# New Mixed-ligand Isocyanide Diphosphine Ruthenium(II) Derivatives. Synthesis of a Potential Metal-containing Tetradentate Ligand

## Javier Ruiz, Victor Riera\* and Marilin Vivanco

Instituto de Química Organometálica, Universidad de Oviedo, 33071 Oviedo, Spain

Reaction of *trans*-[RuCl<sub>2</sub>(CNPh)<sub>4</sub>] with an excess of Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm) in refluxing toluene gave two complexes *cis,cis,trans*-[RuCl<sub>2</sub>(CNPh)<sub>2</sub>(dppm-*P*)<sub>2</sub>] **1** and *mer*-[RuCl(CNPh)<sub>3</sub>(dppm)]Cl **2a**; whereas in the reaction of *trans*-[RuCl<sub>2</sub>(CNBu<sup>t</sup>)<sub>4</sub>] with dppm under the same conditions only *mer*-[RuCl-(CNBu<sup>t</sup>)<sub>3</sub>(dppm)]Cl **2b** was obtained. Complex **1** reacted with TIPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> to give [RuCl(CNPh)<sub>2</sub>(dppm)(dppm-*P*)]PF<sub>6</sub> **3**, a cationic complex containing both a monodentate and a chelated dppm ligand. Complex **1** is remarkable in having two monohapto dppm ligands and can be used in the synthesis of heterometallic species. Thus, treatment of **1** with AgClO<sub>4</sub> or HgCl<sub>2</sub> gave the heterometallic complex [(dppm)(PhNC)<sub>2</sub>CIRu( $\mu$ -dppm)AgCl]ClO<sub>4</sub> **4** or [{(dppm)(PhNC)<sub>2</sub>CIRu-( $\mu$ -dppm)HgCl<sub>2</sub>}]Cl<sub>2</sub> **5** respectively.

Tertiary phosphine halide complexes of ruthenium(II) have received much attention in the literature<sup>1</sup> due to their relevance to homogeneous catalysis, with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] being one of the most active catalysts in the hydrogenation of alkenes.<sup>2</sup> The corresponding diphosphine (L-L) derivatives have also been widely studied, mainly those of the type  $[RuX_2(L-L)_2]$  (X = halide).<sup>3</sup> Mixed-ligand isocyanide phosphine complexes of general formula  $[RuX_2(CNR)_2(PR'_3)_2]^4$  (various isomers; R,  $\mathbf{R}' = alkyl \text{ or } aryl)$  are also known. However, to our knowledge there is no report of mononuclear mixed-ligand isocyanide diphosphine ruthenium(II) derivatives. In this respect we present here the synthesis and spectroscopic characterization of neutral and cationic octahedral ruthenium(II) complexes of the type  $cis, cis, trans-[RuCl_2(CNPh)_2(dppm-P)_2] = 1$ , mer-[RuCl(CNR)<sub>3</sub>(dppm)]Cl (R = Ph **2a** or Bu<sup>t</sup> **2b**), [RuCl(CNPh)<sub>2</sub>(dppm)(dppm-P)]PF<sub>6</sub> **3**, and the silver and mercury adducts of 1, [(dppm)(PhNC)<sub>2</sub>ClRu(µ-dppm)AgCl]- $ClO_4 4 and [{(dppm)(PhNC)_2ClRu(\mu-dppm)HgCl_2}_2]Cl_2 5.$ 

A high-yield one-pot synthesis of  $[RuCl_2(CNPh)_4]^5$  is also described in this paper (Experimental section). This isocyanide complex is a valuable starting material for the preparation of a variety of neutral and cationic ruthenium(II) derivatives as shown in this work.

### **Results and Discussion**

Treatment of trans-[RuCl<sub>2</sub>(CNPh)<sub>4</sub>] with an excess of dppm in refluxing toluene gives a mixture of neutral cis, cis, trans-[RuCl<sub>2</sub>(CNPh)<sub>2</sub>(dppm-P)<sub>2</sub>] 1 and cationic mer-[RuCl(CN-Ph)<sub>3</sub>(dppm)]Cl 2a which can easily be separated by the different solubilities in toluene (see Experimental section). The spectroscopic and analytical data (Tables 1 and 2) are in accordance with the structures proposed for these complexes in Scheme 1. Thus for 1 the cis arrangement of the phenyl isocyanides is supported by the presence in its infrared spectrum of two intense v(CN) bands at 2140 and 2086 cm<sup>-1</sup>. In its <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum the two mutually *trans* monohapto dppm ligands appear as two virtual triplets ( $\delta$  25.8 and -28.1) due to a deceptively simple AA'XX' spin system. The same pattern has been found for *trans*-[Pt(C=CR)<sub>2</sub>(dppm-P)<sub>2</sub>] (R = Ph or p-MeC<sub>6</sub>H<sub>4</sub>).<sup>6a</sup> Moreover, the <sup>13</sup>C NMR spectrum of 1 shows a triplet at  $\delta$  163.7 for the CNPh carbons, arising from coupling to the two phosphorus atoms directly bonded to ruthenium. Interestingly the methylene carbons of the

diphosphine appear as a doublet of triplets centred at  $\delta$  20.9. Since there is only one <sup>13</sup>C atom per molecule, due to the very low natural abundance of <sup>13</sup>C, the methylene carbons form the X part of an AA'MM'X spin system, where A and A' are the two <sup>31</sup>P atoms bonded to ruthenium and M and M' the two uncoordinated <sup>31</sup>P atoms. So, the observed <sup>13</sup>C NMR spectrum can be explained considering a deceptively simple AA'MM'X spin system, with <sup>5</sup>J(M'X) = 0<sup>7</sup> (see Experimental section).

Complex 1 can be regarded as a potential tetradentate ligand through the two free phosphorus atoms and the two chlorine atoms, thus being a promising starting material for the synthesis of heterometallic species. In this context, Shaw and co-workers<sup>6</sup> have shown the ability of complexes of the type  $[PtX_2(dppm-P)_2]$  (X = C=CR or CN) to act as bidentate ligands toward a lot of metallic fragments, and the same group has demonstrated that the rhenium complexes  $[ReH_5(dppen)_2(dppm-P)]$ (dppen = Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>)<sup>8</sup> and  $[ReH_5{P(C_6H_{11})_3}_2-(dppm-P)]$ <sup>9</sup> behave as tridentate ligands toward a second metal through the phosphorus and two hydrogen atoms.

The other product obtained in the reaction of cis-[RuCl<sub>2</sub>-(CNPh)<sub>4</sub>] with dppm corresponds to **2a**. The conductivity value in acetone is in the range observed for 1:1 electrolytes, and this accounts for its low solubility in most common non-polar organic solvents. The v(CN) pattern in the infrared spectrum (Table 2) is typical for a *mer* arrangement of the isocyanide, and this disposition is also supported by the presence of two doublets in its <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum arising from the two inequivalent phosphorus atoms of the diphosphine. In iron chemistry we have already described similar cationic mixed-ligand isocyanide diphosphine complexes.<sup>10</sup>

In order to evaluate the influence of the nature of the isocyanide in the substitution reactions, the alkyl isocyanide derivative cis-[RuCl<sub>2</sub>(CNBu')<sub>4</sub>]<sup>11</sup> was also treated with an excess of dppm in refluxing toluene. The only product formed was *mer*-[RuCl(CNBu')<sub>3</sub>(dppm)]Cl 2b. The absence of any neutral complex similar to 1 may be due to the more basic character of CNBu' compared with CNPh, which facilitates substitution of the chloride in the co-ordination sphere of ruthenium.

On the other hand, the elimination of a chloride ligand of complex 1 by treatment with  $TIPF_6$  gives 3, a cationic complex containing both a monodentate and a chelated dppm ligand. The presence of two strong v(CN) bands in the IR spectrum indicates that the *cis* arrangement of the isocyanide is



Scheme 1 (i) dppm; (ii) TlPF<sub>6</sub>; (iii) AgClO<sub>4</sub>; (iv) HgCl<sub>2</sub>; (v) AgCl

Table 1	${}^{31}P-{}^{1}H$	NMR	data f	or compounds	1-5"
				0	

Com- plex	<i>T/</i> ℃	$\delta^{b}$				Coupling constants (Hz) <sup>c</sup>					
		P <sub>A</sub>	P <sub>B</sub>	Pc	P <sub>D</sub>	$\overline{{}^{2}J(\mathbf{P}_{\mathbf{A}}\mathbf{P}_{\mathbf{B}})}$	$^{2}J(\mathbf{P_{A}P_{C}})$	$^{4}J(\mathbf{P}_{\mathbf{A}}\mathbf{P}_{\mathbf{D}})$	$^{2}J(\mathbf{P_{C}P_{D}})$	$^{2}J(P_{B}P_{C})$	Other
1	20			25.8 (t)	-28.1 (t)			$^{2}J(\mathbf{P_{C}P_{D}})$	$+ {}^{4}J(P_{C}P_{D})$	() = 38	
2a	20	6.9 (d)	-27.0 (d)			45					
2b	20	8.4 (d)	-25.7 (d)			45					
3	20	-4.2 (ddd)	-22.1 (t)	24.1 (ddd)	-28.7 (dd)	34	282	8	42	29	
4	20	-4.3 (ddd)	-21.7 (dd)	20.7 (dd)	-9 (br)	37	284	10	0	30	${}^{1}J(\mathrm{AgP}_{\mathrm{D}}) = 683^{d}$
	-85	-3.4	-21.2	18.5	-7.7 (d,br)	n.r.	280	n.r.	n.r.	n.r.	
5	20	-4.4 (ddd)	-22.2 (t)	20.8 (dd)	5.9 (br)	35	287	11		30	
	-85	-3.1 (ddd)	-22.3 (t)	18.8 (ddd)	14.9 (s)	32	285	9	19	30	${}^{1}J(\text{HgP}_{\text{D}}) = 6880$

<sup>*a*</sup> Chemical shifts ( $\delta$ ) in ppm positive to high frequency relative to external 85% H<sub>3</sub>PO<sub>4</sub>. In CD<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup> s = Singlet, d = doublet, dd = doublet of doublets, dd = doublet, br = broad. <sup>*c*</sup> n.r. = Not resolved. <sup>*d*</sup> Separate couplings to <sup>109</sup>Ag and <sup>107</sup>Ag not resolved.

Table 2 Infrared, analytical and conductivity data for compounds 1-5

		Analysi	$\Lambda_{\rm M}^{\rm c}$		
Compound	$IR^{a}/cm^{-1}$	C	Н	N	$\Omega^{-1}$ cm <sup>2</sup>
1	2140s	67.25	4.55	2.75	
	2086s	(67.00)	(4.75)	(2.45)	
2a	2189w	63.35	4.20	5.05	100
	2151s	(63.80)	(4.30)	(4.85)	
2b	2205w	59.35	5.90	5.15	118
	2169s	(59.60)	(6.15)	(5.20)	
3	2155s	61.45	4.20	2.05	125
	2116s	(61.20)	(4.35)	(2.25)	
4	2157s	56.30	3.80	2.25	112
	2119s	(56.75)	(4.00)	(2.05)	
5	2163s	54.70	4.00	1.85	227
	2123s	(54.20)	(3.85)	(1.95)	
a s = Strong, given in parer	w = weak; m otheses. $^{\circ} 5 \times 1^{\circ}$	easured in 0 <sup>-4</sup> mol dm <sup>-1</sup>	$CH_2Cl_2$ . <sup>3</sup> in aceto	<sup>b</sup> Calcula ne.	ated values

maintained during substitution. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum unambiguously established the disposition of the diphosphines shown in Scheme 1. As shown in Table 1, coupling constants between inequivalent phosphorus atoms are observed except for <sup>2</sup> $J(P_BP_D)$ . Of note is <sup>2</sup> $J(P_AP_C)$  of 282 Hz which is typical of *trans* phosphines co-ordinated to ruthenium(II).

When the abstraction of the halide from complex 1 was carried out with AgClO<sub>4</sub> a quite different result was obtained. In this case chelation of one dppm also takes place but at the same time the AgCl formed co-ordinates the free phosphorus of the remaining monodentate diphosphine. Thus, the heterometallic complex 4 was obtained. The structure proposed in Scheme 1 is supported by the analytical and spectroscopic data given in Tables 1 and 2. The conductivity value in acetone indicates that 4 is a 1:1 electrolyte and so the  $ClO_4^-$  anion is not coordinated. The IR spectrum in the v(CN) region is again typical of a cis isocyanide (two strong bands), and the wavenumbers of the bands are only 3 cm<sup>-1</sup> higher than those of 3, indicating that the long-range electronic interaction between silver and ruthenium is rather weak. In fact, 3 can be considered as a precursor of 4, thus on treating 3 with 1 equivalent of AgCl the cationic complex 4 was obtained, although when prepared in this way the counter anion is  $PF_6^-$  (see Scheme 1).

Major information about the structure of complex 4 is gained from its <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum. At room temperature it consists of four signals; the three corresponding to  $P_A$ ,  $P_B$  and  $P_C$  appear at chemical shifts close to those of the related phosphorus atoms in 3. The phosphorus co-ordinated to silver,  $P_D$ , appears as a broad resonance at  $\delta - 9$ ; the broadness of this signal may be due to a rapid exchange of the phosphorus bonded to silver which usually occurs in silver-phosphine complexes. The values for the coupling constants between all phosphorus atoms in 4 are very similar to those in 3 (see Table 1) with the exception of  ${}^{2}J(P_{C}P_{D})$  which in this case is not observed. At -85 °C the resonance corresponding to P<sub>D</sub> is split into a broad doublet, indicating that the phosphine exchange at silver has stopped, although the resolution of the spectrum was not good enough to separate couplings to  ${}^{107}Ag$  and  ${}^{109}Ag$ , the average value of  ${}^{1}J({}^{107}AgP_{D})$  and  ${}^{1}J({}^{109}AgP_{D})$  being 683 Hz.

In the reaction of complex 1 with 1 equivalent of HgCl<sub>2</sub> the heterometallic Ru/Hg complex 5 was obtained, for which we propose the dimeric structure in Scheme 1. In tungsten carbonyl chemistry a complex closely related to 5 has been described, [{(OC)<sub>5</sub>WPPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}<sub>2</sub>Hg<sub>2</sub>Cl<sub>4</sub>],<sup>12</sup> although in that case the diphosphine was dppe. From the <sup>31</sup>P NMR spectrum of 5 it can be readily deduced that chelation of one dppm at ruthenium occurs, and at the same time the free phosphorus of the other dppm co-ordinates to mercury. Thus, at room temperature the  ${}^{31}$ P NMR spectrum consists of four signals, P<sub>A</sub>, P<sub>B</sub> and P<sub>C</sub> having similar chemical shifts and coupling constants to those of the corresponding phosphorus in 3 and 4. The signal of  $P_{\rm D}$  appears as a very broad resonance at  $\delta$  5.9. As with complex 4, the broadness of this signal may be due to a rapid exchange of the phosphorus bonded to mercury. On decreasing the temperature the exchange process ceases, thus at  $-85 \text{ }^\circ\text{C}\text{ }P_D$ appears as a slightly broad signal with <sup>199</sup>Hg satellites (I = $\frac{1}{2}$  [<sup>1</sup>J(HgP) = 6880 Hz]. These data do not preclude a monomeric neutral structure for 5 of the type [(dppm)-(PhNC)<sub>2</sub>ClRu(µ-dppm)HgCl<sub>3</sub>]. A similar tetrahedral environment around Hg [with the framework Hg(P)Cl<sub>3</sub>] is present in the anion  $[Hg(PEtMe_2)Cl_3]^{-.13}$  However, the conductivity value for 5 in acetone is typical for a 2:1 electrolyte and so two chloride groups must be dissociated, thus supporting the cationic dimeric structure we propose for 5. Moreover, the high value of  ${}^{1}J(\text{HgP})$  (6880 Hz) is in accordance with the presence in the complex of a dimer  $Hg_2P_2(\mu-Cl)_2Cl_2$  core. In this respect it is well established that for mononuclear complexes the values for  ${}^{1}J(\text{HgP})$  are always less than 5000 Hz, whereas for dinuclear phosphine halide mercury complexes this value is about 7000 Hz.<sup>14</sup>

In conclusion in this work we have carried out the synthesis of several mixed-ligand isocyanide dppm ruthenium(II) derivatives, amongst them the remarkable neutral complex  $[RuCl_2(CNPh)_2(dppm-P)_2]$  1, which can be considered as a potential tetradenate ligand. However, in the treatment of 1 with Group 11 (AgClO<sub>4</sub>) and 12 (HgCl<sub>2</sub>) metallic fragments, the abstraction of a chloride group occurs with concomitant chelation of a dppm ligand at ruthenium, giving rise to the heterometallic Ru/Ag and Ru/Hg complexes 4 and 5 respectively. We are currently investigating the co-ordination ability of 1 towards a variety of early and middle transitionmetal fragments.

#### Experimental

General Remarks.—All reactions were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Solvents were dried and purified by standard techniques and distilled under nitrogen prior to use. All reactions were monitored by IR spectroscopy (Perkin-Elmer FT 1720-X spectrophotometer). The C, H and N analyses were performed on a Perkin-Elmer 240B elemental analyser. Proton, <sup>13</sup>C and <sup>31</sup>P NMR spectra were measured with Bruker AC-300 and AC-200 instruments. Chemical shifts are given in ppm, relative to internal SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) or external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). The complex *trans*-[RuCl<sub>2</sub>(CNBu<sup>t</sup>)<sub>4</sub>], <sup>11</sup> phenyl isocyanide <sup>15</sup>

The complex *trans*-[RuCl<sub>2</sub>(CNBu<sup>1</sup>)<sub>4</sub>],<sup>11</sup> phenyl isocyanide<sup>15</sup> and dppm<sup>16</sup> were prepared as described elsewhere. All other reagents were obtained from commercial sources and used without further purification.

Preparations.—trans-[RuCl<sub>2</sub>(CNPh)<sub>4</sub>]. A mixture containing RuCl<sub>3</sub>·3H<sub>2</sub>O (0.1 g, 0.38 mmol), phenyl isocyanide (0.3 g, 2.9 mmol), cyclohexa-1,3-diene (1 cm<sup>3</sup>), toluene (20 cm<sup>3</sup>) and ethanol (1 cm<sup>3</sup>) was heated at 90 °C for 15 min. After this period of time a yellow solid corresponding to *trans*-[RuCl<sub>2</sub>(CNPh)<sub>4</sub>] appeared. It was filtered off, washed with toluene (2 × 20 cm<sup>3</sup>) and dried under vacuum. Yield: 0.18 g (81%). IR(CH<sub>2</sub>Cl<sub>2</sub>) v(CN) 2139s cm<sup>-1</sup>.

cis,cis,trans-[RuCl<sub>2</sub>(CNPh)<sub>2</sub>(dppm-P)<sub>2</sub>] 1 and mer-[RuCl(CNPh)<sub>3</sub>(dppm)]Cl 2a. A solution of trans-[RuCl<sub>2</sub>-(CNPh)<sub>4</sub>] (0.18 g, 0.308 mmol) and dppm (0.42 g, 1.09 mmol) in toluene (20 cm<sup>3</sup>) was refluxed for 24 h. A white precipitate corresponding to complex 2a was formed. This was filtered off, washed with toluene (20 cm<sup>3</sup>) and dried under vacuum (0.11 g, 41%). The remaining toluene solution was evaporated to dryness and the residue washed with hot hexane (40 cm<sup>3</sup>) to eliminate the excess of dppm. The white solid which remains insoluble in hexane corresponds to 1. This was filtered off and dried under vacuum. Yield: 0.15 g (42.5%). NMR(CD<sub>2</sub>Cl<sub>2</sub>): 1,  $\delta_{\rm H}$  4.06 (br, 4 H, P<sub>2</sub>CH<sub>2</sub>) and 6.1–7.8 (50 H, C<sub>6</sub>H<sub>5</sub>);  $\delta_{\rm C}$  20.9 [dt, P<sub>2</sub>CH<sub>2</sub>, <sup>1</sup>J(P<sub>c</sub>C) + <sup>3</sup>J(P<sub>c</sub>C) = 24, <sup>1</sup>J(P<sub>p</sub>C) = 31] and 163.7 [t, CNPh, <sup>2</sup>J(PC) = 12]; **2a**,  $\delta_{\rm H}$  5.82  $[t, 2H, P_2CH_2, {}^2J(PH) = 10]$  and 6.4-8.3 (35 H,  $C_6H_5$ );  $\delta_C 44.5$  $[t, P_2CH_2, {}^1J(PC) = 28], 152.5 [d, 1 C, {}^2J(PC_{trans}) = 106 \text{ Hz}]$ and 155 (br, 2 C, CNPh)

*mer*-[RuCl(CNBu<sup>1</sup>)<sub>3</sub>(dppm)]Cl **2b**. To a solution of *trans*-[RuCl<sub>2</sub>(CNPh)<sub>4</sub>] (0.1 g, 0.198 mmol) in toluene (20 cm<sup>3</sup>) was added an excess of dppm (0.23 g, 0.6 mmol) and the resultant mixture was refluxed for 24 h. Complex **2b** was formed as a white microcrystalline precipitate. This was filtered off, washed with cold toluene (20 cm<sup>3</sup>) and dried under vacuum. Yield: 0.12 g, 75%.  $\delta_{\rm H}$ (CDCl<sub>3</sub>): 0.75 (s, 18 H, CNBu<sup>1</sup>), 1.68 (s, 9 H, CNBu<sup>1</sup>), 7.19 [t, 2 H, P<sub>2</sub>CH<sub>2</sub>, <sup>2</sup>J(PH) = 7 Hz] and 7.5–8.2 (20 H, C<sub>6</sub>H<sub>5</sub>).

[RuCl(CNPh)<sub>2</sub>(dppm)(dppm-P)]PF<sub>6</sub> 3. The salt TIPF<sub>6</sub> (61 mg, 0.174 mmol) was added to a solution of complex 1 (0.2 g, 0.174 mmol) in dichloromethane (30 cm<sup>3</sup>) and the resultant suspension was stirred for 2 h. The white precipitate of TICl was then filtered off and the colourless solution concentrated to 3 cm<sup>3</sup>. Hexane (10 cm<sup>3</sup>) was added and the mixture set aside at -20 °C for 48 h. The resultant white microcrystalline solid of the required product was filtered off, washed with hexane (20 cm<sup>3</sup>) and dried under vacuum. Yield: 0.19 g, 87%.

[(dppm)(PhNC)<sub>2</sub>ClRu( $\mu$ -dppm)AgCl]ClO<sub>4</sub> **4**. The salt AgClO<sub>4</sub> (17 mg, 0.082 mmol) was added to a solution of complex **1** (95 mg, 0.082 mmol) in dichloromethane (30 cm<sup>3</sup>) and the resultant suspension was stirred for 1 h. After this period the white precipitate of AgClO<sub>4</sub> had completely dissolved. Concentration of the solution to 3 cm<sup>3</sup>, addition of hexane (10 cm<sup>3</sup>) and cooling (-20 °C) gave a white solid of the required product **4**. This was filtered off, washed with hexane (20 cm<sup>3</sup>) and dried under vacuum. Yield: 78 mg, 70%.

[{(dppm)(PhNC)<sub>2</sub>ClRu( $\mu$ -dppm)HgCl<sub>2</sub>]<sub>2</sub>]Cl<sub>2</sub>5. Mercury(II) chloride (23 mg, 0.085 mmol) was added to a solution of complex 1 (98 mg, 0.085 mmol) in dichloromethane (30 cm<sup>3</sup>) and the resultant mixture was stirred for 3 h. A colourless solution was formed. This was concentrated to 3 cm<sup>3</sup>, hexane was added and the mixture set aside at -20 °C for 24 h. This gave a white solid of 5 which was filtered off, washed with hexane (20 cm<sup>3</sup>) and dried. Yield: 94 mg, 78%.

#### Acknowledgements

We gratefully acknowledge the financial assistance of Dirección General de Investigación Científica y Técnica (Project PB91-0678).

## References

- 1 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, New York, 1984, pp. 487-529.
- 2 L. H. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Plenum, New York, 1983.

- 3 J. Chatt and R. G. Hayter, J. Chem. Soc., 1961, 772, 896; J. T. Maque and J. P. Mitchener, Inorg. Chem., 1972, 11, 2714; R. Mason, and J. T. Micheler, *Morg. Chem.*, 1972, 11, 2114, R. Mason,
  D. W. Meek and G. R. Scollary, *Inorg. Chim. Acta*, 1976, 16, L11;
  M. Bressan and P. Rigo, *Inorg. Chem.*, 1975, 14, 2286; B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1982, 21, 1037.
  4 B. E. Prater, *J. Organomet. Chem.*, 1971, 27, C17; *J. Organomet. Chem.*, 1972, 34, 379; J. Chatt, R. L. Richards and G. H. D. Royston, *L. Chem. San Delter, Terres*, 1422, 1432.
- J. Chem. Soc., Dalton Trans., 1973, 1433.
- 5 F. Faraone and V. Marsala, Inorg. Chim. Acta, 1978, 27, L109.
- 6 (a) P. G. Pringle and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 581; (b) D. M. McEwan, P. G. Pringle and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 859; (c) W. S. McDonald, P. G. Pringle and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 861; (d) P. G. Pringle and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 956.
- 7 D. E. Axelson and C. E. Holloway, J. Chem. Soc., Chem. Commun., 1973, 455; M. Aktar, P. D. Ellis, A. G. MacDiarmid and J. D. Odom, Inorg. Chem., 1972, 11, 2917; D. A. Redfield, L. W. Cary and

- J. H. Nelson, *Inorg. Chem.*, 1976, **15**, 732. 8 X. L. R. Fontaine, T. P. Layzell and B. L. Shaw, *J. Chem. Soc.*, *Dalton* Trans., 1994, 379.
- 9 S. W. Carr, X. L. R. Fontaine and B. L. Shaw, J. Chem. Soc., Dalton Trans., 1991, 1025.
- 10 V. Riera, J. Ruiz and F. Mayor, J. Organomet. Chem., 1984, 276, 47. 11 J. M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard
- and F. G. A. Stone, J. Chem. Soc., Dalton Trans., 1979, 1003. 12 R. L. Keiter, K. M. Fasig and L. W. Cary, Inorg. Chem., 1975, 14, 201.
- 13 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, Acta Crystallogr., Sect. B, 1980, 36, 708; Inorg. Chim. Acta, 1978, 28, L169.
- 14 S. O. Grim, P. J. Lui and R. L. Keiter, Inorg. Chem., 1974, 13, 342. 15 W. D. Weber, G. W. Gokel and I. K. Ugi, Angew. Chem., Int. Ed.
- Engl., 1972, 11, 530.
- 16 A. M. Aguiar and J. Beisler, J. Organomet. Chem., 1964, 29, 1660.

Received 19th October 1994; Paper 4/06404F

J. CHEM. SOC. DALTON TRANS. 1995