mixture stirred for 1 h. The solution was concentrated under reduced pressure and hexane added to give a yellow precipitate, which was filtered off, washed with hexane, and dried in vacuo. Yield 100 mg (58%). Anal. Found: C, 45.72; H, 5.08; N, 4.87. $C_{22}H_{31}N_2O_5ClPRh$ calcd.: C, 46.12; H, 5.45; N, 4.89%. Melting point: 71.5 °C.

Preparation of [RhCl(CO)L(P(OMe)₃)] (15, n = 8). The procedure described for **14**, but starting from 400.0 mg (0.79 mmol) of **3** and 93 μl (0.79 mmol) of P(OMe)₃, gave a yellow microcrystalline solid. Yield 350 mg (73%). Anal. Found: C, 48.52; H, 6.11; N, 4.75. $C_{24}H_{35}N_2O_5ClPRh$ calcd.: C, 47.97; H, 5.87; N, 4.66%. Melting point 77.1 °C; $\Delta H = 31.2 \text{ kJ mol}^{-1}$.

Preparation of [RhCl(CO)L(P(OMe)₃)] (16, n = 14). The procedure described for **14**, but starting from 100.0 mg (0.17 mmol) of **4** and 20 μl (0.17 mmol) of P(OMe)₃, gave a yellow microcrystalline solid. Yield 89 mg (76%). Anal. Found: C, 51.92; H, 7.44; N, 3.96. $C_{30}H_{38}N_2O_5ClPRh$ calcd.: C, 52.59; H, 6.91; N, 4.08%. Melting point 68.7 °C; $\Delta H 62.8 \text{ kJ mol}^{-1}$.

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