Phenyl Complexes of Ruthenium(II): Competition between Carbonyl Substitution and Formation of Benzoyl Complexes, and an *X*-Ray Study of a Benzoyl Complex†

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Complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Y(PMe_2Ph)_2]$ (X = H, Y = Cl, I, or O_2CMe; X = OMe, Cl, or NMe_2, Y = Cl) react with Me_3CNC in $CHCl_3$ solution to yield carbonyl substitution products $[Ru(CO)(CNCMe_3)(C_6H_4X\text{-}4)Y(PMe_2Ph)_2]$ and benzoyl complexes $[Ru(CO)(CNCMe_3)_2(COC_6H_4X\text{-}4)(PMe_2Ph)_2]^+$ in proportions which vary widely according to the conditions used and the nature of X and Y. The most probable route to the benzoyl complexes appears to be *via* intermediates of formula $[Ru(CO)(CNCMe_3)(COC_6H_4X\text{-}4)Y(PMe_2Ph)_2]$. The structure of $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$ has been determined by *X*-ray crystallography.

Methyl complexes of ruthenium(II) of the type $[Ru(CO)_2Me(X)(PMe_2Ph)_2]$ (X = Cl, Br, or I) rapidly form σ-acyl complexes $[Ru(CO)(COMe)X(PMe_2Ph)_2L]$ (L = CO or PMe_2Ph) when treated in solution with CO or PMe_2Ph.[1] The related complex $[Ru(CO)_2Me(I)(PPh_3)_2]$ also readily undergoes combination of methyl and carbonyl ligands, and the η^2-acyl complex $[Ru(CO)(COMe)I(PPh_3)_2]$ has been isolated and studied by *X*-ray crystallography.[2] The 4-methylphenyl complexes $[Ru(CO)_2(C_6H_4Me\text{-}4)X(PPh_3)_2]$ behave similarly,[3] and again an η^2-acyl complex, $[Ru(CO)(COC_6H_4Me\text{-}4)I(PPh_3)_2]$, has been characterized by *X*-ray work.[2] In marked contrast, the complex $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ exists both in the solid state and in solution in this form rather than as the acyl complex $[Ru(CO)(COPh)Cl(PMe_2Ph)_2]$, and it does not react with CO to give $[Ru(CO)_2(COPh)Cl(PMe_2Ph)_2]$. When treated with PMe_2Ph it forms only the carbonyl substitution product $[Ru(CO)Ph(Cl)(PMe_2Ph)_3]$.[4]

In this paper we describe the reactions of phenyl complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Y(PMe_2Ph)_2]$ (X = H, Y = Cl, I, or O_2CMe; X = OMe, Cl, or NMe_2, Y = Cl) with Me_3CNC. In these reactions, carbonyl substitution and acyl complex formation are in competition, and variation in either X or Y can greatly affect the product distribution.

Results and Discussion

Details of the i.r. and ^1H n.m.r. spectra of new complexes described below are given in Tables 1 and 2 respectively, and ^{13}C n.m.r. data are listed in Table 3.

Reactions of Complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Y(PMe_2Ph)_2]$ *with* Me_3CNC.—Treatment of a $CHCl_3$ solution of $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ [complex (**1a**), of structure (**1**), where X = H and Y = Cl] with an equimolar quantity of Me_3CNC caused the solution to turn yellow. Recrystallization of the crude product yielded colourless crystals of the carbonyl substitution product $[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$ (**2a**), known to possess structure (**2**), where X = H and Y = Cl.[5] The i.r. spectrum of the yellow mother-liquor from the recrystallization, however, included bands attributable neither to the starting materials nor to (**2a**). The reaction was repeated in a solution saturated with CO, in the hope of inhibiting the carbonyl substitution reaction, and from both the colour and the i.r. spectrum of the reaction mixture it was evident that a greater proportion of the yellow material [complex (**3a**, Cl^- salt)] had been formed. When all the Me_3CNC had been consumed, a considerable quantity of complex (**1a**) remained in the solution, indicating that (**3a**) contained more than one isonitrile ligand. Addition of more Me_3CNC completed the conversion into the mixture of (**2a**) and (**3a**). We were unable to achieve complete separation of the two products, but i.r. and n.m.r. spectra shed light on the nature of (**3a**). The i.r. spectrum indicated the presence of a carbonyl ligand and two mutually *cis* Me_3CNC ligands, and the pattern of resonances for the methyl protons and carbon atoms in the PMe_2Ph ligands showed that (**3a**) contained a pair of mutually *trans* PMe_2Ph ligands.‡ Two features of the ^{13}C n.m.r. spectrum indicated a benzoyl rather than a phenyl ligand: firstly there was a weak triplet resonance [$|^2J(P\text{–}C)| = 11.0$ Hz] at δ 260.5 (a characteristic chemical shift value for an acyl carbon atom[8]), and secondly the resonance for C^1 in the phenyl group (identified with the aid of a spectrum recorded under conditions of weak noise decoupling) showed no splitting by the phosphorus nuclei, whereas the C^1 resonances for complexes (**1a**) and (**2a**) were triplets with $|^2J(P\text{–}C)| = ca.$ 14 Hz. We concluded that (**3a**) was probably the cation $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]^+$ of structure (**3**), where X = H; and this was subsequently confirmed by an *X*-ray study of its tri-iodide salt (see below).

The reaction between $[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$ (**1b**) and Me_3CNC in a 1:2 molar ratio in $CHCl_3$ solution yielded $[Ru(CO)(CNCMe_3)(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$ (**2b**), and $[Ru(CO)(CNCMe_3)_2(COC_6H_4OMe\text{-}4)(PMe_2Ph)_2]^+$ (**3b**). In CO-saturated solution nearly all the product was (**3b**), and treatment of a propanone solution of the crude product with $NaClO_4$ yielded (after removal of NaCl) crystals of pure $[Ru(CO)(CNCMe_3)_2(COC_6H_4OMe\text{-}4)(PMe_2Ph)_2]ClO_4$. The balance between the two modes of reaction was, however, still delicately poised: from a reaction carried out at 333 K, with N_2 passing through the solution to remove CO, we were able to isolate pure (**2b**) in reasonable yield.

The reactions of two other substituted phenyl complexes, $[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$ (**1c**) and $[Ru(CO)_2(C_6H_4NMe_2\text{-}4)Cl(PMe_2Ph)_2]$ (**1d**) with Me_3CNC were also investigated. Complex (**1c**) yielded predominantly the substi-

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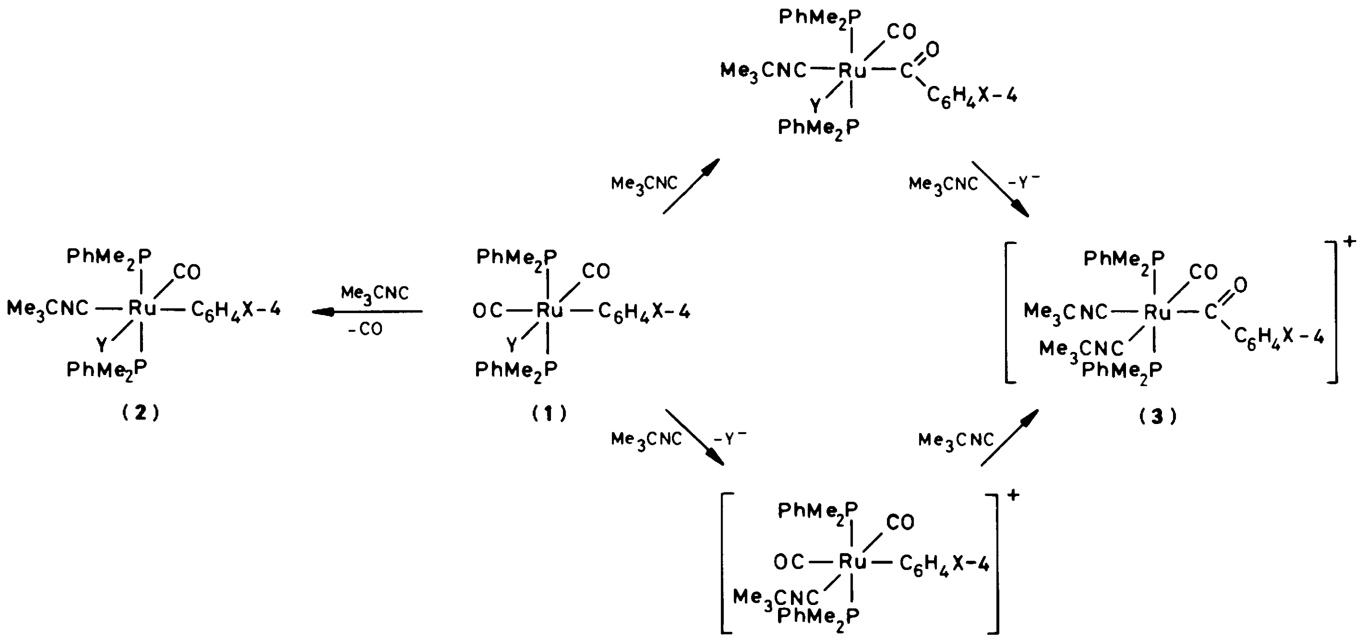
† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ The ways in which phosphorus ligands may be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and coworkers.[6,7]



Scheme. (**a**) X = H, Y = Cl; (**b**) X = OMe, Y = Cl; (**c**) X = Cl, Y = Cl; (**d**) X = NMe$_2$, Y = Cl

Table 1. Infrared data (cm^{-1}) for the complexes*

Complex	Number	ν(C–O)	ν(C–N)
[Ru(CO)(CNCMe$_3$)Ph(Cl)(PMe$_2$Ph)$_2$]	(**2a**)	1 934	2 160
[Ru(CO)(CNCMe$_3$)$_2$(COPh)(PMe$_2$Ph)$_2$]Cl	(**3a**, Cl$^-$ salt)	2 010	2 200, 2 170
[Ru(CO)(CNCMe$_3$)(C$_6$H$_4$OMe-4)Cl(PMe$_2$Ph)$_2$]	(**2b**)	1 938	2 160
[Ru(CO)(CNCMe$_3$)$_2$(COC$_6$H$_4$OMe-4)(PMe$_2$Ph)$_2$]ClO$_4$	(**3b**, ClO$_4^-$ salt)	1 995	2 200, 2 170
[Ru(CO)(CNCMe$_3$)(C$_6$H$_4$Cl-4)Cl(PMe$_2$Ph)$_2$]	(**2c**)	1 940	2 170
[Ru(CO)(CNCMe$_3$)$_2$(COC$_6$H$_4$NMe$_2$-4)(PMe$_2$Ph)$_2$]Cl	(**3d**, Cl$^-$ salt)	1 998	2 200, 2 160
[Ru(CO)(CNCMe$_3$)Ph(O$_2$CMe)(PMe$_2$Ph)$_2$]		1 930	2 165
[Ru(CO)(CNCMe$_3$)$_2$(COPh)(PMe$_2$Ph)$_2$]I$_3$	(**3a**, I$_3^-$ salt)	2 005	2 200, 2 170
[Ru(CO)$_2$Ph(ClO$_4$)(PMe$_2$Ph)$_2$]		2 053, 1 980	
[Ru(CO)(CNCMe$_3$)Ph(ClO$_4$)(PMe$_2$Ph)$_2$]		1 951	2 175
[Ru(CO)(CNCMe$_3$)$_2$Ph(PMe$_2$Ph)$_2$]ClO$_4$		1 995	2 190, 2 160

* In CHCl$_3$ solution. Only bands due to carbonyl ligands and to nitrile C–N stretching modes are listed.

tution product [Ru(CO)(CNCMe$_3$)(C$_6$H$_4$Cl-4)Cl(PMe$_2$Ph)$_2$] (**2c**) under all conditions tried, and (**2c**) was isolated and characterized. In contrast (**1d**) was almost entirely converted into the benzoyl complex [Ru(CO)(CNCMe$_3$)$_2$(COC$_6$H$_4$NMe$_2$-4)(PMe$_2$Ph)$_2$]$^+$ (**3d**). The chloride salt of (**3d**) could not be obtained in crystalline form, but the nature of the complex was clear from the spectroscopic evidence.

The balance between carbonyl substitution and acyl complex formation was also altered by changing the nature of the ligand Y$^-$ in [Ru(CO)$_2$Ph(Y)(PMe$_2$Ph)$_2$]. Whereas the chloro-complex (**1a**) yielded a mixture of (**2a**) and (**3a**), [Ru(CO)$_2$Ph(O$_2$CMe)(PMe$_2$Ph)$_2$] formed only the substitution product [Ru(CO)(CNCMe$_3$)Ph(O$_2$CMe)(PMe$_2$Ph)$_2$], which was fully characterized, and [Ru(CO)$_2$Ph(I)(PMe$_2$Ph)$_2$] appeared to yield only (**3a**), which was isolated as its iodide salt. In solution, and in the presence of light and air, this was converted into the tri-iodide salt of (**3a**), [Ru(CO)(CNCMe$_3$)$_2$(COPh)(PMe$_2$Ph)$_2$]I$_3$, which was studied by *X*-ray crystallography (see below).

Mechanism of the Conversion of Complex (**1**) *into* (**3**).—It seemed most unlikely that the phenyl complexes [Ru(CO)$_2$(C$_6$H$_4$X-4)Y(PMe$_2$Ph)$_2$] of structure (**1**) were converted directly into the benzoyl complexes [Ru(CO)(CNCMe$_3$)$_2$(COC$_6$H$_4$X-4)(PMe$_2$Ph)$_2$]$^+$ of structure (**3**), but spectroscopic studies failed to reveal the presence of intermediates during the reactions. Two possible routes from (**1**) to (**3**) are shown in the Scheme: substitution of the anionic ligand Y$^-$ to give [Ru(CO)$_2$(CNCMe$_3$)(C$_6$H$_4$X-4)(PMe$_2$Ph)$_2$]$^+$ could be followed by combination of phenyl and carbonyl ligands, or formation of the acyl complex [Ru(CO)(CNCMe$_3$)(COC$_6$H$_4$X-4)Y(PMe$_2$Ph)$_2$] could be followed by substitution of Y$^-$. In the hope of determining which was the correct route, we attempted to synthesize one of the possible intermediates, [Ru(CO)$_2$(CNCMe$_3$)Ph(PMe$_2$Ph)$_2$]$^+$, by an alternative route.

The reaction of [Ru(CO)$_2$Ph(Cl)(PMe$_2$Ph)$_2$] and AgClO$_4$ in propanone solution yielded a precipitate of AgCl, and from the filtrate colourless crystals were obtained. From elemental analysis figures, and from the similarity of the i.r. and n.m.r. spectra of the complex to those of [Ru(CO)$_2$Ph(Cl)(PMe$_2$Ph)$_2$], we concluded that the product was [Ru(CO)$_2$Ph(ClO$_4$)(PMe$_2$Ph)$_2$], with the chlorate(VII) anion probably weakly bonded to the metal. Unfortunately, treatment of this complex with an equimolar quantity of Me$_3$CNC in CDCl$_3$ solution did *not* yield the desired [Ru(CO)$_2$(CNCMe$_3$)Ph(PMe$_2$Ph)$_2$]$^+$. Instead some of the [Ru(CO)$_2$Ph(ClO$_4$)(PMe$_2$Ph)$_2$] remained unreacted, some (**3a**) was formed, and another species was present in solution as well. When the

Table 2. Proton n.m.r. data for the complexes*

Complex	Number	PMe_2Ph	$CNCMe_3$	Other resonances	Assignment
$[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$	**(2a)**	1.56 (t, 6)	0.94 (s, 9)		
		1.43 (t, 6)			
$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]Cl$	(**3a**, Cl^- salt)	1.84 (t, 6)	1.50 (s, 9)		
		1.82 (t, 6)	1.36 (s, 9)		
$[Ru(CO)(CNCMe_3)(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$	**(2b)**	1.56 (t, 6)	0.93 (s, 9)	3.77 (s, 3)	4-MeO
		1.42 (t, 6)			
$[Ru(CO)(CNCMe_3)_2(COC_6H_4OMe\text{-}4)(PMe_2Ph)_2]ClO_4$	(**3b**, ClO_4^- salt)	1.74 (t, 6)	1.49 (s, 9)	3.78 (s, 3)	4-MeO
		1.71 (t, 6)	1.30 (s, 9)		
$[Ru(CO)(CNCMe_3)(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	**(2c)**	1.53 (t, 6)	0.98 (s, 9)		
		1.40 (t, 6)			
$[Ru(CO)(CNCMe_3)_2(COC_6H_4NMe_2\text{-}4)(PMe_2Ph)_2]Cl$	(**3d**, Cl^- salt)	1.78 (t, 6)	1.50 (s, 9)	2.98 (s, 6)	$4\text{-}Me_2N$
		1.50 (t, 6)	1.30 (s, 9)		
$[Ru(CO)(CNCMe_3)Ph(O_2CMe)(PMe_2Ph)_2]$		1.47 (t, 6)	0.96 (s, 9)	2.02 (s, 3)	O_2CMe
		1.38 (t, 6)			
$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$	(**3a**, I_3^- salt)	1.80 (t, 6)	1.50 (s, 9)		
		1.73 (t, 6)	1.34 (s, 9)		
$[Ru(CO)_2Ph(ClO_4)(PMe_2Ph)_2]$		1.80 (t, 6)			
		1.44 (t, 6)			
$[Ru(CO)(CNCMe_3)Ph(ClO_4)(PMe_2Ph)_2]$		1.63 (t, 6)	0.98 (s, 9)		
		1.37 (t, 6)			
$[Ru(CO)(CNCMe_3)_2Ph(PMe_2Ph)_2]ClO_4$		1.61 (t, 6)	1.51 (s, 9)		
		1.53 (t, 6)	1.24 (s, 9)		

* In $CDCl_3$ solution. Resonances due to aromatic ring protons are not included. For PMe_2Ph methyl protons, $|^2J(P\text{–}H) + {}^4J(P\text{–}H)| =$ *ca.* 7.5 Hz.

Table 3. Carbon-13 n.m.r. data for the complexes[a]

					Phenyl ring[d]				
Complex	Number	CO[b]	$CNCMe_3$[c]	$CNCMe_3$[c]	C^1	C^2,C^6	C^3,C^5	C^4	PMe_2Ph[e]
$[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$	**(2a)**	201.7	55.8	29.6	161.6	142.5	126.0	121.3	13.0
						138.7			12.1
$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]Cl$	(**3a**, Cl^- salt)	197.7	59.1	29.9	151.5	127.8	125.9	130.1	17.1
		260.5	58.9	29.6					16.9
$[Ru(CO)(CNCMe_3)(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$[f]	**(2b)**	201.7	56.1	30.0	148.4	142.4	112.4	156.0	13.4
						139.3			12.8
$[Ru(CO)(CNCMe_3)_2(COC_6H_4OMe\text{-}4)(PMe_2Ph)_2]ClO_4$[g]	(**3b**, ClO_4^- salt)	198.2	59.1	30.2	144.3	128.1	112.8	161.2	17.1
		257.2	58.8	30.0					16.9
$[Ru(CO)(CNCMe_3)(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	**(2c)**	201.3	56.2	29.9	159.2	143.2	125.9	128.2	13.3
						140.8			12.8
$[Ru(CO)(CNCMe_3)_2(COC_6H_4NMe_2\text{-}4)(PMe_2Ph)_2]Cl$[h]	(**3d**, Cl^- salt)	198.1	58.7	30.0	139.1	130.4	109.8	151.5	16.9
		255.6	58.3	29.8					16.4
$[Ru(CO)(CNCMe_3)Ph(O_2CMe)(PMe_2Ph)_2]$[i]		204.5	55.8	29.8	164.1	143.1	126.1	121.6	14.3
						136.8			12.1
$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$	(**3a**, I_3^- salt)	197.6	59.0	30.2	151.5	127.8	125.8	130.0	17.2
		261.1	58.8	29.8					16.8
$[Ru(CO)_2Ph(ClO_4)(PMe_2Ph)_2]$		200.6			156.8	141.5	128.1	123.8	12.8
		191.7				134.8	127.6		12.4
$[Ru(CO)(CNCMe_3)Ph(ClO_4)(PMe_2Ph)_2]$		204.3	56.7	29.6	160.5	142.5	126.9	122.4	14.0
						135.6	126.8		11.1
$[Ru(CO)(CNCMe_3)_2Ph(PMe_2Ph)_2]ClO_4$		199.3	59.2	30.1	154.0	142.7	127.8	122.8	16.4
			58.3	30.0					15.7

[a] In $CDCl_3$ solution. The weak broad $CNCMe_3$ resonances and the PMe_2Ph resonances have been omitted. [b] Carbonyl ligand resonances were triplets with $|^2J(P\text{–}C)|$ *ca.* 13 Hz. For acyl complexes, the second entry is the triplet resonance [$|^2J(P\text{–}C)|$ *ca.* 11 Hz] for the acyl group. [c] Singlet resonances. [d] For aryl complexes: C^1 resonances were triplets with $|^2J(P\text{–}C)|$ *ca.* 14 Hz; C^2,C^6 resonances were broad; others were singlets. For acyl complexes all resonances were singlets. [e] Triplet resonances: $|^1J(P\text{–}C) + {}^3J(P\text{–}C)|$ *ca.* 33 Hz. [f] C_6H_4OMe at δ 54.8 (s). [g] C_6H_4OMe at δ 55.5 (s). [h] $C_6H_4NMe_2$ at δ 40.1 (s). [i] O_2CMe resonances at δ 175.7 [t, $|^3J(P\text{–}C)| = 2.0$ Hz] and 25.2 (s).

reaction was repeated using a 1:2 molar ratio of $[Ru(CO)_2Ph(ClO_4)(PMe_2Ph)_2]$ to $CNCMe_3$, complete conversion into a mixture of (**3a**) and the new complex was achieved. We suspected that the latter might be the cation $[Ru(CO)(CNCMe_3)_2Ph(PMe_2Ph)_2]^+$, and were able to confirm this by preparing a material with the same ^1H and ^{13}C n.m.r. spectra by another route. This involved the reaction of complex (**2a**) with $AgClO_4$ in propanone, isolation and characterization of the product $[Ru(CO)(CNCMe_3)Ph(ClO_4)(PMe_2Ph)_2]$, and a further reaction of this complex with Me_3CNC. We were unable to crystallize the resulting chlorate(VII) salt, $[Ru(CO)(CNCMe_3)_2Ph(PMe_2Ph)_2]ClO_4$, but its i.r. spectrum indicated the presence of the carbonyl and two mutually *cis* Me_3CNC ligands; and this was confirmed by the ^{13}C n.m.r. spectrum, which also demonstrated the presence of a phenyl ligand and a mutually *trans* pair of PMe_2Ph ligands. Thus the products of reaction of $[Ru(CO)_2Ph(ClO_4)(PMe_2Ph)_2]$ with Me_3CNC were complex (**3a**) and $[Ru(CO)(CNCMe_3)_2Ph(PMe_2Ph)_2]^+$. *Assuming* that both were formed by initial displacement of the chlorate(VII) ligand to give $[Ru(CO)_2(CNCMe_3)Ph(PMe_2\text{-}$

Table 4. Fractional atomic co-ordinates (× 10^4) for $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$

Atom	*x*	*y*	*z*
I(1)	4 823(1)	1 234(1)	3 820(1)
I(11)	3 284(1)	1 385(1)	4 700(1)
I(12)	6 335(1)	1 207(1)	2 921(1)
I(2)	73(1)	3 826(1)	6 170(1)
I(21)	−1 455(1)	3 940(1)	7 040(1)
I(22)	1 592(1)	3 670(1)	5 317(1)
I(3)	9 848(1)	1 180(1)	8 763(1)
I(31)	8 329(1)	724(1)	9 224(1)
I(32)	11 378(1)	1 586(1)	8 315(1)
I(4)	5 362(1)	3 730(1)	1 123(1)
I(41)	3 797(1)	3 397(1)	1 443(1)
I(42)	6 888(1)	4 015(1)	756(1)
Ru(1)	9 828(1)	1 931(1)	4 293(1)
Ru(2)	5 317(1)	4 356(1)	6 778(1)
Ru(3)	5 233(1)	716(1)	7 954(1)
Ru(4)	9 552(1)	3 029(1)	820(1)
P(11)	8 672(2)	2 325(1)	4 643(1)
P(12)	10 938(2)	1 463(1)	4 044(1)
C(131)	9 753(6)	1 955(5)	5 284(5)
N(132)	9 713(5)	1 912(4)	5 856(4)
C(133)	9 598(6)	1 717(5)	6 553(6)
C(141)	10 316(6)	2 837(5)	4 062(5)
N(142)	10 563(5)	3 352(4)	3 879(4)
C(143)	10 863(6)	3 987(5)	3 596(5)
C(151)	9 244(6)	1 020(5)	4 598(5)
O(152)	8 899(4)	898(3)	5 224(4)
C(161)	9 869(5)	1 880(4)	3 383(5)
O(162)	9 886(4)	1 895(4)	2 825(4)
P(21)	6 470(2)	4 186(1)	6 753(1)
P(22)	4 232(2)	4 639(1)	6 714(1)
C(231)	5 598(5)	5 313(5)	6 691(5)
N(232)	5 773(4)	5 851(4)	6 596(4)
C(233)	5 998(6)	6 511(5)	6 331(5)
C(241)	4 854(6)	4 354(5)	7 838(5)
N(242)	4 589(5)	4 281(4)	8 437(4)
C(243)	4 258(6)	4 068(5)	9 169(5)
C(251)	5 858(5)	4 366(5)	5 676(5)
O(252)	6 235(4)	4 843(3)	5 373(3)
C(261)	5 084(6)	3 451(5)	6 811(5)
O(262)	4 968(4)	2 903(3)	6 843(4)
C(134)	10 329(7)	1 899(6)	6 630(6)
C(135)	9 395(7)	1 004(6)	6 592(6)
C(136)	8 988(7)	2 084(6)	7 068(6)
C(144)	11 684(6)	3 955(5)	3 239(6)
C(145)	10 648(6)	4 476(5)	4 192(6)
C(146)	10 518(6)	4 116(5)	3 071(6)
C(153)	9 137(6)	523(5)	4 088(5)
C(154)	8 504(6)	107(5)	4 316(5)
C(155)	8 386(6)	−347(5)	3 876(6)
C(156)	8 891(7)	−425(6)	3 225(6)
C(157)	9 521(6)	−41(5)	2 975(6)
C(158)	9 647(6)	451(5)	3 426(5)
C(211)	6 893(6)	3 507(5)	6 221(6)
C(212)	7 150(7)	4 846(6)	6 390(6)
C(213)	6 519(6)	4 055(5)	7 586(5)
C(214)	6 471(7)	4 566(6)	8 040(6)
C(215)	6 519(8)	4 435(7)	8 697(7)
C(216)	6 620(8)	3 809(7)	8 851(7)
C(217)	6 653(8)	3 313(7)	8 412(7)
C(218)	6 607(6)	3 419(5)	7 769(6)
C(221)	4 359(6)	5 049(5)	5 920(6)
C(222)	3 747(6)	5 213(5)	7 395(6)
C(223)	3 548(6)	3 989(5)	6 803(5)
C(224)	3 259(6)	3 847(5)	5 312(6)
C(225)	2 731(7)	3 351(6)	6 401(6)
C(226)	2 487(7)	2 978(6)	7 017(6)
C(227)	2 760(7)	3 118(6)	7 515(6)
C(228)	3 306(6)	3 617(5)	7 419(6)
C(234)	5 350(6)	6 918(6)	5 702(6)
C(235)	6 669(6)	6 748(6)	6 479(6)
C(236)	6 180(6)	6 478(5)	5 541(5)
P(31)	6 366(2)	773(1)	7 011(1)
P(32)	4 133(2)	545(1)	8 930(1)
C(331)	5 269(6)	−255(5)	7 946(5)
N(332)	5 328(5)	−797(4)	7 985(4)
C(333)	5 471(6)	−1 442(5)	8 117(6)
C(341)	4 680(6)	705(5)	7 316(5)
N(342)	4 360(5)	773(4)	6 971(4)
C(343)	3 986(6)	884(5)	6 503(5)
C(351)	5 801(4)	696(4)	8 629(4)
O(352)	6 178(4)	242(3)	8 577(4)
C(361)	5 242(6)	1 622(5)	7 977(5)
O(362)	5 251(4)	2 182(4)	7 964(4)
P(41)	8 389(2)	2 491(1)	1 334(1)
P(42)	10 667(2)	3 605(1)	197(1)
C(431)	9 444(5)	3 000(5)	−107(5)
N(432)	9 355(5)	3 049(4)	−614(4)
C(433)	9 165(6)	3 229(5)	−1 194(5)
C(441)	10 045(6)	2 180(5)	671(5)
N(442)	10 330(5)	1 714(4)	634(4)
C(443)	10 678(6)	1 113(5)	646(5)
C(451)	9 006(6)	3 903(5)	975(5)
O(452)	8 670(4)	4 018(3)	621(4)
C(461)	9 623(5)	3 094(5)	1 698(5)
O(462)	9 653(4)	3 102(3)	2 238(4)
C(111)	8 139(7)	2 261(6)	5 581(7)
C(112)	8 082(7)	1 873(6)	4 290(6)
C(113)	8 617(6)	3 158(5)	4 442(5)
C(114)	8 485(6)	3 287(5)	3 842(5)
C(115)	8 435(6)	3 926(5)	3 665(6)
C(116)	8 487(7)	4 426(6)	4 103(6)
C(117)	8 617(6)	4 297(5)	4 713(6)
C(118)	8 692(6)	3 664(5)	4 863(5)
C(121)	10 855(7)	709(6)	4 495(6)
C(122)	11 570(7)	1 977(6)	4 295(7)
C(123)	11 466(6)	1 278(5)	3 140(5)
C(124)	11 691(7)	1 787(6)	2 669(6)
C(125)	12 115(7)	1 663(6)	1 955(7)
C(126)	12 277(7)	1 050(6)	1 727(6)
C(127)	12 026(7)	534(6)	2 189(6)
C(128)	11 628(6)	657(5)	2 893(6)
C(321)	4 216(6)	202(6)	9 699(6)
C(322)	3 468(6)	−16(5)	8 777(6)
C(323)	3 633(6)	1 256(5)	9 258(5)
C(324)	3 344(6)	1 532(5)	8 850(6)
C(325)	2 981(7)	2 099(6)	9 079(6)
C(326)	2 918(7)	2 375(6)	9 710(6)
C(327)	3 219(7)	2 121(6)	10 107(6)
C(328)	3 577(6)	1 556(5)	9 894(5)
C(334)	4 804(7)	−1 879(6)	8 207(6)
C(335)	5 621(6)	−1 393(5)	8 785(6)
C(336)	6 151(6)	−1 646(6)	7 500(6)
C(344)	3 195(7)	627(6)	6 884(6)
C(345)	4 374(6)	520(5)	5 832(5)
C(346)	4 047(6)	1 608(6)	6 397(6)
C(353)	5 958(6)	1 244(5)	9 030(6)
C(354)	6 590(6)	1 287(5)	9 177(6)
C(355)	6 722(6)	1 796(6)	9 589(6)
C(356)	6 216(6)	2 243(5)	9 870(6)
C(357)	5 594(6)	2 227(5)	9 740(6)
C(358)	5 464(6)	1 732(5)	9 312(5)
C(411)	7 783(6)	2 895(5)	2 120(6)
C(412)	7 886(6)	2 415(5)	780(6)
C(413)	8 363(6)	1 660(5)	1 619(5)
C(414)	8 413(6)	1 561(5)	2 247(6)
C(415)	8 399(6)	940(6)	2 476(6)
C(416)	8 369(6)	411(6)	2 045(6)
C(417)	8 308(7)	519(6)	1 420(6)
C(418)	8 335(6)	1 147(5)	1 189(6)
C(421)	10 597(6)	4 343(5)	−210(5)
C(422)	11 260(6)	3 165(5)	−559(5)
C(423)	11 249(6)	3 840(5)	655(5)

Table 4 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(244)	4 516(6)	4 547(6)	9 604(6)	C(424)	11 531(6)	4 474(5)	650(5)
C(245)	4 529(6)	3 409(5)	9 169(5)	C(425)	11 994(6)	4 647(6)	1 016(6)
C(246)	3 439(7)	4 039(6)	9 374(6)	C(426)	12 161(6)	4 166(5)	1 363(6)
C(253)	5 837(5)	3 796(4)	5 199(5)	C(427)	11 884(6)	3 527(5)	1 339(6)
C(254)	6 461(6)	3 705(5)	4 637(5)	C(428)	11 433(6)	3 359(5)	996(5)
C(255)	6 481(6)	3 192(5)	5 151(6)	C(434)	9 850(7)	3 116(6)	−1 862(6)
C(256)	5 852(6)	2 802(5)	4 258(5)	C(435)	9 001(6)	3 930(6)	−1 097(6)
C(257)	5 222(5)	2 897(5)	4 842(5)	C(436)	8 508(6)	2 794(5)	−1 157(6)
C(258)	5 208(5)	3 391(5)	5 313(5)	C(444)	10 390(7)	585(6)	297(6)
C(311)	6 832(7)	29(6)	6 812(6)	C(445)	10 477(6)	966(5)	1 429(5)
C(312)	7 025(6)	1 351(5)	7 137(6)	C(446)	11 492(6)	1 256(6)	271(6)
C(313)	6 346(6)	1 004(5)	6 187(5)	C(453)	8 964(6)	4 395(5)	1 547(5)
C(314)	6 529(6)	585(5)	5 622(5)	C(454)	9 543(6)	4 540(5)	1 762(5)
C(315)	6 492(7)	786(6)	4 989(6)	C(455)	9 478(6)	5 024(5)	2 257(5)
C(316)	6 283(7)	1 402(6)	4 945(6)	C(456)	8 839(6)	5 364(5)	2 545(5)
C(317)	6 111(6)	1 808(5)	5 517(5)	C(457)	8 279(6)	5 219(5)	2 322(6)
C(138)	6 146(6)	1 616(5)	6 142(5)	C(458)	8 333(6)	4 744(5)	1 825(5)

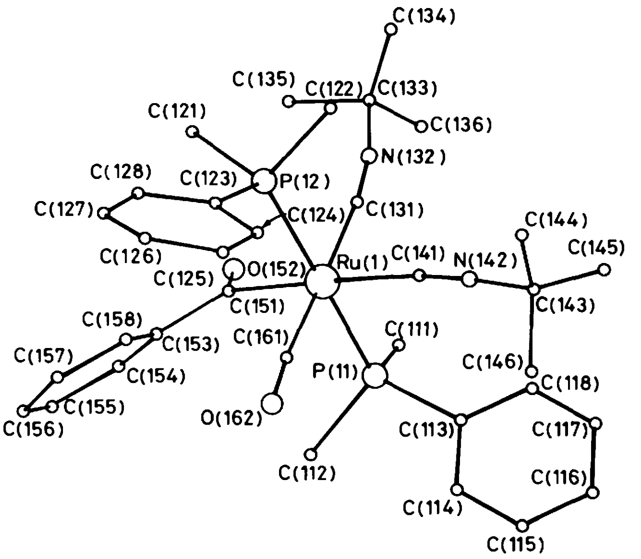


Figure. Structure of $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]^+$ (**3a**), in its tri-iodide salt. Only one of the four cations in the asymmetric unit is shown. In the atom numbering scheme, the first digit identifies each atom as belonging to this cation (cation 1). In Tables 5 and 6 the first digit is omitted

$Ph)_2]^+$, the latter could be ruled out as the intermediate in the conversion of (**1a**) into (**3a**), since no $[Ru(CO)(CNCMe_3)_2Ph(PMe_2Ph)_2]^+$ was formed as a by-product in this conversion. We therefore concluded that the correct route from (**1**) to (**3**) (see Scheme) probably involved initial combination of phenyl and carbonyl ligands, yielding $[Ru(CO)(CNCMe_3)(COC_6H_4\text{-}X\text{-}4)Y(PMe_2Ph)_2]$, which then underwent substitution of Y^- by Me_3CNC.

Structure of the Tri-iodide Salt of Complex (**3a**).—The asymmetric unit was found to contain four independent cations and four tri-iodide anions. The variations in geometry between the four cations are for the most part relatively minor, and the stereochemistry and atom numbering scheme for a single cation are shown in the Figure. Here and in Table 4, where the atomic co-ordinates are listed, the first digit simply identifies each atom as belonging to a particular cation: thus for the cation shown this digit is always a 1. In Tables 5 and 6, which contain selected bond lengths and angles respectively, the first digit is omitted.

Table 5. Selected bond lengths (Å) for $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$

	Molecule 1	Molecule 2	Molecule 3	Molecule 4
Ru–P(1)	2.347(3)	2.351(3)	2.353(2)	2.363(3)
Ru–P(2)	2.363(3)	2.357(3)	2.360(2)	2.360(3)
Ru–C(31)	2.015(12)	2.020(9)	2.025(10)	2.031(11)
C(31)–N(32)	1.172(15)	1.145(12)	1.150(13)	1.150(15)
N(32)–C(33)	1.450(15)	1.469(12)	1.450(14)	1.473(16)
Ru–C(41)	2.037(9)	2.037(9)	2.040(13)	2.043(10)
C(41)–N(42)	1.156(12)	1.162(12)	1.157(16)	1.148(14)
N(42)–C(43)	1.454(12)	1.478(12)	1.481(17)	1.481(14)
Ru–C(51)	2.128(10)	2.125(9)	2.139(12)	2.141(10)
C(51)–O(52)	1.241(12)	1.230(11)	1.230(12)	1.223(15)
C(51)–C(53)	1.519(11)	1.525(10)	1.474(10)	1.521(10)
Ru–C(61)	1.868(10)	1.899(10)	1.880(10)	1.894(11)
C(61)–O(62)	1.154(13)	1.143(12)	1.163(13)	1.152(14)
I–I(1)	2.949(1)	2.914(1)	2.910(1)	2.979(1)
I–I(2)	2.880(1)	2.906(1)	2.906(1)	2.873(1)

The ligand arrangement around the metal in the cation (**3a**) is not greatly distorted from regular octahedral. The Ru–P bond lengths range from 2.347(3) to 2.363(3) Å, values which fall within the normal range for bonds to mutually *trans* pairs of PMe_2Ph ligands in ruthenium(II) complexes.[9] The carbonyl ligand is arranged so that Ru–C–O is approximately linear [175.1(8)—177.3(10)°], and the same applies to the core of the isonitrile ligand *trans* to the benzoyl ligand [C–N–C angles from 170.1(9) to 176.6(9)°]. Possibly as a result of steric interactions, the Me_3C group in the other isonitrile ligand is bent away from the benzoyl ligand, making the C–N–C angles rather smaller [167.4(10)—169.4(12)°]. In all four molecules the Ru–C bond to the isonitrile ligand *trans* to the benzoyl ligand is longer than that to the isonitrile *trans* to CO (as might be expected from the strong *trans*-labilizing effect of acyl ligands[1]), but the differences are rather small in relationship to the standard deviations for the bond lengths.

The presence of a σ-bonded benzoyl ligand in (**3a**) is confirmed by the structure determination. The Ru–C bond lengths to this ligand [2.125(9)—2.141(10) Å] are not significantly different from that [2.142(15) Å] for the same bond in $[Ru(CO)(CNCMe_3)(COPh)Ph(PMe_2Ph)_2]$,[10] which is in keeping with the fact that in both complexes the benzoyl ligand is *trans* to isonitrile. In both structures the acyl and phenyl groups are far from being coplanar, indicating that there is little delocalization between them. In $[Ru(CO)(CNCMe_3)(COPh)Ph(PMe_2Ph)_2]$, the fact that the phenyl ligand lies in the plane defined by the metal and the four carbon atoms to which it is attached causes the acyl group in the benzoyl ligand to be markedly tilted (by *ca.* 57°) out of this plane, but in (**3a**), where there is no phenyl ligand, the tilt is much less (between *ca.* 13 and 20°).

Experimental

Except where otherwise stated, complexes were prepared under an atmosphere of nitrogen, using dry, oxygen-free solvents, and the boiling range of the light petroleum used was 313—333 K. Analytical data for the complexes are listed in Table 7. Details of the instruments used to obtain i.r. and ^1H and ^{13}C n.m.r. spectra have been given elsewhere.[11]

Synthesis of Ruthenium Complexes.—Details of the preparation of the parent complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Y(PMe_2Ph)_2]$ have been given in an earlier paper.[12]

$[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$ (**2a**). A solution of $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ (0.09 g) and Me_3CNC (0.10 cm^3) in $CHCl_3$ (20 cm^3) was stirred until the i.r. spectrum of the solution showed that none of the parent complex remained. After removal of the solvent under reduced pressure, the crude product was recrystallized from a mixture of ethanol and light petroleum and washed with light petroleum (yield 39%).

$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]Cl$ (**3a**, Cl^- *salt*). A solution of $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ (0.10 g) in $CHCl_3$ (20 cm^3) was saturated with CO and treated with Me_3CNC (0.10 cm^3). After 48 h the solvent was removed under reduced pressure. Spectra of the product showed it to be somewhat contaminated with $[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$. Attempted purification by fractional crystallization was unsuccessful.

Table 6. Selected bond angles (°) for $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$

	Molecule 1	Molecule 2	Molecule 3	Molecule 4
P(1)–Ru–P(2)	174.0(1)	172.9(1)	173.5(1)	172.8(1)
P(1)–Ru–C(31)	91.0(3)	88.3(3)	89.0(3)	89.1(3)
P(2)–Ru–C(31)	84.6(3)	85.1(3)	85.1(3)	84.2(3)
P(1)–Ru–C(41)	91.7(3)	92.8(3)	92.7(3)	91.7(3)
P(2)–Ru–C(41)	92.8(3)	91.5(3)	90.4(3)	91.5(3)
P(1)–Ru–C(51)	84.3(3)	84.1(3)	87.9(2)	86.7(3)
P(2)–Ru–C(51)	91.0(3)	91.5(3)	88.8(2)	90.0(2)
P(1)–Ru–C(61)	88.3(3)	90.4(4)	89.8(3)	90.4(3)
P(2)–Ru–C(61)	95.9(3)	95.5(4)	96.0(3)	96.2(3)
C(31)–Ru–C(41)	95.0(4)	95.7(4)	94.5(5)	95.4(4)
C(31)–Ru–C(51)	82.7(4)	83.4(4)	83.8(4)	83.8(4)
C(31)–Ru–C(61)	177.7(4)	177.1(3)	176.8(5)	177.0(4)
C(41)–Ru–C(51)	175.3(4)	176.8(5)	178.2(4)	178.3(4)
C(41)–Ru–C(61)	87.2(4)	87.1(4)	88.5(5)	87.5(4)
C(51)–Ru–C(61)	95.0(4)	93.8(4)	93.2(5)	93.3(4)
Ru–C(31)–N(32)	174.2(9)	175.6(8)	173.0(11)	172.6(8)
C(31)–N(32)–C(33)	167.4(10)	168.3(10)	169.4(12)	168.4(9)
Ru–C(41)–N(42)	172.8(11)	172.6(8)	172.2(8)	174.6(10)
C(41)–N(42)–C(43)	175.2(11)	170.1(9)	176.6(9)	175.6(9)
Ru–C(51)–O(52)	120.2(8)	121.1(7)	118.6(8)	120.6(7)
Ru–C(51)–C(53)	123.6(6)	124.3(5)	126.8(6)	123.7(7)
O(52)–C(51)–C(53)	115.8(8)	114.6(7)	112.6(11)	115.5(8)
Ru–C(61)–O(62)	175.1(8)	176.7(11)	177.3(10)	176.6(8)
I(1)–I–I(2)	174.7(1)	178.1(1)	177.8(1)	177.3(1)

$[Ru(CO)(CNCMe_3)(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$ (**2b**). A solution of $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ (0.075 g) and Me_3CNC (0.03 cm^3) in $CHCl_3$ (30 cm^3) was heated at 333 K, using a stream of nitrogen to purge the solution of CO. After 5 h the solution was cooled, and the solvent was removed under reduced pressure. The product was recrystallized from a mixture of propanone and ethanol, and washed with light petroleum containing a little ethanol (yield 55%).

$[Ru(CO)(CNCMe_3)_2(COC_6H_4OMe\text{-}4)(PMe_2Ph)_2]ClO_4$ (**3b**, ClO_4^- *salt*). To a stirred solution of $[Ru(CO)_2(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$ (0.09 g) in CO-saturated propanone (25 cm^3) was added Me_3CNC (0.035 cm^3). After 20 h $AgClO_4$ (0.033 g) was added, and the AgCl formed was filtered off 1 h later. Slow reduction of the volume of the filtrate under a stream of N_2 gave pale yellow crystals which were washed with light petroleum (yield 59%).

$[Ru(CO)(CNCMe_3)(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$ (**2c**). This was prepared in the same way as $[Ru(CO)(CNCMe_3)(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$, using $[Ru(CO)_2(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$ (0.19 g) and Me_3CNC (0.041 cm^3), with a reaction time of 2 h (yield 80%).

$[Ru(CO)(CNCMe_3)_2(COC_6H_4NMe_2\text{-}4)(PMe_2Ph)_2]Cl$ (**3d**, Cl^- *salt*). A solution of $[Ru(CO)_2(C_6H_4NMe_2\text{-}4)Cl(PMe_2Ph)_2]$ (0.06 g) in $CHCl_3$ (8 cm^3) was treated with Me_3CNC (0.025 cm^3). When the i.r. spectrum of the solution indicated that the reaction was complete, the solvent was removed under reduced pressure. Attempted crystallization of the residual oil was unsuccessful.

$[Ru(CO)(CNCMe_3)Ph(O_2CMe)(PMe_2Ph)_2]$. A solution of $[Ru(CO)_2Ph(O_2CMe)(PMe_2Ph)_2]$ (0.01 g) and Me_3CNC (0.002 cm^3) in $CHCl_3$ (10 cm^3) was stirred until the i.r. spectrum showed that the reaction was complete. The solvent was removed under reduced pressure, and the product recrystallized from a mixture of ethanol and light petroleum (yield 76%).

$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I$ (**3a**, I^- *salt*). A solution of $[Ru(CO)_2Ph(I)(PMe_2Ph)_2]$ (0.06 g) and Me_3CNC (0.025 cm^3) in $CHCl_3$ (5 cm^3) was stirred in the absence of light for 16 h. Ethanol (5 cm^3) was added, and the volume of the solution was reduced under a stream of N_2. The yellow powder obtained was washed with light petroleum containing a little ethanol (yield 53%).

$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I_3$ (**3a**, I_3^- *salt*). The reaction of $[Ru(CO)_2Ph(I)(PMe_2Ph)_2]$ (0.09 g) and Me_3CNC (0.035 cm^3) in $CHCl_3$ (5 cm^3) for 18 h yielded a yellow solution. After removal of the solvent under reduced pressure,

Table 7. Analytical data

		Found (%)			Calculated (%)		
Compound	Number	C	H	N	C	H	N
$[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$	(**2a**)	55.90	6.10	2.45	55.95	6.05	2.35
$[Ru(CO)(CNCMe_3)(C_6H_4OMe\text{-}4)Cl(PMe_2Ph)_2]$	(**2b**)	55.25	5.95	2.30	55.20	6.05	2.20
$[Ru(CO)(CNCMe_3)_2(COC_6H_4OMe\text{-}4)(PMe_2Ph)_2]ClO_4$	(**3b**, ClO_4^- salt)	52.15	5.80	3.60	52.15	5.90	3.45
$[Ru(CO)(CNCMe_3)(C_6H_4Cl\text{-}4)Cl(PMe_2Ph)_2]$	(**2c**)	52.80	5.50	2.20	52.90	5.55	2.20
$[Ru(CO)(CNCMe_3)Ph(O_2CMe)(PMe_2Ph)_2]$		57.55	6.35	2.15	57.70	6.30	2.25
$[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]I$	(**3a**, I^- salt)	50.85	5.70	3.30	50.80	5.65	3.50
$[Ru(CO)_2Ph(ClO_4)(PMe_2Ph)_2]$		47.05	4.65		47.25	4.45	
$[Ru(CO)(CNCMe_3)Ph(ClO_4)(PMe_2Ph)_2]$		50.70	5.40	2.20	50.55	5.45	2.10

the residue was dissolved in propanone (10 cm^3) and light petroleum (b.p. 333—353 K) was added until a slight turbidity appeared. A little propanone was added to clear the solution, which was then left exposed to light and air at 280 K. Orange-brown crystals were slowly formed, and were washed with light petroleum (yield 24%).

[Ru(CO)$_2$Ph(ClO$_4$)(PMe$_2$Ph)$_2$]. To a solution of [Ru(CO)$_2$-Ph(Cl)(PMe$_2$Ph)$_2$] (0.14 g) in propanone (50 cm^3) was added AgClO$_4$ (0.053 g). The solution was stirred in the absence of light for 24 h. The precipitate of AgCl was filtered off and ethanol was added to the filtrate, which was then cooled to 280 K, giving colourless crystals (yield 81%).

[Ru(CO)(CNCMe$_3$)Ph(ClO$_4$)(PMe$_2$Ph)$_2$]. This was prepared in the same way as [Ru(CO)$_2$Ph(ClO$_4$)(PMe$_2$Ph)$_2$], using [Ru(CO)(CNCMe$_3$)Ph(Cl)(PMe$_2$Ph)$_2$] (0.11 g) and AgClO$_4$ (0.04 g) (yield 64%).

[Ru(CO)(CNCMe$_3$)$_2$Ph(PMe$_2$Ph)$_2$]ClO$_4$. The reaction between [Ru(CO)(CNCMe$_3$)Ph(ClO$_4$)(PMe$_2$Ph)$_2$] (0.05 g) and Me$_3$CNC (0.012 cm^3) was carried out in CDCl$_3$ (1 cm^3). When the ^{1}H n.m.r. spectrum of the solution indicated that the reaction was complete, the solvent was removed under reduced pressure, leaving an oil which could not be induced to crystallize.

Crystal-structure Determination of [Ru(CO)(CNCMe$_3$)$_2$-(COPh)(PMe$_2$Ph)$_2$]I$_3$.—The crystal used in the structure determination, of dimensions 0.45 × 0.30 × 0.22 mm, was obtained as described above.

Crystal data. C$_{34}$H$_{45}$I$_3$N$_2$O$_2$P$_2$Ru, M = 1 057.56, triclinic, $P\bar{1}$, a = 20.105(3), b = 20.769(5), c = 20.883(6) Å, α = 92.25(2), β = 66.87(2), γ = 94.41(2)°, U = 7 994.85 Å^3, Z = 8, D_c = 1.757 g cm^{-3}, $F(000)$ = 4 096, μ(Mo-K_α) = 26.96 cm^{-1}, λ = 0.710 69 Å.

X-Ray diffraction data were measured at 123 K on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. Unit-cell dimensions were determined from 2θ measurements of 25 carefully centred reflections, and refined by least squares. Intensity data were collected in the ω–2θ mode with a scan width of 0.6 + 0.35 tan θ to a maximum 2θ value of 56°. The scan rate varied between 1.0 and 4.0 min^{-1} according to the detected intensity. Intensity-control reflections showed no decay over the period of data collection. Intensities were corrected for Lorentz and polarization effects and for variable measuring time, but not for absorption or secondary extinction. 19 726 Reflections were recorded, of which 18 917 were unique, and 4 855 with $I < 2\sigma(I)$ were classified as unobserved.

The ruthenium and iodine positions were determined by direct methods,[13] and a subsequent Fourier difference map revealed the positions of all other non-hydrogen atoms. Refinement was carried out by blocked full-matrix least squares, using a modified version of SHELX 76.[14] Because of the large amount of computing involved, only the ruthenium, iodine, and phosphorus atoms were refined with anisotropic thermal parameters. Refinement converged at R = 0.052, R' = 0.058 for 14 053 observed reflections; $w = 1.000/[\sigma^2(F_o) + 0.001|F_o|^2]$.

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