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XVII *. RADICAL ION-INITIATED SYNTHESES OF RUTHENIUM CLUSTER CARBONYLS CONTAINING TERTIARY PHOSPHINES, PHOSPHITES, ARSINES, $SbPh_3$ OR ISOCYANIDES

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Summary

The syntheses of over sixty known and new derivatives of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ by substitution reactions initiated by sodium diphenylketyl are described. The range of ligands studied includes isocyanides, tertiary phosphines and phosphites, tertiary arsines and $SbPh_3$. The reactions are characterised by high degrees of specificity and conversion; under mild conditions up to four ligands can be introduced. Comparisons with the corresponding thermally induced reactions are made in several cases. The reactions provide routes to mixed ligand derivatives of the cluster carbonyls, although account of relative Lewis base strengths of the ligands may have to be taken. Possible mechanisms of these reactions are discussed briefly, as are the IR ν(CO) spectra of the $Ru_3(CO)_{12-n}L_n$ complexes.

Introduction

The extensive chemistry of $Ru_3(CO)_{12}$ is not paralleled by that of any of its simple substituted derivatives, $Ru_3(CO)_{12-n}(L)_n$, for example, with L = Group VB donor ligand [1]. This contrasts with the situation existing for mononuclear complexes, where tertiary phosphine and arsine complexes abound; these Group VB ligands are essential to the catalytic activity of the ruthenium centre, and allow a degree of tuning of its reactivity. The main reason for these differences lies in the reactivity of the cluster carbonyl. On the one hand, this requires thermal reactions to proceed at elevated temperatures; on the other, the resulting increase in reactivity often results in polysubstitution, further transformation of the ligand after com-

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plexation to the metal cluster, or both. Thus it is well-known that the usual product of reactions between $Ru_3(CO)_{12}$ and tertiary phosphines, PR_3, is the trisubstituted complex $Ru_3(CO)_9(PR_3)_3$; mono- and di-substituted complexes can be obtained with special conditions, such as under CO, or with bulky ligands, as with PCy_3 (vide infra), or as by-products from reactions designed to afford other products. The trisubstituted complex is often unreactive towards small molecules, probably for steric reasons.

With $H_4Ru_4(CO)_{12}$, the result is different, but no less frustrating to the investigator who wishes to study complexes with a particular degree of substitution. A common result is the formation of all possible derivatives $H_4Ru_4(CO)_{12\text{-}n}(PR_3)_n$ (n = 0–4), and although these can be separated using chromatography, the process is tedious and gives only low isolated yields. The selective synthesis of monosubstituted derivatives $H_4Ru_4(CO)_{11}(PR_3)$ by irradiating mixtures of $H_4Ru_4(CO)_{12}$ with tertiary phosphines has been described, however [26].

The problem might be overcome if a method leading to specific and stoichiometric substitution of these clusters could be developed. Our attention was drawn to the results achieved with organometallic radical anions, specifically those obtained from binuclear cobalt carbonyl derivatives, and in particular to their enhanced reactivity towards nucleophiles [2]. As previously communicated, we were able to show that the radical anion generated from $Ru_3(CO)_{12}$ and sodium diphenylketyl, presumably $[Ru_3(CO)_{12}]^{\cdot}$, also reacts readily with Group VB and isocyanide donor ligands to give stoichiometrically substituted products; similar results were obtained with $H_4Ru_4(CO)_{12}$ [3]. This paper records these results in detail, and compares these reactions with analogous thermal substitutions, either already reported, or investigated in connection with this study.

Experimental

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen although subsequent work-up was carried out with no precaution to exclude air. Tetrahydrofuran was freshly distilled from sodium diphenylketyl before use, while other reagent grade solvents were used as received.

Ligands were commercial products and used as received. Literature methods were used to synthesise $Ru_3(CO)_{12}$ [4] and $H_4Ru_4(CO)_{12}$ [5].

IR spectra were obtained with a Perkin–Elmer 683 double-grating spectrophotometer and are accurate to ± 1 cm^{-1}; ^{1}H NMR spectra with Varian T60 (CW) or Bruker WP80 (FT) instruments. Analyses are by the Canadian Microanalytical Service, Vancouver. Tables 1–4 list yields, melting points, analytical and spectroscopic data for the products. Complexes are numbered according to structural type (Fig. 1), with letter(s) indicating ligands present (see caption).

Preparation of sodium diphenylketyl solution. Benzophenone (91 mg, 0.5 mmol) was dissolved in THF (20 cm^3) in a Schlenk tube and finely cut sodium metal was added. The mixture was stirred for 2 h. The resulting deep purple solution was assumed to be ca. 0.025 mmol cm^{-3} in $[Ph_2CO]^{\cdot}$.

Standard reaction procedure. The cluster and the required amount of ligand were dissolved in THF (with warming to ~ 40°C if necessary for the less soluble clusters) in a side-arm flask. The required amount of initiator solution was added dropwise from a syringe, the extent of reaction being monitored by regular infrared examina-

(Continued on p. 328)

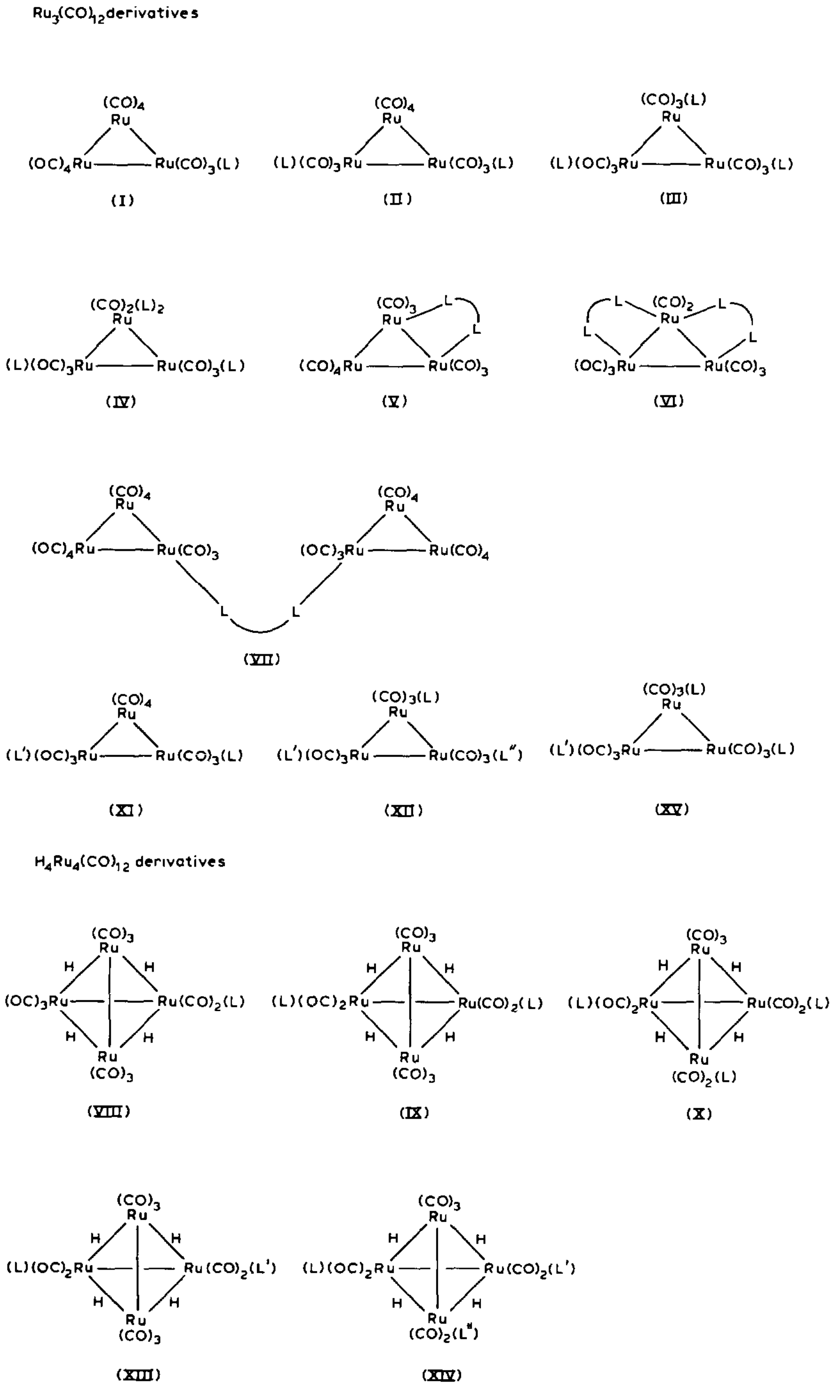

Fig. 1. Structures of complexes. Key to ligands used: (a) PMe_3; (b) PMe_2Ph; (c) PPh_3; (d) $P(C_6H_4Me\text{-}p)_3$; (e) $P(C_6H_4Me\text{-}o)_3$; (f) PCy_3; (g) $P(CH_2CH_2CN)_3$; (h) $P(OMe)_3$; (i) $P(OMe)_2Ph$; (j) $P(OPh)_3$; (k) $P(OC_6H_4Me\text{-}p)_3$; (l) $P(OCH_2)_3CEt$; (m) $AsPh_3$; (n) $SbPh_3$; (o) $CNBu^t$; (p) CNCy; (q) (+)-(*R*)-CNCHMePh; (r) $CNCH_2SO_2C_6H_4Me\text{-}p$ (tosmic); (s) $CH_2(PPh_2)_2$ (dppm); (t) $Ph_2PCH_2CH_2PPh_2$ (dppe); (u) $CH_2(AsPh_2)_2$ (dpam); (v) $Ph_2AsCH_2CH_2AsPh_2$ (dpae)

TABLE 1

PREPARATIONS AND ANALYTICAL DATA FOR COMPLEXES $Ru_3(CO)_{12-n}(L)_n$

Complex	L	Colour	*n*	Yield (%) [a]	M.p. (°C)	Analyses (Found (calcd.)(%)) C	H	Other	M
Ia	PMe_3	red	1	75 (15)	132(dec.)	24.64 (24.46)	2.21 (1.32)		689 (689)
IIa	PMe_3	red	2	60 (60)	192–193	26.12 (26.13)	2.17 (2.46)		737 (737)
IIIa	PMe_3	red	3	76 (90)	168–171	27.34 (27.59)	3.45 (3.47)		785 (785)
IVa	PMe_3	deep red	4	– (0.3)	–	29.38 (28.89)	3.83 (4.36)		833 (833)
Ib	PMe_2Ph	red-orange	1	76 (3)	104–106	30.26 (30.46)	1.23 (1.48)		
Ic	PPh_3	orange	1	81 (37)	131–133	40.86 (39.87)	1.80 (1.73)		
IIc	PPh_3	deep red	2	96 (76)	199–201	50.11 (49.86)	2.53 (2.73)		
IIIc	PPh_3	purple-red	3	85(98)	178–181	57.49 (56.38)	3.71 (3.38)		
Id	$P(C_6H_4Me\text{-}p)_3$	deep orange	1	79	185–186	42.47 (41.97)	2.13 (2.31)		
IIId [b]	$P(C_6H_4Me\text{-}p)_3$	purple	3	87 (88)	184–185				
Ie	$P(C_6H_4Me\text{-}o)_3$	red	1	37	> 300	42.29 (41.97)	2.33 (2.31)		
If	PCy_3	red	1	89 (42)	177–179	38.84 (39.06)	3.61 (3.73)		
IIf	PCy_3	yellow	2	55(80)	211–213	47.21 (48.24)	5.51 (5.81)		
IIg	$P(CH_2CH_2CN)_3$	orange	2	91	157–158	35.61 (34.68)	2.49 (2.49)	N 7.96 (8.67)	
IIIg	$P(CH_2CH_2CN)_3$	orange-red	3	72	180(dec.)	38.07 (38.10)	3.34 (3.19)	N 10.96 (11.11)	

Ih	$P(OMe)_3$	orange	1	81 (43)	61–63	23.04 (22.87)	0.74 (1.23)			737 (737)
IIh	$P(OMe)_3$	red	2	81 (35)	72–73	23.02 (23.12)	1.78 (2.18)			833 (833)
IIIh	$P(OMe)_3$	red	3	70 (15)	111–114	22.87 (23.31)	2.82 (2.93)			929 (929)
Ii [c]	$PPh(OMe)_2$	orange-red	1	74	93.5–95	35.41 (34.93)	2.46 (1.99)			
IIi [c]	$PPh(OMe)_2$	red	2	63 (14)	120–122	38.13 (38.37)	3.21 (2.81)			
IIIi	$PPh(OMe)_2$	red	3	44 (7)	106–108	37.07 (37.19)	2.93 (3.12)			
IVi [b]	$PPh(OMe)_2$	purple	4	91 (57)	165–168					
Ik	$P(OC_6H_4Me\text{-}p)_3$	red	1	64		39.31 (39.88)	1.92 (2.20)	P	3.32 (3.21)	
IIk	$P(OC_6H_4Me\text{-}p)_3$	red	2	26		47.85 (48.49)	3.41 (3.29)	P	4.60 (4.81)	
IIIk	$P(OC_6H_4Me\text{-}p)_3$	red	3	66	153	54.33 (53.32)	4.18 (3.90)	P	5.73 (5.81)	
Il	$P(OCH_2)_3CEt$	orange	1	50	135–137	26.78 (26.40)	1.24 (1.24)			
IIl	$P(OCH_2)_3CEt$	tan	2	57	197–199	34.26 (34.11)	2.65 (2.86)			
IIIl [c]	$P(OCH_2)_3CEt$	yellow-brown	3	92	> 200	31.89 (31.10)	3.45 (3.19)			
Im	$AsPh_3$	orange-brown	1	66		42.88 (42.23)	2.15 (2.12)			
IIm [b]	$AsPh_3$	deep red	2	48 (1.5)						
In	$SbPh_3$	orange	1	44	92–93	36.49 (36.12)	1.31 (1.57)	Sb	10.88 (12.62)	
Io	$CNBu^t$	red	1	78 (86)	114–116	27.46 (27.55)	1.17 (1.31)	N	1.36 (2.02)	696 (696)
IIo [b]	$CNBu^t$	red	2	61 (41)	90–91					751 (751)
Ip	CNCy	red	1	89 (80)	122–125	29.83 (30.01)	1.11 (1.54)	N	1.36 (1.94)	722 (722)

TABLE 1 (continued)

Complex	L	Colour	n	Yield (%) [a]	M.p. (°C)	Analyses (Found (calcd.)(%))			
						C	H	Other	M
Iq	(+)-(R)-CNCHMePh	deep red	1	33	61	32.57 (32.37)	0.77 (1.22)	N 1.96 (1.96)	
IIr	$CNCH_2SO_2C_6H_4Me$-p	red	2	87	132(dec.)	33.70 (34.84)	2.46 (1.86)	N 4.73 (2.88)	975 (975)
Vs	dppm	red	1	90 (28)	174–176	43.76 (43.44)	2.05 (2.29)		
VIs	dppm	dark red-brown	2	26 (12)	178–180	53.46 (53.75)	2.94 (3.42)	P 10.00 (9.56)	
VIIs	dppm	orange-red	0.5	98	169–170	39.58 (40.54)	2.97 (3.01)		
Vu [d]	dpam	red	1	53 (75)	172–173	44.23 (43.95)	2.67 (2.63)		
VIu	dpam	red	2	8 (21)	> 300	47.78 (47.33)	3.65 (3.01)		
Vv	dpae	red	1	78 (60)	172(dec.)	39.76 (40.43)	2.96 (2.26)		

[a] From radical ion-initiated reactions; values in parentheses from thermally induced reactions. In neither case have yields been optimised. [b] Identified by comparison with literature values. [c] C_6H_6 solvate. [d] PhMe solvate.

TABLE 2. PREPARATIONS AND ANALYTICAL DATA FOR MIXED LIGAND COMPLEXES

Complex	Ligands	Colour	Yield (%)	M.p. (°C)	Analyses (Found (calcd.)(%))		
					C	H	Other
$Ru_3(CO)_{12-n}(L)_n$							
XIah [a]	PMe_3 $P(OMe)_3$	red	87	102–104	26.95 (26.06)	2.50 (2.91)	
XIbn	PMe_2Ph $CNBu^t$	red	42	128–132	33.82 (34.33)	2.37 (2.51)	N 1.59 (1.74)

XIdl	$P(C_6H_4Me\text{-}p)_3$ $AsPh_3$	deep red	39	154–156	50.33 (49.30)	3.17 (3.04)	
XIdn	$P(C_6H_4Me\text{-}p)_3$ $CNBu^t$	red	88	151(dec.)	44.51 (44.54)	3.35 (3.11)	N 1.04 (1.44)
XIno	$CNBu^t$ CNCy	deep red	85	130(dec.)	34.03 (34.07)	3.07 (2.60)	N 3.81 (3.61)
XIIach	PMe_3 PPh_3 $P(OMe)_3$	deep red	41	> 300	38.70 (38.95)	3.66 (3.26)	
XIIau	PMe_3 dppe	deep red	81	252(dec.)	47.41 (47.70)	3.82 (3.54)	
XIIhr	$P(OMe)_3$ dpam	bright red	51	223(dec.)	41.40 (42.00)	2.99 (3.03)	
XVIo	$CNBu^t$ $[P(OCH_2)_3CEt]_2$	red-purple	34		32.15 (32.44)	3.18 (3.24)	N 0.99 (1.45)
$H_4Ru_4(CO)_{12-n}(L)_n$							
XIIIbk	PMe_2Ph $P(OC_6H_4Me\text{-}p)_3$	golden yellow	66	136–137	40.53 (39.74)	2.96 (3.08)	
XIIIhi [b]	$P(OMe)_3$ $PPh(OMe)_2$	red	60	oil			
XIVbhi	PMe_2Ph $P(OMe)_3$ $PPh(OMe)_2$	red	75	oil	30.78 (31.63)	3.23 (3.02)	
XIVbjk	PMe_2Ph $P(OCH_2)_3CEt$ $P(OC_6H_4Me\text{-}p)_3$	bright yellow	64	153–155	40.25 (40.25)	3.61 (3.61)	P 5.98 (7.08)

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[a] Et_2O solvate; *M* (mass spectrometry) 785 (calcd. 785). [b] Identified from IR and NMR spectra only.

tion of diluted aliquots. When reaction was complete, THF was pumped off under vacuum and the residue recrystallised from an appropriate solvent.

Full details for all reactions will not be given, the examples below being typical, and indicative of the simplicity of the method and the high yields usually obtained therefrom.

Reactions of $Ru_3(CO)_{12}$

Dimethylphenylphosphine. The radical ion-initiated reaction between $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and PMe_2Ph (55 mg, 0.4 mmol) in THF (8 ml) required 0.1 ml $[Ph_2CO]^{\cdot-}$ solution for complete reaction. Recrystallisation from warm light petroleum gave red-orange Ib (230 mg, 76%).

Triphenylphosphine. Similarly, $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PPh_3 (40 mg, 0.15 mmol) in THF (6 ml) afforded orange crystals of Ic (110 mg, 81%), recrystallised from dichloromethane/light petroleum. Complexes IIc and IIIc were obtained in 96 and 85% yields as dark-red and purple-red solids, respectively, from the appropriate stoichiometric amounts of $Ru_3(CO)_{12}$ and PPh_3.

Tricyclohexylphosphine. Reactions under the usual conditions between $Ru_3(CO)_{12}$ and PCy_3 in the presence of $Na[Ph_2CO]$ afforded If and IIf in 89 and 55% yields, respectively, when 1/1 and 1/2 molar proportions were used. In an attempt to substitute a third CO ligand, a reaction with six-molar excess PCy_3 was carried out. A mixture of $Ru_3(CO)_{12}$ (75 mg, 0.12 mmol) and PCy_3 (200 mg, 0.70 mmol) in THF (25 ml) was treated with $Na[Ph_2CO]$ (ca. 1.2 ml). The solution went dark red immediately (the IR contained ν(CO) bands of $Ru_3(CO)_{11}(PCy_3)$), then changed to orange-yellow after 10 min (the IR now contained ν(CO) bands of $Ru_3(CO)_{10}(PCy_3)_2$); after 45 min at 42°C the solution was cloudy brown. Filtration removed a black solid, and preparative TLC under nitrogen (developing with 3/7 Et_2O/light petroleum) afforded as the only product an off-white powder (26 mg, 11%), dec. > 300°C, whose analysis is consistent with the formulation $Ru(CO)_2(PCy_3)_3$. IR: ν(CO) 2030vs, 1945vs cm^{-1} (Nujol). (Found: C, 67.36; H, 9.98. $C_{56}H_{99}O_2P_3Ru$ calcd.: C, 67.74; H, 10.43%).

Triphenylarsine. (i) A mixture of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and $AsPh_3$ (50 mg, 0.16 mmol) in THF (10 ml) was treated with $Na[Ph_2CO]$ (ca. 1.1 ml). Recrystallisation from a benzene/light petroleum mixture afforded orange-brown Im as a benzene solvate (100 mg, 66%).

(ii) Similarly, $Ru_3(CO)_{12}$ (150 mg, 0.24 mmol) and $AsPh_3$ (140 mg, 0.62 mmol) in THF (6 ml) required $Na[Ph_2CO]$ (2.3 ml) for completion of the reaction. Deep red crystals of IIm (134 mg, 48%) were obtained from benzene/light petroleum.

(+)-(R)-α-Methylbenzyl isocyanide. A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and (+)-(*R*)-CNCHMePh (43 mg, 0.33 mmol) in THF (10 ml) required 0.1 ml initiator solution for complete reaction. The product is extremely soluble in hexane, from which deep red well-formed crystals of Iq (74 mg, 33%) were obtained.

Bis(diphenylphosphino)methane. Complexes Vs and VIs were obtained as the sole products in 90 and 26% yields, respectively, in stoichiometric reactions carried out according to the general procedure outlined above, while if the ratio $Ru_3(CO)_{12}$/dppm was 2/1, the complex $[Ru_3(CO)_{11}]_2(\mu$-dppm) (VIIs) was formed in 98% yield.

Similar reactions carried out with 1,2-bis(diphenylphosphino)ethane to give the complexes Vt, VIt and $[Ru_3(CO)_{11}]_2(\mu$-dppe) (VIIt) have been described earlier [6].

Reactions of $H_4Ru_4(CO)_{12}$

In a typical reaction, a mixture of $H_4Ru_4(CO)_{12}$ (185 mg, 0.25 mmol) and PPh_3 (70 mg, 0.27 mmol) in THF (10 ml) required 0.5 ml of $Na[Ph_2CO]$ solution for complete reaction at room temperature. Evaporation and recrystallisation (light petroleum) gave pale orange crystals of VIIIc (133 mg, 55%).

The following monosubstituted complexes were prepared similarly: light orange $H_4Ru_4(CO)_{11}[P(OMe)_3]$ (VIIIh) (90%); orange $H_4Ru_4(CO)_{11}[P(OPh)_3]$ (VIIIj) (76%) from CH_2Cl_2/light petroleum; bright yellow $H_4Ru_4(CO)_{11}[P(OC_6H_4Me\text{-}p)_3]$ (VIIIk) (65%), m.p. 131–133°C, from EtOH/benzene (Found: C, 36.41; H, 2.31; P, 2.94. $C_{32}H_{25}O_{14}PRu_4$ calcd.: C, 35.97; H, 2.35; P, 2.90%); and orange $H_4Ru_4(CO)_{11}(CNBu^t)$ (VIIIo) (63%) from EtOH/benzene. With two molar equivalents of ligand, red $H_4Ru_4(CO)_{10}(PPh_3)_2$ (IXc) (53%) from MeOH, and red $H_4Ru_4(CO)_{10}(CNBu^t)_2$ (IXo) (34%) from EtOH/benzene were obtained, while a reaction between $H_4Ru_4(CO)_{12}$ (100 mg, 0.13 mmol) and $P(OMe)_3$ (87 mg, 0.7 mmol) gave orange $H_4Ru_4(CO)_9[P(OMe)_3]_3$ (Xh) (65 mg, 47%) from light petroleum. All complexes except VIIIk have been described previously, and were characterised by comparison either with authentic samples, or with the literature values.

Preparation of ruthenium carbonyl derivatives containing different ligands

$Ru_3(CO)_9[P(OMe)_3](dpam)$. A mixture of $Ru_3(CO)_{10}$(dpam) (Vr) (100 mg, 0.09 mmol) and $P(OMe)_3$ (16 mg, 0.13 mmol) in THF (10 ml) was heated to 42°C, and treated with the initiator solution (0.35 ml). After 30 min, solvent was removed (rotary evaporator) and the residue recrystallised (benzene/EtOH) to give bright red crystals of $Ru_3(CO)_9[P(OMe)_3]$(dpam) (XIIhu) (56 mg, 51%).

$Ru_3(CO)_9(PMe_3)(dppe)$. Similarly, a mixture of $Ru_3(CO)_{10}$(dppe) (150 mg, 0.15 mmol) and PMe_3 (19 mg, 0.25 mmol) in THF (9 ml) was treated with 10 drops of $Na[Ph_2CO]$ solution at room temperature. Effervescence occurred, and the solution darkened in colour. After 15 min, solvent was removed, and the product recrystallised (benzene/EtOH) to give deep red $Ru_3(CO)_9(PMe_3)$(dppe) (XIIat) (127 mg, 81%).

$Ru_3(CO)_9(PMe_3)(PPh_3)[P(OMe)_3]$. A mixture of $Ru_3(CO)_{11}[P(OMe)_3]$ (Ih) (100 mg, 0.14 mmol) and PMe_3 (19 mg, 0.25 mmol) in THF (9 ml) was treated with 8 drops of initiator solution. After 10 min gas evolution had ceased, and the IR spectrum indicated that reaction was complete. Solvent was then removed, and the product was recrystallised (Et_2O/pentane) to give pure $Ru_3(CO)_{10}(PMe_3)$-$[P(OMe)_3] \cdot Et_2O$ (XIah) (93 mg, 87%). Isolation of the intermediate complex is not necessary: addition of PPh_3 (32 mg, 0.12 mmol) to the product in THF (8 ml), warming to 47°C, and addition of $Na[Ph_2CO]$ solution (0.95 ml) gave, after 40 min, deep red $Ru_3(CO)_9(PMe_3)(PPh_3)[P(OMe)_3]$ (Xach) (50 mg, 41%) which was recrystallised from an EtOH/benzene/heptane mixture.

$H_4Ru_4(CO)_9(PMe_2Ph)[P(OMe)_3][PPh(OMe)_2]$. Addition of 0.1 ml initiator solution to $H_4Ru_4(CO)_{11}[P(OMe)_3]$ (VIIIh) (246 mg, 0.29 mmol) and $PPh(OMe)_2$ (50 mg, 0.29 mmol) was sufficient to complete the reaction. The product formed a red oil (from light petroleum) (170 mg, 60%), and was identified as $H_4Ru_4(CO)_{10}[P(OMe)_3][PPh(OMe)_2]$ (XIIIhi) from its IR and NMR spectra. Further reaction of (XIIIhi) (169 mg, 0.17 mmol) with PMe_2Ph (25 mg, 0.18 mmol) in THF (3 ml) occurred after addition of 0.3 ml initiator solution. Evaporation of a warm light petroleum extract of the residue afforded a red oil which slowly

solidified, shown to be $H_4Ru_4(CO)_9(PMe_2Ph)[P(OMe)_3][PPh(OMe)_2]$ (XIVbhi) (140 mg, 75%).

$H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$. A mixture of $H_4Ru_4(CO)_{11}[P(OC_6H_4Me\text{-}p)_3]$ (VIIIk) (735 mg, 0.69 mmol) and PMe_2Ph (95 mg, 0.69 mmol) in THF (6 ml) reacted after addition of 0.12 ml initiator solution. Recrystallisation (hexane) gave golden needles of $H_4Ru_4(CO)_{10}(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3]$ (XIIIbk) (540 mg, 66%). This complex (330 mg, 0.28 mmol) reacted with $P(OCH_2)_3CEt$ (45 mg, 0.28 mmol) in THF (4 ml), requiring 3 ml of $Na[Ph_2CO]$ solution. Evaporation and recrystallisation (benzene/light petroleum) gave bright yellow microcrystals of $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3]$-$[P(OCH_2)_3CEt]$ (XIVbkl) (230 mg, 64%).

Reactions between $Ru_3(CO)_{11}(AsPh_3)$, $P(OCH_2)_3CEt$ and $CNBu^t$

A mixture of $Ru_3(CO)_{11}(AsPh_3)$ (Im) (100 mg, 0.11 mmol) and $P(OCH_2)_3CEt$ (28 mg, 0.17 mmol) in THF (5 ml) was treated with 5 drops of the initiator solution. After 15 min at room temperature, removal of solvent and separation of the products by preparative TLC gave: (i) $Ru_3(CO)_{11}[P(OCH_2)_3CEt]$ (Il) (36 mg, 43%); (ii) $Ru_3(CO)_{10}[P(OCH_2)_3CEt]_2$ (IIl) (34 mg, 34%); and $Ru_3(CO)_{10}[P(OCH_2)_3$-$CEt](AsPh_3)$ (XIlm) (17 mg, 15%), all identified from their IR and NMR spectra. If the reaction between $Ru_3(CO)_{11}(AsPh_3)$ and $P(OCH_2)_3CEt$ as above was followed by addition of $CNBu^t$ (8.5 mg, 0.17 mmol), the subsequent product could be separated into several complexes, including: (i) $Ru_3(CO)_9(CNBu^t)[P(OCH_2)_3CEt]_2$ (XV) (36 mg, 34%); (ii) $Ru_3(CO)_{11}[P(OCH_2)_3CEt]$ (Il) (3 mg, 4%); (iii) $Ru_3(CO)_{10}[P(OCH_2)_3CEt]_2$ (IIl) (8 mg, 8%); (iv) $Ru_3(CO)_{10}(CNBu^t)[P(OCH_2)_3$-$CEt]$ (XIlo) (trace) and (v) $Ru_3(CO)_9(CNBu^t)[P(OCH_2)_3CEt](AsPh_3)$ (XIIlmo) (trace). Complexes (IIlo) and (IIIlmo) were identified only from their ^1H NMR spectra.

Thermally induced reactions of $Ru_3(CO)_{12}$

Trimethylphosphine. (i) PMe_3 (55 mg, 0.72 mmol) was distilled into a solution of $Ru_3(CO)_{12}$ (450 mg, 0.70 mmol) in benzene (65 ml). After 9 h at r.t., chromatography (neutral alumina) gave recovered $Ru_3(CO)_{12}$ (379 mg, 84%) and red Ia (72 mg, 15%), both eluted with light petroleum.

(ii) Similarly, a mixture of $Ru_3(CO)_{12}$ (150 mg, 0.23 mmol) and PMe_3 (76 mg, 1.0 mmol) in benzene (65 ml) after 4.5 h at r.t. gave $Ru_3(CO)_{12}$ (50 mg, 33%), red (IIa) (75 mg, 43.5%) (eluted with 5/95 Et_2O/light petroleum) and red IIIa (29 mg, 16%) (eluted with 1/1 Et_2O/light petroleum).

(iii) The reaction between $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PMe_3 (25 mg, 0.33 mmol) in benzene (50 ml) afforded $Ru_3(CO)_{12}$ (26 mg, 26%), Ia (9 mg, 8.4%) and IIa (69 mg, 60%).

(iv) A mixture of $Ru_3(CO)_{12}$ (1750 mg, 2.74 mmol) and PMe_3 (822 mg, 10.8 mmol) was heated in refluxing degassed pentane to give IIIa (1930 mg, 90%) and IVa (7 mg, 0.3%) (eluted with 1/1 Et_2O/light petroleum).

Triphenylphosphine. (i) $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PPh_3 (41 mg, 0.16 mmol) were heated in hexane (50 ml) at 45°C for 1 h. Chromatography (silica gel) gave recovered $Ru_3(CO)_{12}$ (36 mg, 36%), Ic (50 mg, 36.6%) and IIc (40 mg, 23%), eluted with light petroleum or benzene.

(ii) $Ru_3(CO)_{12}$ (900 mg, 1.41 mmol) and PPh_3 (740 mg, 2.82 mmol) in cyclohexane (500 ml) at 55°C for 4 h afforded Ic (90 mg, 7.3%), IIc (1190 mg, 76.3%) and IIIc (186 mg, 9.8%).

(iii) $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PPh_3 (120 mg, 0.46 mmol) in refluxing hexane (50 ml) for 2 h, gave, after cooling, an insoluble purple solid, which was filtered off to give IIIc (205 mg, 97.7%).

Tris(p-tolyl)phosphine. The reaction between $Ru_3(CO)_{12}$ (356 mg, 0.56 mmol) and $P(C_6H_4Me\text{-}p)_3$ (462 mg, 1.52 mmol) in refluxing hexane (3 h) gave purple IIId (727 mg, 88%) after recrystallisation (CH_2Cl_2/hexane).

Tricyclohexylphosphine. (i) After 2.5 h in refluxing hexane (70 ml), a mixture of $Ru_3(CO)_{12}$ (211 mg, 0.33 mmol) and PCy_3 (282 mg, 1.01 mmol) was chromatographed (neutral alumina) to give: (i) yellow IIf (301 mg, 80%), eluted with light petroleum; (ii) red If (38 mg, 13%), eluted with 3/7 dichloromethane/diethyl ether; (iii) a small amount of an unidentified green complex, eluted with 1/1 CH_2Cl_2/Et_2O, which had $\nu(CO)$ at 2094m, 2075w, 2055s, 2033sh, 1988vs, 1960sh cm^{-1} (in $CHCl_3$).

(ii) A similar reaction between $Ru_3(CO)_{12}$ (202 mg, 0.32 mmol) and PCy_3 (95 mg, 0.34 mmol) in heptane (50°C, 1 h) afforded: (i) recovered $Ru_3(CO)_{12}$ (71 mg, 35%); (ii) complex IIf (22 mg, 6%); (iii) complex If (118 mg, 42%).

Trimethyl phosphite. (i) A mixture of $Ru_3(CO)_{12}$ (400 mg, 0.63 mmol) and $P(OMe)_3$ (70 mg, 0.56 mmol) in hexane (150 ml) was heated (50°C, 3 h), and the products separated by chromatography (Florisil) to give; (i) recovered $Ru_3(CO)_{12}$ (78 mg, 20%); (ii) orange Ih (198 mg, 43%), and (iii) red IIh (92 mg, 18%), eluted successively with light petroleum.

(ii) A similar reaction between $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $P(OMe)_3$ (70 mg, 0.56 mmol) in hexane (100 ml) at 50°C for 5 h afforded: (i) recovered $Ru_3(CO)_{12}$(10 mg, 5%); (ii) complex Ih (67 mg, 29%); (iii) complex IIh (91 mg, 35%) and (iv) red IIIh (43 mg, 15%), the latter eluted with 1/3 Et_2O/light petroleum.

(iii) A third experiment used $Ru_3(CO)_{12}$ (400 mg, 0.63 mmol) and $P(OMe)_3$ (220 mg, 1.77 mmol), and heating in refluxing cyclohexane for 3 h resulted in deposition of some dark-coloured material. Chromatography of the filtered reaction mixture gave only complex IIIh (81 mg, 14%).

Bis(diphenylphosphino)methane. The reaction between $Ru_3(CO)_{12}$ (480 mg, 0.75 mmol) and dppm (600 mg, 1.56 mmol) in refluxing cyclohexane (200 ml) for 16 h afforded the following compounds by chromatography (alumina) of the filtered solution: (i) recovered $Ru_3(CO)_{12}$ (42 mg, 9%); (ii) red Vs, eluted with light petroleum, and obtained as a toluene solvate (201 mg, 28%) from toluene/light petroleum; (iii) dark red-brown VIs (82 mg, 12%), eluted with 95/5 Et_2O/C_6H_6. A yellow solid deposited during the reaction was shown to be $Ru_3(\mu_3\text{-}PPh)(\mu\text{-}CHPPh_2)(CO)_7(dppm)$ (220 mg, 25%) by comparison with the literature [7].

Bis(diphenylarsino)methane. (i) A reaction between $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and dpam (76 mg, 0.16 mmol) in refluxing toluene (20 ml) for 1.5 h gave, after chromatography (Florisil): (i) recovered $Ru_3(CO)_{12}$ (11 mg, 11%), and (ii) red (Vu) (123 mg, 75%).

(ii) Similarly, $Ru_3(CO)_{12}$ (400 mg, 0.63 mmol) and dpam (610 mg, 1.29 mmol) in refluxing toluene (50 ml) for 24 h afforded: (i) complex Vu (291 mg, 44%), obtained as a toluene solvate from toluene/octane; (ii) red VIu (196 mg, 21%), eluted with benzene and (iii) an unidentified deep red complex (41 mg), eluted with MeOH, with $\nu(CO)$ at 2020s, 1995sh, 1975vs, 1946sh cm^{-1} (in CH_2Cl_2).

1,2-Bis(diphenylarsino)ethane. Chromatography (alumina) of the mixture obtained by heating $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and dpae (76 mg, 0.16 mmol) in refluxing toluene (75 ml) for 23 h gave: (i) recovered $Ru_3(CO)_{12}$ (29 mg, 29%) and (ii) red Vv (100 mg, 60%), both eluted with light petroleum.

Results

The large number of complexes that we have obtained are best discussed on a ligand-by-ligand basis, and Fig. 1 illustrates the general formulae of the cluster derivatives, and lists the ligands we have used. The majority of complexes were obtained by addition of sodium diphenylketyl to a stoichiometric mixture of $Ru_3(CO)_{12}$ and the ligand in tetrahydrofuran, as described in the Experimental section. We had also commenced a study of certain of these reactions promoted by heat, and these results are also summarised. It is convenient to discuss the results obtained with $Ru_3(CO)_{12}$ first, followed by those with $H_4Ru_4(CO)_{12}$; the final section is devoted to a description of some mixed-ligand complexes.

Reactions of $Ru_3(CO)_{12}$

Trimethylphosphine. To our knowledge, no complexes of types I–IV containing PMe_3 have been described hitherto. First studied was the thermally induced reaction which at Australian summer room temperature proceeded readily to give Ia and IIa, and on moderate heating, complexes IIIa and IVa, the relative proportions depending on the relative amounts of reactants present. This behaviour contrasts with the usual reactions between $Ru_3(CO)_{12}$ and PR_3, which afford the trisubstituted derivatives; the Experimental section records the best of a limited number of experiments designed to optimise the yields of each complex. A minor product from a relatively large scale reaction employing ca. 4 mol equivalents of the phosphine was IV, obtained as a dark-red solid.

As with all complexes described herein, the PMe_3 derivatives were readily characterised by analysis and spectroscopically: the IR spectra are discussed below. The ^1H NMR spectra of Ia, IIa and IIIa contained characteristic doublets for the P*Me* groups; that of IVa contained two equal intensity doublets, suggesting a structure in which two Ru atoms each bears one equatorial PMe_3 substituent, while the third has two PMe_3 substituents, either both axial or both equatorial. Since IIIa is known to have the three PMe_3 ligands attached one to each Ru in an equatorial position [8], the latter is preferred. Presumably steric interaction of the fourth PMe_3 ligand with the other PMe_3 and CO groups on the cluster renders the formation of IVa difficult, leading to its isolation in only very low yield. The mass spectrum of IVa contains a parent ion cluster centred on m/e 833, which fragments by stepwise loss of the eight CO groups.

Dimethylphenylphosphine. Complexes Ib, IIb and IIIb have been described previously [9], being obtained from thermal reactions between $Ru_3(CO)_{12}$ and the phosphine (Ib, 3%; IIb, 17%; IIIb, 19%). The present method offers a significant improvement in yield.

Triphenylphosphine. Complex IIIc is perhaps the best-known of the Group V ligand derivatives of $Ru_3(CO)_{12}$, having been studied on numerous occasions [9,10]. The mono- and di-substituted complexes IIIa and IIIb have also been described by several workers, being obtained from IIIc and CO [11], or from $Ru_3(CO)_{12}$ and $Pt(\eta^2\text{-stilbene})(PPh_3)_2$ [9]. The radical ion-initiated reactions afford these complexes specifically and in high yield. It is also of interest that we have found that these materials can also be obtained from short thermally induced reactions between $Ru_3(CO)_{12}$ and PPh_3, albeit with the necessity for chromatographic purification if Ic or IIc are required.

Tris(p-tolyl)phosphine. Previous reports have described IIId [9], and we obtained this complex, free from either Id or IId, from a reaction between $Ru_3(CO)_{12}$ and $P(C_6H_4Me\text{-}p)_3$ in refluxing hexane. The previously unreported Id was obtained in 79% yield from the radical ion-initiated reaction in THF.

Tris(o-tolyl)phosphine. This sterically demanding ligand does not give simple substitution products in thermal reactions with $Ru_3(CO)_{12}$. Only low yields of Ie were obtained from the radical ion-initiated reaction.

Tricyclohexylphosphine. A maximum of two CO groups can be displaced by the bulky PCy_3 ligand in either thermally or radical ion-induced reactions. Complex IIf is unusual in being eluted before the monosubstituted complex If, perhaps as a result of the hydrocarbon-like envelope of cyclohexyl groups in the former complex which reduces its affinity for the chromatographic adsorbent. With a large excess of PCy_3, breakdown of the cluster occurs to give a low yield of a complex of composition $Ru(CO)_2(PCy_3)_3$; the two ν(CO) bands indicate a *cis*-$Ru(CO)_2$ arrangement. The high ν(CO) frequencies, oxidative stability and high melting point suggest that it is not a simple ruthenium(0) derivative, however.

Tris(2-cyanoethyl)phosphine. The new complexes IIg and IIIg were obtained by the radical ion-initiated reaction; the thermal reaction was not studied.

Trimethyl phosphite. The advantages of our new route to these substituted complexes are again illustrated in the reactions of $P(OMe)_3$, from which high yields of specifically mono-, di- or tri-substituted products were obtained. These contrast with the low yields of mixtures of products obtained on heating the two reactants, and this reaction is one example where the trisubstituted complex is not formed as a preferred product.

Dimethyl phenylphosphinite. Complex IIi and IVi containing $PPh(OMe)_2$ have been obtained previously in low yield from thermal reactions between $Ru_3(CO)_{12}$ and the ligand [9]. Moderate to high yields of the pure complexes Ii and IIIi were obtained by the reactions described here.

Tri-p-tolyl phosphite. Each of the complexes Ik, IIk and IIIk was obtained pure from stoichiometric proportions of reactants; the solubility of IIk proved to be higher than usual, resulting in only 26% isolated yield of this complex.

4-Ethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2]octane. The constrained phosphite $P(OCH_2)_3CEt$ reacted similarly to give the first triruthenium carbonyl complexes containing this ligand.

Triphenylarsine. Only the disubstituted complex IIm was obtained from heating $Ru_3(CO)_{12}$ and $AsPh_3$ in refluxing hexane [9,12]. The radical ion-initiated reaction of appropriate proportions of reactants afforded Im and IIm, the latter identified by comparison with a known sample, but no trisubstituted complex could be obtained.

Triphenylstibine. The only product isolated from the reaction between $Ru_3(CO)_{12}$ and $SbPh_3$, on irradiation in hexane solution, was the mononuclear $Ru(CO)_4(SbPh_3)$, formed by breakup of the Ru_3 cluster [13]. In contrast, our reaction conditions enabled isolation of orange In as the first organostibine derivative of $Ru_3(CO)_{12}$ to be described.

t-Butyl isocyanide. We have recently described the formation of several isocyanide derivatives of ruthenium carbonyl [4], and the present results show that these complexes may also be obtained in high yield by the radical ion-initiated reaction. The CNBu^t derivatives Io and IIo were obtained.

Cyclohexyl isocyanide. As found for most of these reactions, the yield of Ip was considerably greater than that obtained by the thermal reaction [4].

(+)-(R)-α-methylbenzyl isocyanide. Complex Iq, containing an optically active isocyanide ligand, was so soluble in hexane that only a poor isolated yield was obtained.

Bis(diphenylphosphino)methane. The reaction between $Ru_3(CO)_{12}$ and dppm has been described recently [7]. In xylene at 80–85°C, complex VIs was obtained in 73% yield, while at 130°C, oxidative addition of the ligand to the Ru_3 cluster occurred to give $Ru_3(\mu_3\text{-PPh})(\mu\text{-CHPPh}_2)(CO)_7(\text{dppm})$. In our hands, a similar reaction in refluxing cyclohexane afforded both Vs and VIs, together with some of the phosphinidene complex. Complexes Vs and VIs were obtained as the sole products in stoichiometric reactions carried out according to our general procedure; no alteration product was produced in these reactions which went to completion in a few minutes at room temperature. As found with the related bidentate ligand dppe [6], reaction of $Ru_3(CO)_{12}$ with 0.5 mol equivalent of dppm afforded complex VIIs containing two $Ru_3(CO)_{11}$ units bridged by a dppm ligand.

Bis(diphenylarsino)methane. A mixture of Vu and VIu can be obtained from reactions carried out in refluxing toluene, although some evidence for further reaction on longer heating was obtained. The radical ion-initiated syntheses proceeded well for Vu, but unusually only a very low yield of VIu was isolated from the 1/2 reaction.

1,2-Bis(diphenylarsino)ethane. With this ligand, only complex Vv has been isolated, as the only product if the reaction is initiated by $Na[Ph_2CO]$, but mixed with unreacted $Ru_3(CO)_{12}$ (and ligand) in the thermal reaction, and requiring chromatographic purification.

Reactions of $H_4Ru_4(CO)_{12}$

Thermally-induced reactions of $H_4Ru_4(CO)_{12}$ with a number of tertiary phosphines and phosphites have been described, and are characterised by the formation of most, if not all, of the substitution products $H_4Ru_4(CO)_{12-n}L_n$. Similar reactions carried out in the presence of $Na[Ph_2CO]$ were found to give smooth reactions affording high yields of a single pure complex, the composition of which reflected the molar ratio of the reactants. Thus, whereas the reaction between $H_4Ru_4(CO)_{12}$ and $P(OMe)_3$ gave a complex mixture of $H_4Ru_4(CO)_{12-n}[P(OMe)_3]_n$ ($n = 0$–4) complexes which required extensive chromatography to obtain pure complexes [14], we have prepared two of these compounds pure in room temperature reactions between $H_4Ru_4(CO)_{12}$ and one or three molar equivalents of $P(OMe)_3$. We find that increasing amounts of initiator are required as the degree of substitution increases. Similar results were obtained with PPh_3, $P(OC_6H_4Me\text{-}p)_3$ and CNBu^t, the products being characterised by comparison with reported spectroscopic data [15,16].

Preparation of mixed ligand derivatives of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$

As far as we are aware, the only references to derivatives of $Ru_3(CO)_{12}$ containing more than one tertiary phosphine are to the ligand exchange reactions between $Ru_3(CO)_9(PPh_3)_3$ and PEt_3, in which all possible complexes $Ru_3(CO)_9(PEt_3)_n$-

$(PPh_3)_{3-n}$ (n = 1–3) were detected spectroscopically, but not otherwise characterised [10a]. A reaction between $Ru_3(CO)_9(PPh_3)_3$ and PBu_3 is reported to give $Ru_3(CO)_9(PBu_3)_3$, but no intermediate complexes were described [17].

The ready availability of specifically substituted derivatives of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$, such as those described above, suggested that successive reactions with different ligands might afford designed synthesis of new complexes containing two or more different ligands, other than CO. As we have communicated previously, the appropriate experiments showed this to be the case, and we have made complexes containing several different combinations of ligands [18]. The new complexes were characterised by the usual combination of analytical and spectroscopic methods, the significant data being summarised in the Tables. As with polysubstitution with one ligand, we found that reactions leading to trisubstituted complexes required somewhat more radical ion-initiator than those giving mono- or di-substituted derivatives; these reactions are also best carried out by warming the reaction mixture (to ca. 40–50°C) for 15–30 min.

In one instance we found that a ligand other than CO was replaced. The radical-initiated reaction between $Ru_3(CO)_{11}(AsPh_3)$ and $P(OCH_2)_3CEt$ afforded the two complexes $Ru_3(CO)_{12-n}[P(OCH_2)_3CEt]_n$ (n = 1 and 2) in addition to the expected $Ru_3(CO)_{10}[P(OCH_2)_3CEt](AsPh_3)$. The total conversion amounted to 92% (based on separated isolated products). The formation of the phosphite-substitution products can be explained by competitive loss of CO and $AsPh_3$ from the intermediate radical anion (see below). Indeed, free $AsPh_3$ was detected on the thin-layer chromatogram of the reaction products. Not surprisingly, when $CNBu^t$ was added to the above reaction mixture (in the initial expectation that the mixed phosphite-arsine complex was the only product), six complexes were isolated. The major product was $Ru_3(CO)_9(CNBu^t)[P(OCH_2)_3CEt]_2$, and the expected $Ru_3(CO)_9(CNBu^t)$-$[P(OCH_2)_3CEt](AsPh_3)$ was obtained only in trace amounts. These results indicate that although the radical anion-initiated route to mixed ligand clusters can be used successfully in many cases, caution must be exercised in the synthesis of complexes containing ligands of widely differing basicity. In these cases, it is likely that high yields of the desired products will be obtained by only one of the several permutations of the individual synthetic routes, which will be determined by the relative basicities of the ligands employed.

The properties of these complexes are unremarkable, and we note only at this time that the trisubstituted derivatives of $H_4Ru_4(CO)_{12}$ such as (XIVbhi) and (XIVbkl) are chiral, and if they are capable of being resolved, may be useful as optically active hydrogenation or hydroformylation catalysts. Further studies to determine factors influencing the preferred sequence of ligand substitution, and on the catalytic utility of selected complexes, is proceeding.

Mechanistic speculations

We have not made a detailed study of the mechanism of the radical ion-initiated reaction but all our results are consistent with the overall electron transfer catalysed process which we proposed earlier [3] by comparison with other organometallic [2,19,20] and organic systems [21]. This is outlined in eqs. 1–3:

$$Ru_3(CO)_{12} + [Ph_2CO]^{\bar{\cdot}} \rightarrow [Ru_3(CO)_{12}]^{\bar{\cdot}} + Ph_2CO \quad (1)$$

$$[Ru_3(CO)_{12}]^{\bar{\cdot}} + L \rightarrow [Ru_3(CO)_{11}L]^{\bar{\cdot}} + CO \quad (2)$$

$$[Ru_3(CO)_{11}L]^{\cdot -} + Ru_3(CO)_{12} \rightarrow Ru_3(CO)_{11}L + [Ru_3(CO)_{12}]^{\cdot -} \qquad (3)$$

This process relies on the increased susceptibility of the radial anion $[Ru_3(CO)_{12}]^{\cdot -}$ towards nucleophilic attack, when compared with the neutral parent cluster. This probably results from the extra electron entering an Ru–Ru antibonding orbital, thus facilitating Ru–Ru bond cleavage to generate a labile 17e metal centre; a mechanism involving enhanced CO loss from an intact Ru_3 cluster, similar to that proposed recently for reactions at an Fe_3 cluster, seems less likely [22]. On the basis of a brief electrochemical study of $Ru_3(CO)_{12}$, in which it was reported that the $[Ru_3(CO)_{12}]^{\cdot -}$ radical has a very short lifetime (in acetone) [23], Robinson et al. [20] have suggested that substitution at $Ru_3(CO)_{12}$ initiated by $[Ph_2CO]^{\cdot -}$ does not involve an electron transfer catalysed mechanism, but occurs by an alternative, unspecified route. Definite conclusions must await the results of more detailed studies [24].

The following general points can be made about the substitution reactions studied herein:

(1) For $Ru_3(CO)_{12}$, mono-, di- and tri-substitution can be brought about by catalytic amounts of $Ph_2CO^{\cdot -}$, although efficiencies decrease with higher substitution. For example, formation of $Ru_3(CO)_{12-n}[P(OCH_2)_3CEt]_n$ required 2 mol% ($n = 1$), 3 mol% ($n = 2$) and 30 mol% ($n = 3$) of initiator. This is not unexpected; reduction of a cluster to the corresponding anion is rendered more difficult as CO is replaced by poorer π-acceptor ligands PR_3, presumably slowing the electron transfer step (eq. 3). At the same time steric and statistical factors will tend to discourage higher substitution.

(2) For most examples, the infrared spectra of the crude reaction mixtures indicate that quantitative conversion to one product had occurred; yields quoted are isolated yields of recrystallised products, some of which have quite high solubilities in hydrocarbons.

(3) Reactions with PR_3, $P(OR)_3$ and CNR were all efficiently initiated but those with AsR_3, SbR_3 and BiR_3 were decreasingly so, to the extent that no $Ru_3(CO)_{11}(BiPh_3)$ could be isolated. This trend presumably reflects the decreasing nucleophilicity of MR_3 as the atomic weight of M increases.

(4) For neither of the ruthenium clusters studied were products arising from cluster breakdown observed as co-products.

(5) Reactions with $H_4Ru_4(CO)_{12}$ were noticeably less efficient than with $Ru_3(CO)_{12}$. Possible chain-termination processes of $H_4Ru_4(CO)_{12}^{\cdot -}$ (the postulated intermediate) by loss of hydride ligands may be responsible for this. It was noted in stepwise reactions with $H_4Ru_4(CO)_{12}$ that the second substitution was apparently more facile than the first. However, this may be an artefact arising from the poor solubility of $H_4Ru_4(CO)_{12}$ (compared with most $H_4Ru_4(CO)_{12}L$ complexes) which meant that reactions had to be carried out with dilute and/or warmed solutions which are likely to have an adverse affect on the reaction because of decreased electron transfer rates or increased radical-anion decay.

(6) The maximum degree of substitution obtainable with $H_4Ru_4(CO)_{12}$ depends on the incoming nucleophile. Thus with excess $P(OMe)_3$ the trisubstituted $H_4Ru_4(CO)_9[P(OMe)_3]_3$ was the final product, whereas with excess PPh_3 only $H_4Ru_4(CO)_{10}(PPh_3)_2$ could be obtained despite the addition of up to 30 mol% initiator.

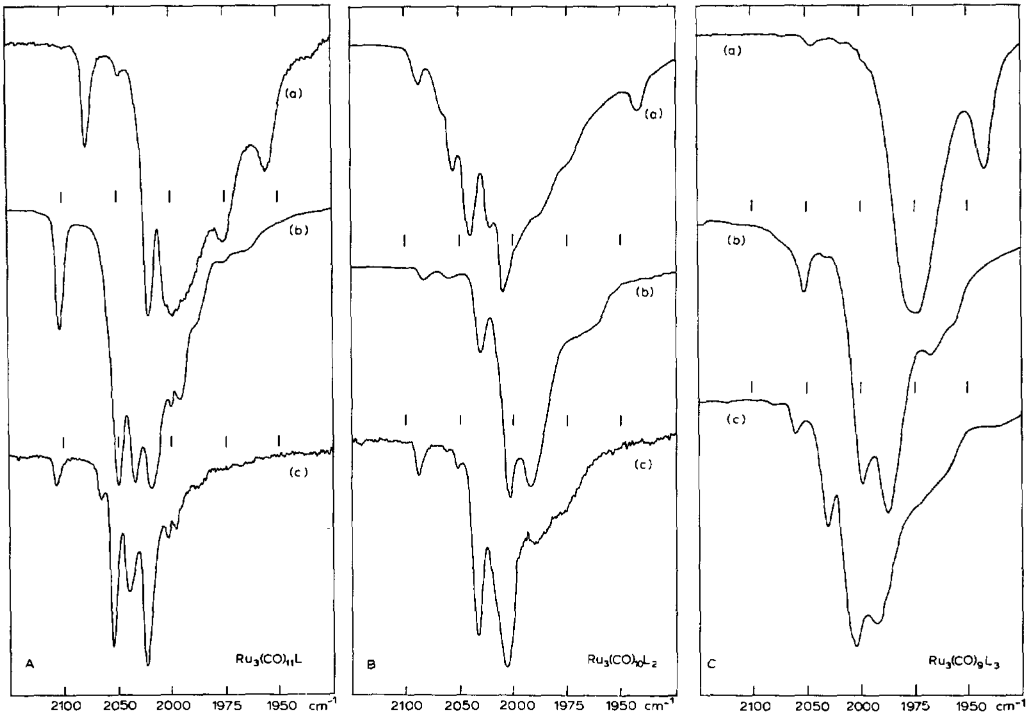

Fig. 2. Typical IR $\nu(CO)$ spectra of $Ru_3(CO)_{11}(L)$ (A), $Ru_3(CO)_{10}(L)_2$ (B), and $Ru_3(CO)_9(L)_3$ (C) complexes. Ligands: (a) PMe_3; (b) $P(OMe)_2Ph$; (c) $P(OMe)_3$.

Spectroscopic studies

The isolation of a number of specifically substituted derivatives of $Ru_3(CO)_{12}$ has enabled us to record definitive $\nu(CO)$ spectra and to establish some features of these spectra in relation to the degree of substitution. Figure 2 shows some typical spectra of the complexes $Ru_3(CO)_{12-n}L_n$, and Table 3 lists the frequencies of the main absorptions for each of the complexes studied.

For $n = 1$, there are three, sometimes four, strong bands between 1985 and 2055 cm^{-1}, together with a weak to medium absorption between 2090–2100 cm^{-1}. As expected the frequencies of all bands decrease as the basicity of the ligand increases. The spectra of the disubstituted complexes show two main bands, the profiles of which indicate that the envelope contains three or more absorptions, between 1965 and 2050 cm^{-1}, with a high-energy absorption between 2070 and 2090 cm^{-1}. There is a general decrease in frequency with the introduction of the second ligand. The trends in the trisubstituted complexes are less obvious, with the $\nu(CO)$ spectra being much less well resolved; the major absorptions again lie between 1965 and 2050 cm^{-1}, as broad envelopes which may be resolved into individual maxima, with the highest energy band being found between 2050 and 2085 cm^{-1}. For $n = 4$, where a wide range of complexes is not available for comparison, the overall absorption pattern is shifted to lower energies by some 20 cm^{-1} from the trisubstituted complexes, reflecting the distribution of electron density from the phosphorus ligands into the CO antibonding orbitals. There is no pronounced band at higher frequencies.

(Continued on p. 343)

TABLE 3. IR AND NMR SPECTROSCOPIC DATA FOR COMPLEXES $Ru_3(CO)_{12-n}(L)_n$

L	Complex	ν(CO) (cm^{-1})	Solvent	^{1}H NMR		
				δ(ppm)	Assignment	Solvent
n = 1						
PMe_3	Ia	2086w,2066sh,2056m,2040s,2023s,2011vs,1990sh,		1.60d (*J* 11 Hz)	Me	$(CD_3)_2CO$
		1978sh,1943m	C_6H_{12}			
PMe_2Ph	Ib	2096m,2044s,2028s,2016s,2000w,1987w	C_6H_{12}	1.97d (*J* 10 Hz)	Me	
				7.52m	Ph	$CDCl_3$
PPh_3	Ic	2097m,2047s,2031sh,2026sh,2017s,2001w,1986w	C_6H_{12}	7.48m		$CDCl_3$
$P(C_6H_4Me\text{-}p)_3$	Id	2098m,2063m,2048s,2032ms,2017vs,2001m,1989m,		2.35s	Me	
		1977sh,1955m	C_6H_{12}	7.28m	C_6H_4	$CDCl_3$
$P(C_6H_4Me\text{-}o)_3$	Ie	2099m,2045s,2030s,2016vs,2000m,1989m,1955sh	CH_2Cl_2	2.45s	Me	
				7.30m	C_6H_4	$CDCl_3$
PCy_3	If	2099m,2082m,2047m,2026s,2016vs,1996s,1985s,		0.53,1.42,1.58,	Cy	
		1970m,1945m	C_6H_{12}	2.23m(br)		$CDCl_3$
$P(OMe)_3$	Ih	2104m,2064w,2051vs,2038s,2019vs,2001s,1997s,		3.68d (*J* 12 Hz)	Me	$CDCl_3$
		1984m	C_6H_{12}			
$PPh(OMe)_2$	Ii	2103m,2051s,2035s,2020s,2002ms,1997ms,1990sh,		3.62d (*J* 12 Hz)	OMe	
		1978sh,1967sh	C_6H_{12}	7.51m	Ph + C_6H_6	$CDCl_3$
$P(OC_6H_4Me\text{-}p)_3$	Ik	2104m,2088w,2050s,2038s,2020vs,2003s,1990m	C_6H_{12}	2.33s	Me	
				7.03m	C_6H_4	$CDCl_3$
$P(OCH_2)_3CEt$	Il	2106w,2051s,2043m,2023s,2002m,1990w	C_6H_{12}	0.84m	Me	
				1.19m	CH_2Me	
				4.25d (*J* 5 Hz)	OCH_2	$CDCl_3$
$AsPh_3$	Im	2100w,2048m,2038sh,2018vs,2000m,1990sh	C_6H_{12}	7.45m	Ph	$CDCl_3$
$SbPh_3$	In	2101m,2050s,2032m,2019vs,2000w,1989w,1976m,		7.40m	Ph	$CDCl_3$
		1965m	C_6H_{12}			
$CNBu^t$	Io	2093m,2047s,2040s,2016s,1998m,1995m; ν(CN) 2170m	C_6H_{12}	1.53s	CMe_3	$CDCl_3$
CNCy	Ip	2090m,2048m,2038vs,2032s,2024m,2011m,2003m,		1.78m(br)	Cy	$(CD_3)_2CO$
		1994sh ν(CN) 2175m	C_6H_{12}			
CNCHMePh	Iq	2095m,2047s,2041s,2022m,2006m,2001m; ν(CN) 2175w	C_6H_{12}	1.76d (*J* 7 Hz)	Me	$CDCl_3$
				5.24q (*J* 7 Hz)	CH	
				7.38m	Ph	
1/2(dppm)	VIIs	2094m,2054sh,2046m,2012sh,1998sh,1978s,1969s,		4.24t (*J* 12 Hz)	CH_2	$CDCl_3$
		1946sh, 1912vw	C_6H_{12}	7.36m	Ph	

n = 2

PMe_3	IIa	2076m,2046w,2019vs,1998vs,1976s,1955m	C_6H_{12}	1.80d (*J* 10 Hz)	Me	$(CD_3)_2CO$
PPh_3	IIc	2072w,2060w,2047m,2034sh,2024s,1990s,1968s,1950m	C_6H_{12}	7.50m	Ph	$CDCl_3$
PCy_3	IIf	2077s,2059w,2045s,2001s,1989m,1979m,1941w	C_6H_{12}	0.75,1.32,1.50,	Cy	$CDCl_3$
				1.88m		
$P(CH_2CH_2CN)_3$	IIg	2076w,2056w,2022m,2000s,1988vs,1950m,1937m		1.39(br)	CH_2	$(CD_3)_2CO$
		ν(CN) 2162w	CH_2Cl_2			
$P(OMe)_3$	IIh	2088w,2050w,2034s,2008vs,1991m,1980sh	C_6H_{12}	3.66d (*J* 12)		$CDCl_3$
$PPh(OMe)_2$	IIi	2081w,2058w,2005s,1986s,1971sh	C_6H_{12}	3.57d (*J* 11 Hz)	OMe	
				7.41m	Ph	$CDCl_3$
$P(OC_6H_4Me\text{-}p)_3$	IIk	2088w,2036m,2010s,1993m,1980sh	C_6H_{12}	2.29s	Me	$(CD_3)_2CO$
				7.10m	C_6H_4	
$P(OCH_2)_3CEt$	IIl	2092w,2053sh,2038s,2022sh,2010vs,1988sh,br	CH_2Cl_2	0.81m,1.14m	Et	
				4.20m	OCH_2	
				7.36s	C_6H_6	
$AsPh_3$	IIm	2080m,2050w,2026s,1997vs,br,1980sh	CH_2Cl_2	7.42m	Ph	$CDCl_3$
$CNBu^t$	IIo	2065m,2020vs,2007sh,1996m,1990s,1986s		1.55s	CMe_3	$(CD_3)_2CO$
		ν(CN) 2155m	C_6H_{12}			
$CNCH_2SO_2C_6H_4Me\text{-}p$	IIr	2095w,2069m,2022vs,2005m,1996m,1990s,1982s				
		ν(CN) 2160m	C_6H_{12}			
dppm	Vs	2083,2023w,2013s,2003s,1987w,1966m,1964sh,1961m	C_6H_{12}	4.29t (*J* 10.5 Hz)	CH_2	
				7.35m	Ph	$CDCl_3$
dpam	Vu	2083m,2067m,2024m,2009vs,1990sh,1964m,1944w	C_6H_{12}	2.26s	Ph*Me*	
				4.11s	CH_2	
				7.36m	Ph	$CDCl_3$
dpae	Vv	2082m,2066w,2048m,2022sh,2013vs,2002vs,1986s,		4.32m	CH_2	
		1964s,1950sh	C_6H_{12}	7.40m	Ph	$CDCl_3$
PMe_3	XIah	2081m,2061w,2047m,2024s,2002vs,1966s,1958sh,		1.69d (*J* 12 Hz)	PMe	
$P(OMe)_3$		1935w	C_6H_{12}		(Et_2O)	$CDCl_3$
				2.40q,1.71t		
				3.66d (*J* 12 Hz)	OMe	
PMe_2Ph	XIbo	2098w,2068w,2045m,2029s,2016s,2004m,1986w		1.49s	CMe_3	
$CNBu^t$		ν(CN) 2168w		1.86d (*J* 9 Hz)	PMe	
				7.42m	Ph	$CDCl_3$
$P(C_6H_4Me\text{-}p)_3$	XIdm	2077w,2062m,2047w,2024s,1998vs,1989sh,1979s,		2.42s,	Me	
		1957s,1908m				
$AsPh_3$				7.51m	$Ph + C_6H_4$	$CDCl_3$
$P(C_6H_4Me\text{-}p)$	XIdo	2066m,2024s,1996s,1978m		1.53s	CMe_3	

TABLE 3 (continued)

L	Complex	ν(CO) (cm^{-1})	Solvent	^{1}H NMR		
				δ(ppm)	Assignment	Solvent
CNBu^t		ν(CN) 2164w	C_6H_{12}	2.38s	Me	
				7.50m	C_6H_4	$(CD_3)_2CO$
$P(OCH_2)_3CEt$	XIIm	2078w,2057w,2038s,2027m,		0.83t (J 6 Hz)	Me	
$AsPh_3$		2014vs,1990m	C_6H_{12}	1.33q (J 7 Hz)	CH_2Me	
				4.23t (J 2 Hz)	OCH_2	
				7.38m	Ph	$CDCl_3$
CNBu^t	XIop	2097w,2065m,2022vs,2001m,1995m,1990sh,1985w		1.55s,	CMe_3	$CDCl_3$
CNCy		ν(CN) 2166w,2159sh	C_6H_{12}	1.65(br)	Cy	
n = 3						
PMe_3	IIIa	2044w,2015sh,1997sh,1975vs,1943s	C_6H_{12}	1.80d (J 10 Hz)	Me	$(CD_3)_2CO$
PPh_3	IIIc	2044m,1978sh,1967br	C_6H_{12}	7.43m	Ph	$CDCl_3$
$P(C_6H_4Me\text{-}p)_3$	IIId	2039vw,2017vw,1977sh,1965s	C_6H_6	2.36s	Me	
				7.25m	C_6H_4	$CDCl_3$
$P(CH_2CH_2CN)_3$	IIIg	2087m,2025vs,1991vs,1920w	CH_2Cl_2	1.40m(br)	CH_2	$(CD_3)_2CO$
		ν(CN) 2166m				
$P(OMe)_3$	IIIh	2062w,2032m,2005vs,1993vs,1964sh	C_6H_{12}	3.64d (J 12 Hz)	OMe	$CDCl_3$
$PPh(OMe)_2$	IIIi	2054w,2034w,1999s,1988vs,1968m,1959sh	C_6H_{12}	3.60d (J 11 Hz)	OMe	
				7.48m	Ph	$CDCl_3$
$P(OC_6H_4Me\text{-}p)_3$	IIIk	2062m,2010s,1998vs,1976sh	C_6H_{12}	2.27s	Me	$CDCl_3$
				7.10m	C_6H_4	
$P(OCH_2)_3CEt$	IIIl	2058m,2012s,sh,1997vs,br,1975s,sh	CH_2Cl_2	0.80m,1.13m	Et	
				4.17m	OCH_2	
PMe_3	XIIach	2050m,1980vs,1957s,1946sh	C_6H_{12}	1.70d (J 12 Hz)	P*Me*	
PPh_3				3.68d (J 11 Hz)	PO*Me*	
$P(OMe)_3$				7.50m	Ph	$CDCl_3$
PMe_3	XIIat	2031m,2009ms,1995s,1987s,1973vs,1940m	C_6H_{12}	2.76s(br)	CH_2 + Me	
dppe				7.46m	Ph	$CDCl_3$
$P(OMe)_3$	XIIhu	2027w,2012s,2003vs,1988s,1967s,1959sh,1952sh	C_6H_{12}	2.99s	OMe	
dpam				5.78s	Ph*Me*	
				7.50m	Ph	$CDCl_3$

n = *4*						
PMe_3	IVa	2072w,2043w,2018m,1990sh,1976vs,1942s,1897s	C_6H_{12}	1.82d (*J* 11 Hz)	Me	
				1.88d (*J* 11 Hz)	Me	$(CD_3)_2CO$
$PPh(OMe)_2$	IVi	2061w,2030mw,2000sh,1986vs,1967vs,1920m	C_6H_{12}	3.08d (*J* 12 Hz)	PO*Me*	
				3.56d (*J* 12 Hz)	PO*Me*	
				7.48m	Ph	$CDCl_3$
dppm	VIs	2056w,2046w,2023m,2012sh,1998sh,1981vs,		4.25t (*J* 11 Hz)	CH_2	
		1970s,1945m	C_6H_{12}	7.36m	Ph	$CDCl_3$
dpam	VIt	2054m,2041w,2026m,2011vs,2006sh,1963vs	C_6H_{12}	4.19s	CH_2	
				7.36m	Ph	$CDCl_3$

TABLE 4

IR AND NMR SPECTROSCOPIC DATA FOR COMPLEXES $H_4Ru_4(CO)_{12-n}(L)_n$

L	Complex	ν(CO) (cm^{-1})	^{1}H NMR	
			δ(ppm)	Assignment ($CDCl_3$)
n = *1*				
PPh_3	VIIIc	2095m,2082m,2068vs,2059s,2028vs,2015m,2009s,1969w		
$P(OMe)_3$	VIIIh	2097w,2069vs,2060vs,2031vs,2018m,2009m,1976w		
$CNBu^t$	VIIIo	2104w,2078s,2070s,2042s,2022s,2012m,1998w,1984w	−17.97s	RuH
		ν(CN) 2178w	1.51s	CMe_3
$P(OPh)_3$	VIIIj	2098m,2072vs,2061s,2036s,2013s		
$P(OC_6H_4Me\text{-}p)_3$	VIIIk	2098m,2071s,2061s,2036s,2028w,2016s,2000sh,1983w	−17.70d (*J* 7 Hz)	RuH
			2.33s	Me
			7.87m	C_6H_4
n = 2				
PPh_3	IXc	2079m,2062s,2052m,2036m,2022vs,2013s,2003w,1977w,1960w		

TABLE 4 (continued)

L	Complex	ν(CO) (cm^{-1})	^{1}H NMR δ(ppm)	Assignment (CDCl$_3$)
CNBu^t	IXo	2092m,2084w,2060s,2034vs,2020s,2000s,1982s	$-$17.7s, $-$18.2s	RuH
		ν(CN) 2168m	1.49s	CMe$_3$
PMe$_2$Ph	XIIIbk	2082s, 2061vs,2043w,2028vs,2017s,2002m,1992w,1955w	$-$17.4t (*J* 7 Hz)	RuH
P(OC$_6$H$_4$Me-*p*)$_3$			1.87d (*J* 9 Hz)	PMe$_2$
			2.30s	Me
			7.11s	C$_6$H$_4$
			7.42m	Ph
P(OMe)$_3$	XIIIi	2079s,2058vs,2032s,2024vs,2018sh,2000s,1983w,1974w,1966w		
PPh(OMe)$_2$				
n = *3*				
P(OMe)$_3$	Xh	2068m,2036s,2014m,1998s,1985m,1978s,1963w		
PMe$_2$Ph	XIVbhi	2061s,2031vs,2010s,1992s,1984w,1971m,1956w,1941w	$-$17.0s(br)	RuH
P(OMe)$_3$			1.78m	P*Me*
PPh(OMe)$_2$			3.55d (*J* 12 Hz)	POMe
			3.57d (*J* 9 Hz)	POMe
			7.40m	Ph
PMe$_2$Ph	XIVbjk	2065s,2041s,2009s,2000m,sh,1986br	$-$17.3m(br)	RuH
P(OCH$_2$)$_3$CEt			0.82m,1.16m	Et
P(OC$_6$H$_4$Me-*p*)$_3$			1.80d (*J* 10 Hz)	PMe$_2$
			2.31s	Me
			4.17d (*J* 5 Hz)	OCH$_2$
			7.11m	C$_6$H$_4$
			7.42m	Ph

These spectra have proved useful in monitoring most of the reactions reported above, and the most diagnostically useful features are the high frequency bands mentioned above. These tend to be separated from the major absorption, and are sufficiently different in frequency that the growth or decay of a particular complex can be conveniently followed for the mono- or di-substituted complexes.

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