Cationic Ruthenium(II) Phosphite Complexes. Preparation and Properties of Monocarbonyl and Isocyanide Derivatives†

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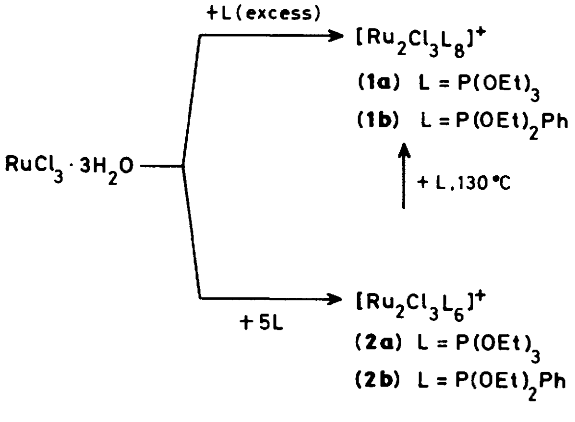
Mono- and tri-μ-chloro ruthenium(II) complexes $[Ru_2Cl_3L_8]BPh_4$ and $[Ru_2Cl_3L_6]BPh_4$ [L = $P(OEt)_3$ or $P(OEt)_2Ph$] were prepared by allowing ruthenium trichloride to react with phosphite in refluxing ethanol. Cationic carbonyl derivatives of the type *trans*-$[RuCl(CO)L_4]^+$ were also prepared by the carbonylation reaction of a phosphite-containing $RuCl_3$ solution. The reaction of all these compounds with isocyanide was examined and led to the synthesis of the new $[RuCl(RNC)_2L_3]^+$, $[Ru(RNC)_3L_3]^{2+}$, and $[RuCl(CO)(RNC)L_3]^+$ derivatives. Characterization of the complexes by i.r. and ^1H and ^{31}P n.m.r. data is also discussed.

A large range of studies on the synthesis, structure, and reactivity of ruthenium(II) complexes containing tertiary phosphine ligands has been reported in recent years.[1] Relatively less attention has been devoted to the phosphite ligands and, except for the report of Robinson and co-workers[2] on carbonyl ruthenium(II) derivatives, all phosphite complexes have been prepared by substitution reactions from phosphine or olefin derivatives.[3] We have previously reported[4] on the chemistry of cobalt(II) and iron(II) carbonyl compounds and now, as an extension of our studies, we report on the reactivity of the salt $RuCl_3$ toward phosphite ligands, and on the carbonylation reaction of phosphite-containing $RuCl_3$ solutions which allowed the synthesis of new ruthenium(II) complexes. Furthermore, the reactivity of these compounds with isocyanides was investigated, and the preparation and characterization of new mixed-ligand complexes is also reported.



Scheme 1.

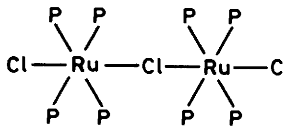
Results and Discussion

Phosphite and Carbonyl Complexes.—The reaction of ruthenium trichloride with an excess of phosphite (ratio > 1:10) in boiling ethanol gives the binuclear complexes $[Ru_2Cl_3L_8]^+$ [L = $P(OEt)_3$ (**1a**) or $P(OEt)_2Ph$ (**1b**)] which were isolated and characterized. On the contrary, operating with a smaller excess of phosphite (ratio 1:5) gave $[Ru_2Cl_3L_6]^+$ (**2**), as shown in Scheme 1.

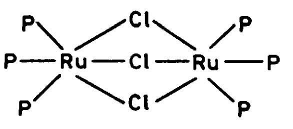
The tri-μ-chloro complexes (**2**) show a remarkable reluctance to react with excess of phosphite to give (**1**), in boiling ethanol or 1,2-dichloroethane, and the starting complexes (**2**) can be recovered unchanged after 48 h of reaction. These data seem to indicate that the formation of the two dimers (**1**) and (**2**) from the reaction of $RuCl_3$ with phosphite follows two different paths since the reaction (**2**) + L $\longrightarrow$ (**1**) does not take place in boiling ethanol. However, at 130 °C in pure phosphite the $[Ru_2Cl_3L_6]^+$ complexes react to give the $[Ru_2Cl_3L_8]^+$ derivatives.

We studied also the reaction of $RuCl_3$ toward phosphites in ethanol in the presence of zinc dust. In this case, however, the reaction proceeds at room temperature to give the known complex $[RuCl_2\{P(OEt)_3\}_4]$[5] whose $^{31}P-\{^1H\}$ n.m.r. spectra (singlet at δ 127.5) suggest a *trans* geometry. Selected physical and spectroscopic data for compounds (**1**) and (**2**), which are stable, white, diamagnetic solids, and 1:1 electrolytes[6] (Λ_M = 56.5—60.5 S cm^2 mol^{-1}), are given in Tables 1 and 2.

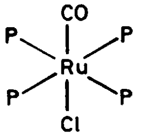
The $^{31}P-\{^1H\}$ n.m.r. spectra of $[Ru_2Cl_3L_8]^+$ cations appear as singlets at room temperature, and remain unchanged from +40 to −70 °C. On the basis of these data and of the stoicheiometry of the complexes, a structure of type (**I**) with only one chlorine bridge may be proposed for these derivatives. On the other hand, at room temperature as well as at −70 °C, the $^{31}P-\{^1H\}$ n.m.r. spectra of the $[Ru_2Cl_3L_6]^+$ complexes appear as complicated multiplets, suggesting magnetic inequivalence of the phosphorus nuclei. However, increasing the sample temperature produces a sequence of changes in the ^{31}P spectra until, at +80 °C for (**2a**) and at +110 °C for (**2b**) respectively, a singlet is observed for both complexes (Table 2). Since a three-membered chloro-bridge structure (**II**) may be proposed for these $[Ru_2Cl_3L_6]^+$ complexes, as previously observed for analogous tertiary phosphine derivatives,[1i] the fact that the



(I)



(II)



(III)

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† *Non-S.I. unit employed*: atm = 101 325 Pa.

Table 1. Physical and analytical data

Complex	M.p. (°C)	Λ_M[a]/S cm^2 mol^{-1}	Analysis[b] (%)			
			C	H	N	Cl
(**1a**) $[Ru_2Cl_3\{P(OEt)_3\}_8]BPh_4$	185	60.5	44.15 (44.20)	7.00 (7.20)		5.35 (5.45)
(**1b**) $[Ru_2Cl_3\{P(OEt)_2Ph\}_8]BPh_4$	208	59.3	56.00 (56.45)	6.15 (6.40)		5.05 (4.80)
(**2a**) $[Ru_2Cl_3\{P(OEt)_3\}_6]BPh_4$	179	56.5	44.30 (44.35)	6.80 (6.80)		6.90 (6.55)
(**2b**) $[Ru_2Cl_3\{P(OEt)_2Ph\}_6]BPh_4$	192	60.5	55.10 (55.55)	6.15 (6.10)		6.05 (5.85)
(**3a**) *trans*-$[RuCl(CO)\{P(OEt)_3\}_4]BPh_4$	196	59.1	51.20 (51.25)	7.00 (7.00)		3.30 (3.10)
(**3b**) *trans*-$[RuCl(CO)\{P(OEt)_2Ph\}_4]BPh_4$	210	51.6	61.20 (61.15)	6.35 (6.30)		3.10 (2.80)
(**4**) $[RuCl(4\text{-}MeC_6H_4NC)_2\{P(OEt)_3\}_3]BPh_4$	185	53.0	58.30 (58.60)	6.75 (6.70)	2.40 (2.35)	3.15 (3.00)
(**5a**) $[Ru(4\text{-}MeC_6H_4NC)_3\{P(OEt)_2Ph\}_3][BPh_4]_2$	188	130.3	72.55 (72.70)	6.25 (6.35)	2.45 (2.50)	
(**5b**) $[Ru(PhNC)_3\{P(OEt)_2Ph\}_3][BPh_4]_2$	214	130.8	72.60 (72.35)	6.10 (6.15)	2.20 (2.55)	
(**5c**) $[Ru(4\text{-}MeOC_6H_4NC)_3\{P(OEt)_2Ph\}_3][BPh_4]_2$	191	128.4	70.50 (70.65)	6.10 (6.15)	2.35 (2.40)	
(**6a**) $[RuCl(CO)(4\text{-}MeC_6H_4NC)\{P(OEt)_3\}_3]BPh_4$	98	51.4	55.60 (55.70)	6.55 (6.60)	1.30 (1.25)	3.45 (3.20)
(**6b**) $[RuCl(CO)(4\text{-}MeC_6H_4NC)\{P(OEt)_2Ph\}_3]BPh_4$	168	51.6	63.15 (63.30)	6.15 (6.05)	1.00 (1.15)	3.25 (2.95)
(**6c**) $[RuCl(CO)(4\text{-}ClC_6H_4NC)\{P(OEt)_2Ph\}_3]BPh_4$	150	51.8	60.65 (61.25)	5.75 (5.70)	0.90 (1.15)	5.95 (5.85)

[a] In nitromethane solution (10^{-3} mol dm^{-3}), at 25 °C. [b] Calculated values given in parentheses.

Table 2. Selected i.r. and n.m.r. data for the ruthenium(II) complexes

Compound	$\nu(CO)$[a]/cm^{-1}	$\nu(CN)$[a]/cm^{-1}	$\delta(^1H)$[b]			$^{31}P\text{-}\{^1H\}$[b,c]	
			$POCH_2CH_3$ (CH₂)	4-Me	$POCH_2CH_3$ (CH₃)	Spin system	δ
(**1a**)			4.20 (m)		1.28 (t)		+132.5 (s)
(**1b**)			3.80 (m)		1.30 (t)		+162.8 (s)
(**2a**)			4.21 (m)		1.26 (t)		+132.2 (m) +132.5 (s)[d]
(**2b**)			3.90 (m)		1.29 (t), 1.33 (t)		+162.7 (m) +162.3 (s)[e]
trans-$[RuCl_2\{P(OEt)_3\}_4]$			4.24 (m)		1.22 (t)		+127.5 (s)
(**3a**)	2 007s (2 005s)		4.29 (m)		1.33 (t)		+115.0 (s)
(**3b**)	1 986s (1 998sh, 1 982s)		3.87 (m)		1.24 (t)		+139.1 (s)
(**4**)		2 181s, 2 157s (2 180s, 2 152s)	4.21 (qnt), 4.29 (qnt)	2.38 (s)	1.31 (t), 1.32 (t)	AB_2	δ_A 128.8, δ_B 122.4 *J*(AB) 58.3
(**5a**)		2 200m, 2 173s (2 197m, 2 170s)	4.25 (qnt)	2.36 (s)	1.49 (t)		+143.6 (s)
(**5b**)		2 200m, 2 172s (2 198m, 2 167s)	4.28 (m)		1.50 (t)		+143.2 (s)
(**5c**)		2 198m, 2 176s (2 200m, 2 172s)	4.25 (m)	3.82 (s)	1.49 (t)		+143.9 (s)
(**6a**)	2 021s (2 010s)	2 189s (2 187s)	4.33 (m)	2.40 (s)	1.33 (t), 1.35 (t), 1.37 (t)	AB_2	δ_A 115.0, δ_B 113.4 *J*(AB) 56.0
(**6b**)	2 000s (1 995s)	2 191s (2 192s)	4.06 (m)	2.34 (s)	1.32 (t), 1.30 (t), 1.28 (t)	AB_2	δ_A 140.9, δ_B 136.6 *J*(AB) 41.4
(**6c**)	2 003s (1 997s)	2 187s (2 188s)	4.06 (m)		1.32 (t), 1.27 (t), 1.26 (t)	AB_2	δ_A 140.8, δ_B 135.9 *J*(AB) 41.1

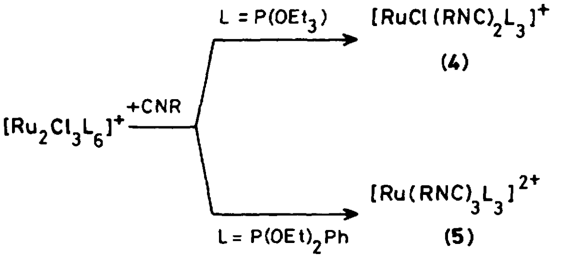
[a] In CH_2Cl_2(KBr). [b] At room temperature in $(CD_3)_2CO$. [c] Positive shifts downfield from 85% H_3PO_4; *J* values are in Hz. [d] At 80 °C in $(CD_3)_2SO$. [e] At 110 °C in $(CD_3)_2SO$.

phosphorus nuclei are inequivalent at room temperature may be tentatively explained on the basis of restricted rotation around the Ru–P bonds as a result of steric interactions between the substituents on neighbouring P atoms.

Study of the chemical properties of compounds (**1**) and (**2**) indicated relatively robust complexes. No evidence for reaction with phosphite, halogenide ions, or CO (1 atm) in boiling ethanol or $ClCH_2CH_2Cl$ was detected. Treatment with nitric oxide for one week did not modify the starting compounds (**1**) and (**2**). With isocyanide, however, the chlorine bridge could be broken to give the substituted derivatives $[RuCl(RNC)_2L_3]^+$ and $[Ru(RNC)_3L_3]^{2+}$ (R = $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, or Ph).

It should be noted that, while binuclear ruthenium(II) complexes of the type $[Ru_2Cl_3(PR'_3)_6]^+$ have been reported with tertiary phosphine or phosphite ligands,[1a,i,3c] no examples of mono-μ-chloro complexes of the type $[Ru_2Cl_3L_8]^+$ have ever been described.

Carbon monoxide (1 atm) reacts with a boiling alcoholic solution of ruthenium trichloride containing an excess of phosphite [$P(OEt)_3$ or $P(OEt)_2Ph$] to give a colourless solution from which the cationic monocarbonyl complexes *trans*-$[RuCl(CO)L_4]BPh_4$ (**3**) may be isolated. In the case of the $P(OEt)_2Ph$ ligand, the reaction product contained not only (**3**) but also $[Ru_2Cl_3L_8]^+$, which could be removed by fractional crystallization. The reaction was carried out by varying the molar ratio $RuCl_3$: L in the range 1 : 3—1 : 10 as well as by reacting with CO for several days, but in every case



Scheme 2.

monocarbonyls were always obtained. It may also be noted that, in the case of the carbonylation of alcoholic $FeCl_2$ solution containing phosphite ligand, the formation of monocarbonyls of the type $[FeCl(CO)L_4]^+$ was always observed[4d] and the results seem to be attributable to the properties of the phosphites used.

Complexes (3) are white solids, diamagnetic, and 1:1 electrolytes (Λ_M = 51.6—59.1 S cm^2 mol^{-1}, Table 1). Their i.r. spectra show only one strong ν(CO) band at 1 986—2 007 cm^{-1} (in CH_2Cl_2 solution, Table 2), while the ^{31}P-{^1H} n.m.r. spectra in the temperature range +40 to −70 °C are singlets, in agreement with a *trans* geometry (**III**) for the complexes.

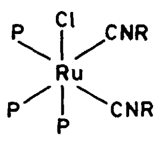
Monocarbonyl complexes of Ru^{II} with phosphites are rare and, apart from some hydride compounds,[3a,c,e] they are the type $[RuCl_2(CO)L_3]$, generally obtained by substitution of CO in the dicarbonyl complexes $[RuCl_2(CO)_2L_2]$.[2,3b] In effect, the reaction of $RuCl_3\cdot3H_2O$ in boiling 2-methoxyethanol with CO and phosphite afforded dicarbonyl complexes.[2] In the present case, the carbonylation reaction in ethanol allowed preparation of the first cationic monocarbonyl Ru^{II} derivatives.

Isocyanide Complexes.—The reaction of complexes (**2**) with aryl isocyanides in boiling 1,2-dichloroethane proceeds with the break of the chlorine bridge and formation of the mixed-ligand derivatives $[RuCl(RNC)_2\{P(OEt)_3\}_3]^+$ (**4**) or $[Ru(RNC)_3\{P(OEt)_2Ph\}_3]^{2+}$ (**5**) as shown in Scheme 2.

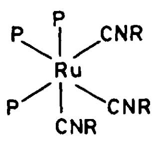
The stoicheiometry of the products depends on the nature of the phosphite used: *i.e.*, with L = $P(OEt)_3$, the di(isocyanide) compound (**4**) is obtained, whereas with L = $P(OEt)_2Ph$, the tri(isocyanide) (**5**) is formed. We studied the progress of the reaction by i.r. spectra, operating at different complex:isocyanide ratios (1:2—1:20), to test whether different complexes could be obtained. However, the results show that in every case the same complexes are always obtained. The $[RuCl_3L_8]^+$ derivatives also react with isocyanides to give complexes (**4**) or (**5**), respectively, but in this case the reaction rate is very slow. For example, in boiling $ClCH_2CH_2Cl$ only 30% of the isocyanide complex was obtained after reaction for 48 h.

The formation of the two different complexes (**4**) and (**5**) with the two phosphines used, $P(OEt)_3$ and $P(OEt)_2Ph$, could be attributed to their different π-acceptor properties rather than to their steric hindrance: the dicationic derivative $[Ru(RNC)_3L_3]^{2+}$ is obtained only with $P(OEt)_2Ph$, which is a less π-accepting but more bulky ligand than is $P(OEt)_3$. The di(isocyanide) derivative, on the contrary, was obtained with $P(OEt)_3$, whose better π-acceptor properties require the presence of the σ-donor Cl^- ligand in the complex.

The new Ru^{II} complexes are white diamagnetic solids, and their elemental analyses, i.r. and n.m.r. data (Tables 1 and 2) are consistent with the formulations given. Complex (**4**) is a 1:1 electrolyte in nitromethane and its i.r. spectrum shows two ν(CN) bands at 2 181 and 2 157 cm^{-1} (in CH_2Cl_2 solution), indicating two mutually *cis* isocyanides. In the temperature range +40 to −70 °C, the ^{31}P-{^1H} n.m.r. spectra show an AB_2 pattern which may be simulated with the values reported in Table 2. Furthermore, in the methylene region, the ^1H n.m.r. spectra show two quintets (ratio 1:2) due to the phosphite ligands in mutually *cis* positions. The presence of two mutually *trans* phosphites should be indicated by a complicated multiplet in the CH_2 region, due to the virtual coupling between the two phosphorus atoms. On this basis a *fac* structure (**IV**) may reasonably be proposed in solution for this complex.



(**IV**)



(**V**)

The tri(isocyanide) derivatives (**5**) behave as 1:2 electrolytes in CH_3NO_2 solution (Λ_M = 128.4—130.8 S cm^2 mol^{-1}) and their i.r. spectra show, in the ν(CN) region, one band of medium intensity at 2 198—2 200 cm^{-1} and one strong absorption at 2 172—2 176 cm^{-1} in CH_2Cl_2 solution. The ^{31}P-{^1H} n.m.r. spectra are singlets at room temperature and remain unchanged at −70 °C, indicating the presence of three equivalent phosphite ligands, as expected for a *fac* geometry (**V**) for the complexes.

The monocarbonyl derivatives *trans*-$[RuCl(CO)L_4]^+$ (**3**) also react with isocyanide, to afford the mixed-ligand complexes $[RuCl(CO)(RNC)L_3]^+$ (**6**) (see below), both in stoicheiometric

$$\underset{(3)}{[RuCl(CO)L_4]^+} + RNC \longrightarrow \underset{(6)}{[RuCl(CO)(RNC)L_3]^+} + L$$

or excess amounts of RNC. The i.r. spectra show a ν(CN) absorption at 2 187—2 191 cm^{-1}, while the ν(CO) band appears at 2 000—2 021 cm^{-1}. The latter band increases by *ca.* 15 cm^{-1} compared to that of the *trans*-$[RuCl(CO)L_4]^+$ complexes, in agreement with the better π-acceptor properties of the isocyanide compared to the phosphite ligand. On the other hand, the ^{31}P-{^1H} n.m.r. spectrum is an AB_2 multiplet (Table 2) between +40 and −70 °C, indicating that the two phosphines must be mutually *trans*. However, the presence of four different ligands around the Ru atom does not allow us to assign a geometry to these compounds on the basis of these data alone. Isocyanide complexes of ruthenium(II) with tertiary phosphine or carbonyl ligands have been reported previously,[7] but no example of a phosphite derivative has ever been prepared. Now, by reacting the new derivatives (**2**) and (**3**) with CNR, the synthesis of these mixed-ligand derivatives may be achieved.

In view of the high ν(CN) value, we hoped that these ruthenium(II) isocyanide complexes would undergo reactions with amines or alcohols to give carbene complexes. However, no reactions were observed by treating complexes (**4**), (**5**), and (**6**) with either of these reagents, indicating that the CNR ligand is not susceptible to nucleophilic attack.

Experimental

Materials.—All solvents used were purified by standard methods and distilled under a stream of nitrogen immediately before use; $RuCl_3\cdot3H_2O$ (Alfa Ventron) was used as received. Triethyl phosphite (Ega Chemie) was purified by distillation under nitrogen. Diethoxyphenylphosphine was prepared following the method of Rabinowitz and Pellon.[8] Substituted phenyl isocyanides were obtained by the method of Ziehn and co-workers.[9] Other reagents were purchased commercially in the highest available purity and used as received.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Solid-state spectra were obtained from KBr pellets or Nujol mulls; solution spectra were obtained using potassium bromide cells. Solution ^1H n.m.r. spectra were obtained with a Varian EM-390 or Varian FT-80A spectrometer using $SiMe_4$ as internal standard. Fourier-mode, proton-noise-decoupled ^{31}P n.m.r. spectra were collected on a Varian FT-80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, downfield shifts being considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of complexes in nitromethane at 25 °C were measured with a 'Halosis' bridge. Solution susceptibilities were determined by the Evans method.[10]

Synthesis of the Complexes.—All synthetic work was performed under an inert atmosphere, using standard Schlenk techniques. Once isolated, the complexes were air-stable for 2—3 d.

$[Ru_2Cl_3L_8]BPh_4$ [L = $P(OEt)_3$ (**1a**) *or* $P(OEt)_2Ph$ (**1b**)]. To a solution of $RuCl_3{\cdot}3H_2O$ (1 g, *ca.* 4 mmol) in ethanol (70 cm^3) an excess of the appropriate phosphite (40 mmol) was added and the reaction mixture heated under reflux for 24 h. The resulting yellow solution was filtered, concentrated to half its original volume, and $NaBPh_4$ (1.7 g, 5 mmol) was then added to give a white precipitate which was crystallized from ethanol (yield $\geqslant$90%).

$[Ru_2Cl_3L_6]BPh_4$ [L = $P(OEt)_3$ (**2a**) *or* $P(OEt)_2Ph$ (**2b**)]. The appropriate phosphite (20 mmol) was added to a solution of $RuCl_3{\cdot}3H_2O$ (1 g, *ca.* 4 mmol) in ethanol (50 cm^3). The reaction mixture was heated under reflux for 24 h and, after filtration, concentrated to *ca.* 50%. The addition of $NaBPh_4$ (1.7 g, 5 mmol) afforded a white precipitate which was separated and crystallized from ethanol (yield $\geqslant$60%).

$[RuCl_2\{P(OEt)_3\}_4]$. Zinc dust was added to a solution of $RuCl_3{\cdot}3H_2O$ (1 g, *ca.* 4 mmol) in ethanol (50 cm^3) containing an excess of $P(OEt)_3$ (4 cm^3, 24 mmol) and the reaction mixture was stirred until the colour turned yellow (10—15 min). After filtration, the solution was concentrated to *ca.* 20 cm^3 and cooled to −30 °C. Yellow crystals, which were filtered off and dried under vacuum, separated out after 1—2 d (yield $\geqslant$65%) (Found: C, 34.25; H, 7.15; Cl, 8.10. Calc. for $C_{24}H_{60}Cl_2O_{12}P_4Ru$ C, 34.45; H, 7.25; Cl, 8.45%).

$[RuCl(CO)\{P(OEt)_3\}_4]BPh_4$ (**3a**). A solution of $RuCl_3{\cdot}3H_2O$ (1 g, *ca.* 4 mmol) and triethyl phosphite (4 cm^3, 24 mmol) in ethanol (50 cm^3) was heated under reflux under CO (1 atm) until the colour of the solution turned light yellow (2—3 h). After filtration, the solution was concentrated to half its original volume; addition of $NaBPh_4$ (1.7 g, 5 mmol) caused the precipitation of a white product which was crystallized from ethanol (yield $\geqslant$25%).

$[RuCl(CO)\{P(OEt)_2Ph\}_4]BPh_4$ (**3b**). This compound was prepared following the method reported above for (**3a**). In this case, however, a mixture of the complexes $[RuCl(CO)\{P(OEt)_2Ph\}_4]BPh_4$ and $[Ru_2Cl_3\{P(OEt)_2Ph\}_8]BPh_4$ was obtained and their separation was achieved by fractional crystallization. In a typical separation, 2 g of the crude product were mixed with 30 cm^3 of warm ethanol (40 °C) and enough dichloromethane (4—7 cm^3) to produce a homogeneous solution at *ca.* 35 °C. The solution was cooled slowly to 4 °C to give white crystals which were recrystallized from ethanol to give $[RuCl(CO)\{P(OEt)_2Ph\}_4]BPh_4$ in pure form (yield $\geqslant$20%). Further cooling of the solution to −30 °C gave white crystals of $[Ru_2Cl_3\{P(OEt)_2Ph\}_8]BPh_4$ (yield $\geqslant$40%). The total yield of the two Ru^{II} complexes was *ca.* 70%, of which *ca.* one third was the monocarbonyl.

$[RuCl(4\text{-}MeC_6H_4NC)_2\{P(OEt)_3\}_3]BPh_4$ (**4**), To a solution of $[Ru_2Cl_3L_6]BPh_4$ (0.5 g, 0.3 mmol) in 1,2-dichloroethane (40 cm^3) was added an excess of *p*-tolyl isocyanide (0.47 g, 4 mmol) and the reaction mixture heated under reflux for 4 h. The solvent was removed under reduced pressure and the oil obtained was triturated with ethanol (20 cm^3) containing $NaBPh_4$ (0.2 g, 0.6 mmol). After 5—10 h a white solid formed, which was collected and crystallized from ethanol (yield $\geqslant$60%).

$[Ru(RNC)_3\{P(OEt)_2Ph\}_3][BPh_4]_2$ [R = $4\text{-}MeC_6H_4$ (**5a**), Ph (**5b**), *or* $4\text{-}MeOC_6H_4$ (**5c**)]. These complexes were prepared following the method reported above for (**4**), starting from $[Ru_2Cl_3\{P(OEt)_2Ph\}_6]BPh_4$. In this case, however, the dicationic tri(isocyanide) complexes were obtained.

$[RuCl(CO)(RNC)L_3]BPh_4$ [L = $P(OEt)_3$, R = $4\text{-}MeC_6H_4$ (**6a**); L = $P(OEt)_2Ph$, R = $4\text{-}MeC_6H_4$ (**6b**) *or* $4\text{-}ClC_6H_4$ (**6c**)]. A solution of $[RuCl(CO)L_4]BPh_4$ (0.4 mmol) in 1,2-dichloroethane (40 cm^3) containing the appropriate isocyanide (1.2 mmol) was heated under reflux for 3 h. The solvent was removed, leaving an oil which was triturated with ethanol (15 cm^3). The white solid which formed after 1—2 h was collected and crystallized from ethanol (yield $\geqslant$80%).

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