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Cluster chemistry

LIII *. Preparation and some substitution reactions of bis(arylimido)triruthenium complexes: X-ray structures of $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ and $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(L)$ ($L = CNC_6H_3Me_2\text{-}2,6$ and PPh_3)

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Abstract

Azoarenes, ArN=NAr′, react with $Ru_3(CO)_{12}$ to give $Ru_3(\mu_3\text{-}NAr)(\mu_3\text{-}NAr')(CO)_9$ (Ar = Ph, Ar′ = Ph, C_6H_4Me-3, $C_6H_4CF_3$-3, C_6H_4F-3 (**11**), C_6H_4F-4; Ar = Ar′ = C_6H_4Me-3) in moderate yields; for Ar = Ar′ = Ph or C_6H_4Me-3, the mononuclear cyclometallated $Ru(C_6H_3RN{=}NC_6H_4R\text{-}3)_2(CO)_2$ (R = H or Me) were also obtained in low yield. $Fe_3(CO)_{12}$ and azobenzene afford $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ in very low yield. An X-ray study of **11** confirms the structural assignments made on the basis of the spectroscopic measurements: an Ru_3 triangle with a non-bonded Ru...Ru vector is capped on both sides by a μ_3-arylimido moiety. Electron transfer-catalysed reactions with isocyanides, tertiary phosphines and phosphites proceed to give CO-substituted products in moderate yields: complexes $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(L)$ ($L = CNC_6H_3Me_2$-2,6 (**15**), PPh_3 (**16**), $P(OMe)_3$), $\{Ru_3(\mu_3\text{-}NPh)_2(CO)_8\}_2(\mu\text{-}(PPh_2)_2C_2)$ and $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}LL)(CO)_7$ (LL = dppm, dppe) were obtained. X-ray structural studies of **15** and **16** show that the isocyanide ligand occupies an axial position, whereas the tertiary phosphine takes up an equatorial position, both on a terminal ruthenium atom. Crystals of **11**, **15** and **16** crystallize in the monoclinic system with space group $P2_1/n$, a 11.496(2), b 14.020(2), c 15.735(2) Å, β 99.43(1)°, $Z = 4$ for **11**; space group $P2_1/n$, a 11.933(2), b 18.952(2), c 14.370(4) Å, β 100.29(2)°, $Z = 4$ for **15**; and space group Pc, a 17.507(3), b 11.657(2), c 19.518(4) Å, β 100.41(2)°, $Z = 4$ for **16**. The structures were refined by

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* For Part LII, see ref. 38.

least-squares methods and at convergence $R = 0.037$, $R_w = 0.048$ for 3653 statistically significant reflections for **11**; $R = 0.041$, $R_w = 0.046$ for 3903 reflections for **15**; and $R = 0.039$, $R_w = 0.047$ for 5291 reflections for **16**.

Introduction

The first report of cluster complexes of the iron triad containing the M_3N_2 skeletal framework was that describing the reaction between MeN_3 and $Fe_2(CO)_9$ [1]; the product, $Fe_3(\mu_3\text{-}NMe)_2(CO)_9$ (**1**), was fully characterised by an X-ray study in 1969 [2]. Subsequently, the reaction between $Fe_3(CO)_{12}$ and nitroethane to give the ethyl analogue of **1** was described by Aime and coworkers [3], and Alper and Paik showed that similar complexes were formed in reactions with nitroarenes [4]. The reduction of nitroarenes to arylamines by $Fe_3(CO)_{12}$ in methanol [5] and by $Ru_3(CO)_{12}$ [6] had been discovered previously.

More detailed investigations of these $M_3(CO)_{12}$-catalysed reactions resulted in the isolation and X-ray characterisation of the complexes $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_9$ (**2**) [7] and $M_3(\mu_3\text{-}NPh)_2(CO)_9$ (M = Fe (**3**) [8], M = Ru (**4**) [9]). CO exchange in $Fe_3(\mu_3\text{-}NR)_2(CO)_9$ [10] and studies of their dynamic properties by ^{13}C NMR have been reported [11], while more recently, the synthesis of formyl, acyl and carbene derivatives in the iron system, and interesting carbene-nitrene and CO-alkyne-nitrene coupling reactions have been elucidated [12]. Similar complexes have been isolated from reactions of $M_3(CO)_{12}$ with azides [13], or nitroso compounds [14], while their reactions with hydrogen have given $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NAr)_2(CO)_8$ (**5**), which has been shown to be an efficient olefin hydrogenation catalyst [15].

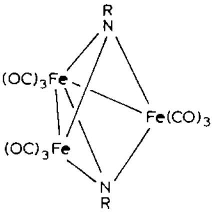
After the reactivity of unsaturated organic compounds containing olefinic or acetylenic centres towards metal carbonyls had been established, a natural extension was to compounds containing CH=N and N=N groups. The first results of these studies appeared in 1965, when it was reported inter alia that reactions between azobenzene and iron carbonyls afforded the binuclear complexes, $Fe_2(\mu\text{-}NHC_6H_4NPh)(CO)_6$ (**6**) [16]. The o-semidine-derived structure was confirmed by an X-ray study [17]. In the full account, the reaction between azotoluene and $Fe_3(CO)_{12}$ was also described as producing a trinuclear complex ascribed the structure $Fe_3(\mu_3\text{-}NHC_6H_3MeNC_6H_4Me)(CO)_9$ (**7**) on the basis of similarities in the spectral properties of complexes **6** and **7** [18]. Reactions between azobenzene and $Ru_3(CO)_{12}$ were examined several years later, and the major product was a trinuclear complex, which was assigned a structure related to that of **7**, again on the basis of similarities in their spectra [19].

The properties of the M_3N_2 complexes resemble those of the supposed semidine derivative (**7**), and we have reinvestigated some of this chemistry. We have confirmed that the trinuclear complexes have the trinuclear bis(arylimido) cluster structure, both spectroscopically and by an X-ray structure of the product obtained from $PhN{=}NC_6H_4F\text{-}3$. Also described herein are some CO-substitution reactions of these complexes, together with the structures of the isocyanide and PPh_3 complexes; some of this work has been described in a preliminary communication, together with the structure of $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}dppm)(CO)_7$ [20]. The synthesis of similar complexes from $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_9$ and azoarenes, and the reaction of complexes **4** with H_2 to give the olefin-hydrogenation catalysts $Ru_3(\mu_3\text{-}NAr)_2(\mu\text{-}H)_2(CO)_8$ (**5**), have been described recently [15].

Results

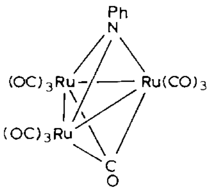
We have found that the reactions of azoarenes with $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ proceed as originally described, but that the trinuclear complexes so formed have the M_3N_2 skeleton, a formal cleavage of the N=N double bond in the azoarene occurring. Thus, the purple trinuclear complex $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (**3**) was obtained in very low yield from the reaction between $Fe_3(CO)_{12}$ and azobenzene in refluxing benzene. Similarly, $Ru_3(CO)_{12}$ afforded orange $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**5**) in 20% yield, accompanied by a smaller amount of the mononuclear cyclometallated complex $\overline{Ru(C_6H_4N=N}Ph)_2(CO)_2$ (**8**), and a dark brown solid which has not yet been identified. A slightly higher yield of **5** was obtained by carrying out the reaction under CO. Analogous trinuclear complexes were obtained from the reactions of $Ru_3(CO)_{12}$ with $C_6H_4RN=NC_6H_4R'$; only the mixed complexes $Ru_3(\mu_3\text{-}NR)(\mu_3\text{-}NR')(CO)_9$ (R = H, R′ = 3-Me (**9**), R = H, R′ = 3-CF_3 (**10**), R = H, R′ = 3-F (**11**), R = H, R′ = 4-F (**12**)) were obtained from the asymmetric azobenzenes, no evidence for the formation of the homo-bis-arylimido complexes being obtained. In the case of azotoluene, both $Ru_3(\mu_3\text{-}NC_6H_4Me\text{-}3)_2(CO)_9$ (**13**) and the dimethyl analogue of **8**, $\overline{Ru(C_6H_3MeN=N}C_6H_4Me)_2(CO)_2$ (**14**), were isolated.

The identities of these complexes were established by elemental microanalyses, comparison of their IR $\nu(CO)$ spectra with the literature values (for **3** and **4**), and from the unit cells of **3** and **4**, which were identical (within experimental error) with those reported in the literature. The similarities in the physical properties of the other trinuclear complexes suggested that they also contained the Ru_3N_2 skeleton,



(1) R = Me

(3) R = Ph



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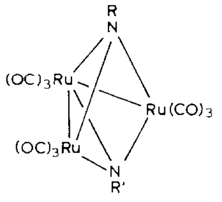
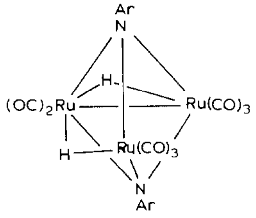
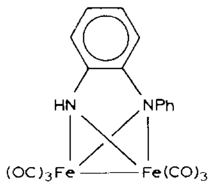


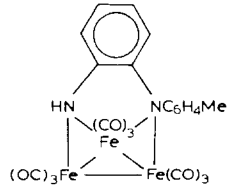
	R	R′
(4)	Ph	Ph
(9)	Ph	C_6H_4Me-3
(10)	Ph	$C_6H_4CF_3$-3
(11)	Ph	C_6H_4F-3
(12)	Ph	C_6H_4F-4
(13)	C_6H_4Me-3	C_6H_4Me-3



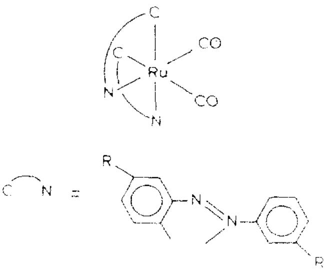
(5) Ar = Ph



(6)

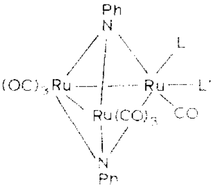


(7)

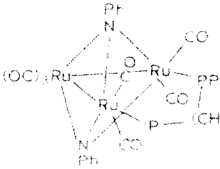


(8) R = H

(14) R = Me



	L	L'
(**15**)	CNxy	CO
(**16**)	CO	PPh_3
(**17**)	CO	$P(OMe)_3$
(**18**)	CO	$\frac{1}{2}$(dppa)



(**19**) n = 1

(**20**) n = 2

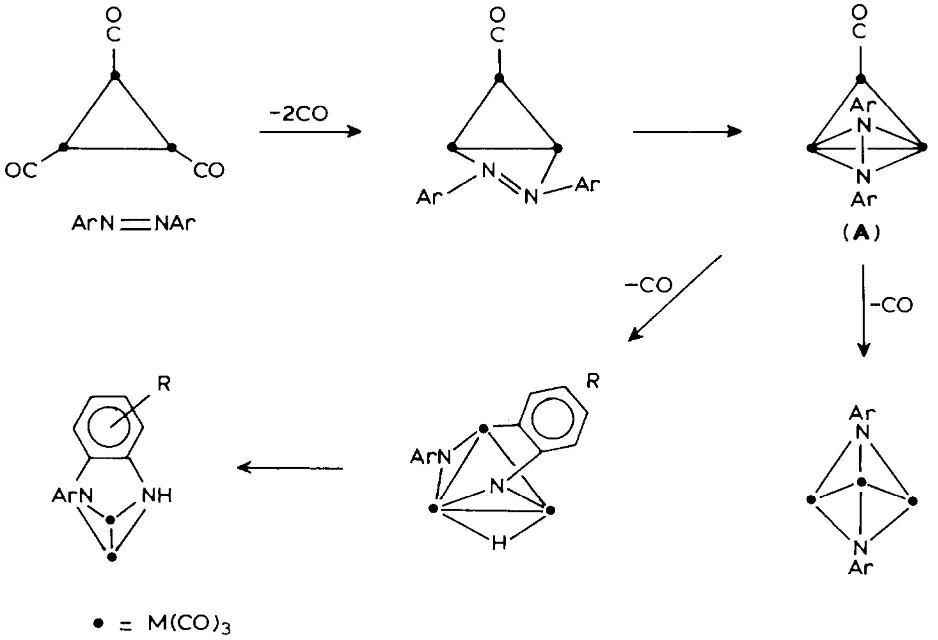
and this was confirmed by an X-ray study of the 3-fluorophenyl complex **11** (see below). For **13**, the single methyl resonance found in the ^1H NMR spectrum showed the two methyl groups were in identical environments. The ^{13}C NMR spectra of **3** and **4** were virtually identical, containing only three absorptions between δ 123–130 ppm, showing that both phenyl groups are chemically equivalent, and furthermore, were not consistent with the *o*-semidine-derived structures proposed earlier.

The fast atom bombardment (FAB) mass spectrum of **4** contains ions $[M-n\text{CO}]^-$ (n = 0–9), together with a series of weak ions corresponding to $[Ru_3(CO)_n]^-$ (n = 7–12), or more likely, $[Ru_3N_2(CO)_n]^-$ (n = 6–11), formed by loss of the phenyl groups and intermolecular transfer of CO ligands.

The mononuclear complex **8** contained two ν(CO) bands in its IR spectrum, while the ^1H NMR spectrum showed the characteristic multiplets associated with an *ortho*-metallated phenylazophenyl group. The compound was fully characterised by a single-crystal X-ray study, which showed that the CO groups were *trans* to the carbon of one, and the nitrogen of the second, cyclometallated ligand [21]. This structure is identical with that found for the osmium analogue, obtained from similar reactions between $Os_3(CO)_{12}$ and azobenzene [22]. As has been found before, there are few differences in the bond parameters between the two complexes. It is interesting to note that these two complexes, and also $Ru\{\overline{(RC_6H_3O)P}(OC_6H_4R\text{-}4)_2\}_2(L)_2$ (R = H, L = $P(OPh)_3$ [23]; R = Me, L = CO [24]) have one aryl carbon *trans* to the chelate donor atom, and the other *trans* to L, in contrast to the situation found for $Ru(bq)_2(CO)_2$ (bq = benzo[*h*]quinolin-10-yl-C^{10},N), in which both nitrogen atoms are *trans* to the CO groups [25], and the rhodium complex $\overline{Rh(C_6H_4N{=}N}Ph)_2(O_2CMe)$, in which the two nitrogens are mutually *trans*, and the metallated carbons mutually *cis* [26]. The origins of these differences are not clear at the present time.

Mechanism of the reaction

The formation of the trinuclear bis-arylimido complexes from azoarenes requires that the N=N double bond is cleaved at some stage of the reaction. It is likely that the first step of the transformation involves coordination of the azoarene to the cluster by the nitrogen atoms, perhaps giving an intermediate in which one of the M–M bonds is bridged by the azoarene such as **A** (Scheme 1). Slippage of the azoarene and further interaction with the third metal atom results in N–N bond cleavage together with electron rearrangement following capping leading to opening



Scheme 1

of the M_3 triangle. The intermediacy of **A** has not been established in the ruthenium system, but in an analogous reaction, $Os_3(CO)_{12-x}(CH_3CN)_x$ ($x = 1$ or 2) reacts with dimethyl azodicarboxylate to give $Os_3\{\mu_3\text{-}N(CO_2Me)NC(O)OMe\}(CO)_{11}$, which when heated in benzene affords $Os_3\{\mu_3\text{-}N_2(C(O)OMe)_2\}(CO)_{10}$ [27]. Stabilisation of this intermediate is aided by coordination of the ester carbonyl oxygen atoms.

The eventual cleavage of the N–N bond is also consistent with the formation of the *o*-semidine derivatives such as **6**. An alternative reaction can take place when one nitrogen is coordinated to one metal atom, namely the well-known cyclometallation reaction. Interaction of the aryl C–H bond with the cluster results in formation of an Ru–C bond and addition of the hydrogen atom to the cluster, as found with the aryldiazo complex $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}N{=}NPh)(CO)_8$ recently [28]. However, reaction with a second molecule of azoarene affords the mononuclear complexes **8** or **14**, the hydrogen being eliminated with the other two metal carbonyl fragments; ruthenium carbonyl hydrides are unstable ($RuH_2(CO)_4$) or unknown ($Ru_2H_2(CO)_8$), and we have found that the possible cluster hydride, $Ru_4(\mu\text{-}H)_4(CO)_{12}$, reacts readily with azobenzene to give at least nine products.

Substitution reactions

No chemistry of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$, apart from its hydrogenation to give $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NPh)_2(CO)_8$ [15], has been reported previously. We have found that ready substitution of CO by isocyanide or tertiary phosphine ligands occurs under electron-transfer catalysed conditions. Thus, with *m*-xylyl isocyanide, red-orange $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(CNxy)$ (**15**) was isolated in 40% yield. The IR spectrum contained a ν(CN) band at 2156 cm^{-1}, together with a complex ν(CO) pattern, the number of bands suggesting the presence of isomers. However, the ^{1}H NMR spectrum showed the presence of only one environment for the Me groups. To determine the position of substitution, an X-ray study of **15** was undertaken, and this revealed that one of the axial CO groups on an outer ruthenium atom had been replaced by the isocyanide ligand. In other respects, the structure resembles that of the parent compound.

Similar reactions between $\mathrm{Ru_3(CO)_{12}}$ and monodentate tertiary phosphines, such as $\mathrm{PPh_3}$, or phosphites, such as $\mathrm{P(OMe)_3}$, afforded monosubstituted complexes whose IR ν(CO) spectra differed from that of complex **15** in having only seven bands. The position of substitution was established as the equatorial site on one of the terminal ruthenium atoms by means of an X-ray study of the $\mathrm{PPh_3}$ complex **16**; the similarity of the IR ν(CO) spectra suggests that the $\mathrm{P(OMe)_3}$ complex **17** has the same stereochemistry. The linear bis-tertiary phosphine, $\mathrm{C_2(PPh_2)_2}$ (dppa), gave a red-orange complex with an IR ν(CO) spectrum similar to those of **16** and **17**, and with an elemental microanalysis and molecular weight (FAB MS) consistent with its being the 'binuclear' $\{\mathrm{Ru_3}(\mu_3\text{-NPh})_2\mathrm{(CO)_8}\}_2(\mu\text{-dppa})$ (**18**).

Reactions of **4** with the bidentate tertiary phosphines dppm and dppe afforded the complexes **19** and **20**, respectively; the latter was obtained in only very low yield. Both complexes had similar IR ν(CO) spectra, and the X-ray study reported earlier [20] showed that the dppm ligand spanned the non-bonded Ru ... Ru vector, with the phosphorus atoms occupying the two equatorial sites. Characterisation of complexes **16** and **19** was aided by their mass spectra. In the electron impact (EI) mass spectrum of **16**, the strongest ion was $[\mathrm{PPh_3}]^+$, indicating that thermal decomposition has occurred in the hot (150 °C) source. Ions corresponding to $[M - n\mathrm{CO}]^+$ ($n = 0$–8) were very weak. In contrast, the FAB mass spectrum of **19** contained strong ions $[M - n\mathrm{CO}]^+$ ($n = 0$–7), together with other fragment ions corresponding to loss of the arylimido groups.

The substitution positions are the same as found for the parent carbonyl, $\mathrm{Ru_3(CO)_{12}}$ [29]. Isocyanides occupy axial positions in $\mathrm{Ru_3(CO)_{11}(CNBu^t)}$ and $\mathrm{Ru_3(CO)_{10}(CNBu^t)_2}$ [30], while tertiary phosphines and phosphites go into equatorial sites, as found in many such derivatives that have been studied. Bidentate phoshines also occupy equatorial sites on adjacent ruthenium atoms in complexes such as $\mathrm{Ru_3(CO)_{10}(dppm)}$ [31], $\mathrm{Ru_3(CO)_8(dppm)_2}$ [32] and $\mathrm{Ru_3(CO)_{10}(dppe)}$ [33].

In ETC reactions of $\mathrm{Ru_3(CO)_{12}}$, the intermediate $[\mathrm{Ru_3(CO)_{12}}]^{\cdot}$ anion radical is assumed to have a 17e centre, which are known to be readily substituted. The extra electron is accommodated in the LUMO which has metal–metal antibonding character [34]. Kochi and coworkers [35] have made a detailed study of $\mathrm{Fe_3}(\mu_3\text{-PPh})_2\mathrm{(CO)_9}$, a complex closely related to $\mathrm{Ru_3}(\mu_3\text{-NPh})_2\mathrm{(CO)_9}$, and of its reactions with a range of phosphorus donor ligands, and have found that 'closed' and 'open' radical anions, the latter formed by 'slippage' of the PPh group, are formed. The consequent weakening or cleavage of the Fe–P bond generates a 17e metal centre which is substitution labile. Their studies offer an explanation for the dppe ligand bridging the non-bonded metal atoms in $\mathrm{Fe_3}(\mu_3\text{-PPh})_2(\mu\text{-dppe})\mathrm{(CO)_7}$, exactly paralleling the structure of $\mathrm{Ru_3}(\mu_3\text{-NPh})_2(\mu\text{-dppm})\mathrm{(CO)_7}$ reported earlier [20]. We consider that similar intermediates are formed in the ETC-substitution reactions of the ruthenium complex.

X-ray structures of $Ru_3(\mu_3\text{-}NAr)_2(CO)_9$ and substituted derivatives

As mentioned above, the X-ray structures of $M_3(\mu_3\text{-NPh})_2(CO)_9$ (M = Fe [8], Ru [9]) and of the related complexes $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(CO)_9$ [7] and $Ru_3(\mu\text{-H})_2(\mu_3\text{-NPh})_2(CO)_8$ [15] have been reported; unit cell data for complexes **3** and **4** obtained in this work were the same as reported in the above accounts, and constitute confirmatory identification of these compounds. We have also determined the molecular structures of $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-NC}_6H_4F\text{-3})(CO)_9$ (**11**) and of the substituted complexes $Ru_3(\mu_3\text{-NPh})_2(CO)_8(L)$ (L = CNxy (**15**) and L = PPh_3 (**16**)) and $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppm})(CO)_7$ (**19**); details of the latter appeared in our preliminary communication [20]. Full details of these structural determinations are given in the Experimental section. Plots of each of the molecules **11**, **15** and **16** are given in Fig. 1–3, respectively: a commentary on significant structural features (Table 2) follows.

All four complexes contain an 'open' Ru_3 triangle capped on both sides by a μ_3-arylimido ligand (aryl = Ph except for one group, 3-FC_6H_4, in **11**). The Ru_3N_2 core is thus based on a trigonal bipyramidal arrangement with the N atoms occupying axial positions. The carbonyl ligands in the complexes are basically terminal and any deviation from linearity arises either as a result of steric pressures within the complexes or significant intermolecular interactions as will be discussed below. Substitution of a carbonyl in **4** by CN(*m*-xylyl) in **15** and by PPh_3 in **16** occurs at one of the 'end' Ru atoms rather than at the middle Ru atom.

The molecular geometry found for **11** (Fig. 1) is essentially the same as that found for the parent bis-imido compound **4** [9], there being no outstanding differences between comparable interatomic parameters in these molecules. The asymmetry in the Ru(1)–Ru(2) and Ru(2)–Ru(3) bonds (distances 2.702(1) and 2.615(1) Å) is similar to that reported for **4** [9] and is examined further below. The

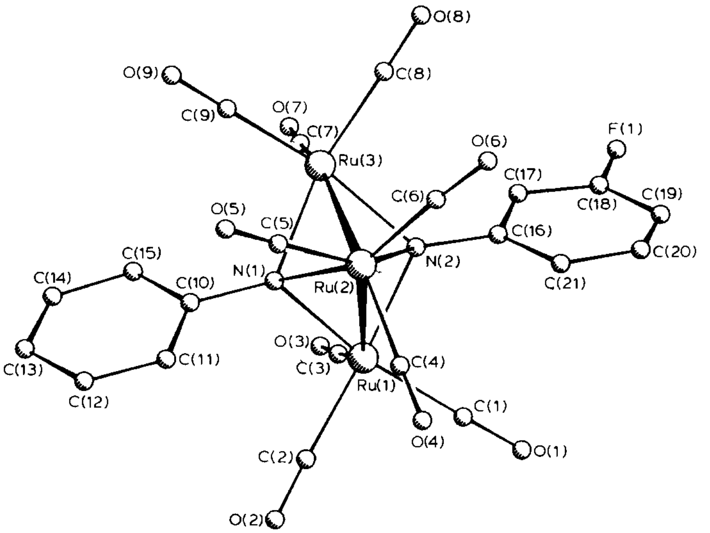


Fig. 1. Molecular structure of $Ru_3(\mu_3\text{-NPh})(\mu_3\text{-NC}_6H_4F\text{-3})(CO)_9$ (**11**), showing atom numbering scheme.

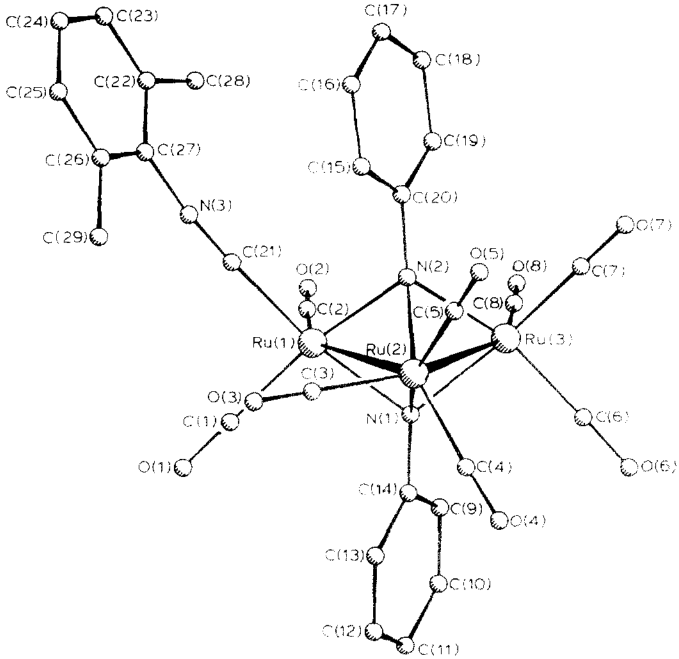


Fig. 2. Molecular structure of $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)$ (**15**), showing atom numbering scheme.

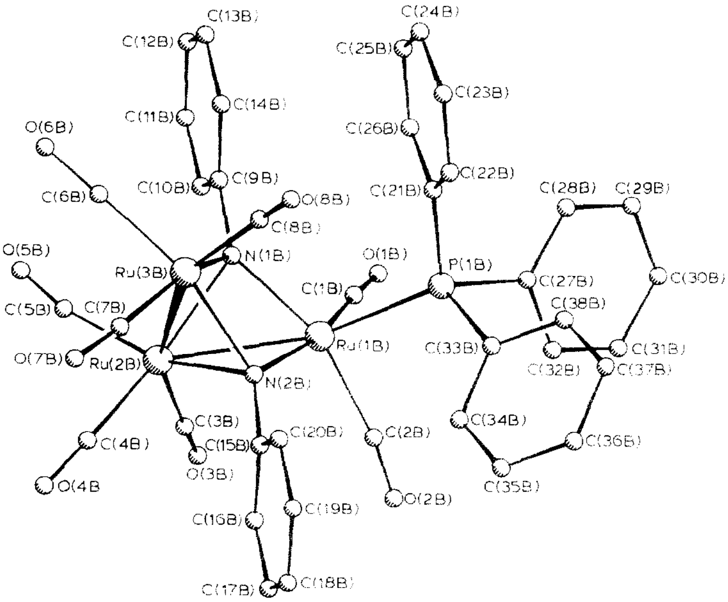


Fig. 3. Molecular structure of $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(PPh_3)$ (**16**) (molecule B), showing atom numbering scheme.

Ru(1)...Ru(3) separation of 3.291(1) Å is not indicative of a bonding interaction between these atoms. Not unexpectedly the presence of the *m*-fluorine atom on one of the phenyl groups in **11** does not exert any significant influence on the overall structure. However, the crystal structure analysis does confirm the nature of the reaction product derived from the reaction of $Ru_3(CO)_{12}$ with asymmetric azoarenes.

In complex **15**, the isocyanide ligand replaces an 'axial' CO group on a terminal ruthenium atom (Fig. 2). In these trigonal bipyramidal M_3N_2 complexes, the six CO groups that are not approximately coplanar with the Ru_3 core may be termed 'axial', although the Ru–C–N vector is inclined at 96.3° to the Ru_3 plane, with the N(1)–Ru(1)–C(21) angle 162.7(2)°. This may be compared with the corresponding N–Ru–P angle of approximately 109° found in **16** (see below). However, the overall structure and disposition of the ligands is remarkably similar to those found in **4** and **11**. The Ru–C–O angles range between 174.6(6) and 179.7(3) Å, while the Ru(1)–C(21)–N(3) angle is 175.9(5)°.

In **16** one of the carbonyl groups on a terminal Ru atom of **4** has been substituted for a PPh_3 ligand (Fig. 3). The PPh_3 molecule coordinates the Ru_3 triangle equatorially; for molecule A of the asymmetric unit, the P atom lies 0.11 Å above the Ru_3 plane (i.e. in the direction of the N(1A) atom) and in molecule B the P atom lies 0.03 Å below the Ru_3 plane. The asymmetry in the Ru–Ru bonds found in the structures of **4** and **11** persists in **16** in which the longer Ru–Ru bond involves the Ru atom coordinated by PPh_3. The Ru–P distance of 2.318(3) Å (2.327(3) Å for molecule B) is equal within experimental error to that found for the closely related compound (**19**) in which the dppm ligand equatorially spans the non-bonded Ru...Ru vector such that the Ru_3P_2 atoms are almost coplanar [20]. The presence of the bulky PPh_3 ligand is responsible for the deviation from linearity of the Ru(1)–C(2)–O(2) bond (167.1(9)°) as is shown in Fig. 3. There are no major differences between chemically equivalent parameters defining the two molecules of **16** which comprise the asymmetric unit for this compound.

A common feature of the bis-μ_3-phenylimidotriruthenium structures reported above, as well as the earlier examples, is the unequal distances of the Ru–Ru bonds in the Ru_3 triangles. It has been suggested [9] that it is the relative disposition of the ligands which is responsible for the disparate Ru–Ru distances. We now develop this point further. As can be seen from Table 2, in each of the molecules there exists a weak intermolecular interaction, of ca. 3.0 Å, between the terminal Ru atom and a carbonyl group bonded to the middle Ru atom. The geometry of this interaction is such that the 'semi-bridging' carbonyl is coplanar with the Ru_3 triangle and, further, it is noted that the greatest deviation from linearity of the Ru–C–O groups in these structures (except for that mentioned for **15** above) is found for the carbonyl groups involved in these intermolecular interactions. It is proposed that the presence of these additional, albeit weak, Ru...CO contacts is a major contributing factor to the minor asymmetry observed in the Ru–Ru bonds.

There is a systematic variation in the non-bonded Ru...Ru distances in these clusters which can be related to the substitution pattern of the coordination geometries. For the compounds **4**, **11** and **15** the non-bonded Ru...Ru distances lie in the narrow range 3.284(1)–3.291(1) Å. An expansion of the Ru...Ru distance of ca. 0.3 Å is found in **19** and of ca. 0.7 Å in **16**. The opening of the Ru_3 triangles is undoubtedly related to the presence of the sterically demanding phosphine substituents in equatorial positions in these structures.

The separation of the imido N atoms in the clusters lies in the range 2.41(1)–2.45(1) Å and it has been suggested by others that some direct interaction between these atoms is likely [9].

Conclusion

The trinuclear complexes obtained from previously described reactions between $M_3(CO)_{12}$ (M = Fe [18], M = Ru [19]) and azoarenes have been shown to be bis-μ_3-arylimidotrimetal clusters, $M_3(\mu_3\text{-NAr})_2(CO)_9$, by spectroscopic and X-ray structural comparisons with examples of known structure obtained from other nitrogen-containing precursors. Electron transfer-catalysed substitution reactions with 2e donor ligands result in the formation of axially- (isocyanide) or equatorially-substituted products (tertiary phosphines and phosphites); the latter reactions are analogous to those of $Fe_3(\mu_3\text{-PPh})_2(CO)_9$ [35], and are assumed to proceed in a similar manner via opening of the Ru_2N triangle.

Experimental

General conditions. All reactions were run under nitrogen except those involving CO or H_2; no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Solvents were dried and distilled (dme and thf from sodium diphenylketyl) before use. Pressure reactions were carried out in a small stainless steel laboratory autoclave (Carl Röth, Karlsruhe) of internal volume 100 ml, equipped with an internal glass liner.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^{1}H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 8 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip. Spectra are recorded as m/z (calculated for ^{102}Ru or ^{305}Ru$_3$), assignment, % relative intensity. Peaks marked ★ are centres of multiplets consisting of overlapping ions related by loss of one or two H from the indicated ion.

Starting materials. $Fe_3(CO)_{12}$ was obtained from Strem Chemicals, Danvers, Mass., and used after drying in vacuum; $Ru_3(CO)_{12}$ was prepared by a literature method [28]. Azoarenes were either commercial products, or were prepared by condensation of the appropriate amine with PhNO or C_6F_5NO.

Reaction between $Fe_3(CO)_{12}$ and azobenzene

A mixture of $Fe_3(CO)_{12}$ (1.00 g, 1.99 mmol) and azobenzene (1.00 g, 5.48 mmol) in benzene (90 ml) was heated at reflux point for 4.5 h. After cooling, solvent was removed in vacuum, and the residue chromatographed (Florisil). Light petroleum eluted a purple band (mixture of $Fe_3(CO)_{12}$, $Fe_3(\mu_3\text{-NPh})_2(CO)_9$ (3) and azobenzene, see below) and diethyl ether/light petroleum (1/3) eluted an orange band (azobenzene, identified by comparison with an authentic sample). Preparative TLC of the purple band (silica, light petroleum eluant) gave four bands. Band 1 ($R_f = 0.90$), green, trace, $Fe_3(CO)_{12}$ (IR identification). Band 2 ($R_f = 0.78$), purple, $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (**3**) (30 mg, 2.5%), recrystallised (n-hexane), m.p. 138 °C (dec). Found: C, 41.74, H, 1.80; N, 4.63%; $C_{21}H_{10}N_2O_9Fe_3$ calcd. C, 41.91; H, 1.67; N, 4.65%. IR (cyclohexane): ν(CO) 2059vs, 2037vs, 2017vs, 2011s, 1986s, 1972s cm^{-1} (lit. [18] 2050vs, 2028s, 2008s, 1987m, 1970w cm^{-1}). ^1H NMR: δ ($CDCl_3$) 7.28–6.99 ppm (m, Ph). ^{13}C NMR: δ ($CDCl_3$) 209.6–191.6 (m, CO); 128.4, 125.5, 123.1 ppm (m, Ph). The identity of complex **3** was confirmed from its unit cell: monoclinic, space group $P2_1/n$, a 11.34, b 13.66, c 15.42 Å, β 100.0°, V 2352 $Å^3$ (lit. [8]: monoclinic, $P2_1/n$, a 11.282(2), b 13.658(1), c 15.379(4) Å, $\beta = 99.81(2)°$, V 2335.1 $Å^3$). Band 3, ($R_f = 0.60$) orange, azobenzene (TLC identification). Band 4, ($R_f = 0.42$) red (trace), $Fe_2(\mu_2\text{-}C_6H_4NHNC_6H_5)(CO)_6$ (**6**) (IR identification).

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

(a) Azobenzene

(i) Under nitrogen. A mixture of $Ru_3(CO)_{12}$ (500 mg, 0.78 mmol) and azobenzene (285 mg, 1.56 mmol) was heated in refluxing n-octane (80 ml) until the reaction was judged to be complete (monitoring the disappearance of the 2061 cm^{-1} band of $Ru_3(CO)_{12}$ (ca. 4 h)). Solvent was removed under reduced pressure and the residue was chromatographed (Florisil). Light petroleum eluted an orange band, which was recrystallised (n-pentane) to give $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**4**) (115 mg, 20%), m.p. 157 °C (Found: C, 34.18; H, 1.43; N, 3.79%, M, 740. $C_{21}H_{10}N_2O_9Ru_3$ calcd.: C, 34.20; H, 1.37; N, 3.80%; M, 739.) IR (cyclohexane): ν(CO) 2098w, 2077vs, 2053vs, 2027vs, 2020vs, 2016vs, 1995s, 1984m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 6.7–7.3 (m, Ph). ^{13}C NMR: δ ($CDCl_3$) 123.2, 124.2, 128.4 (Ph), 191.7 ppm (m, CO). FAB mass spectrum: 739, $[M^+]$, 31; 711, $[M - CO]^+$, 93; 683, $[M - 2CO]^+$, 100; 655, $[M - 3CO]^+$, 17; 641, $[Ru_3(CO)_{12}]^+$ or $[Ru_3N_2(CO)_{11}]^+$ ($\equiv M'$), 14; 627, $[M - 4CO]^+$, 59; 613, $[M' - CO]^+$, 10; 599, $[M - 5CO]^+$, 21; 585, $[M' - 2CO)]^+$, 10; 571, $[M - 6CO]^+$, 41; 557, $[M' - 3CO]^+$, 14; 543, $[M - 7CO]^+$, 48; 529, $[M' - 4CO]^+$, 21; 515, $[M - 8CO]^+$, 31; 501, $[M' - 5CO]^+$, 31; 487, $[M - 9CO]^+$, 31. The identity of complex **4** was confirmed from its unit cell: orthorhombic, space group $Pna2_1$, a 19.72, b 9.65, c 13.03 Å, V 2478 $Å^3$ (lit. [9]: orthorhombic, $Pna2_1$, a 19.730(2), b 9.67(1), c 13.043(1) Å, V 2487.7 $Å^3$). Light petroleum/CH_2Cl_2 (9/1) eluted an orange band, which was recrystallised (n-hexane) to give $\overline{Ru(C_6H_4N=N}C_6H_5)_2(CO)_2$ (**8**) (20 mg, 3.8%) m.p. 130 °C (dec) (Found: C, 60.18; H, 3.64; N, 10.73; $C_{26}H_{18}N_4O_2Ru$ calcd.: C, 60.11; H, 3.49; N, 10.78%.) IR (cyclohexane); ν(CO) 2036vs, 1986vs cm^{-1}. ^1H NMR: δ ($CDCl_3$) 8.7–6.5 (m, Ph). The brown band eluted by dichloromethane was recrystallised (CH_2Cl_2/hexane) to give a brownish-black powder (unidentified, 490 mg), with ν(CO) (CH_2Cl_2) at 2034s(br), 1984s(br) cm^{-1}.

(ii) Under CO. A mixture of $Ru_3(CO)_{12}$ (500 mg, 0.78 mmol) and azobenzene (145 mg, 0.79 mmol) was heated in refluxing n-octane (70 ml) for 7 h with CO gas (high purity) bubbling through. After cooling, solvent was removed under reduced pressure and the residue chromatographed (Florisil). After multiple chromatography [necessary to separate $Ru_3(CO)_{12}$ and $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$] pure $Ru_3(CO)_{12}$ (50 mg, 10%; IR identification) and $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**4**) (130 mg, 25%; IR identi-

(Continued on p. 212)

Table 1

Reactions of $Ru_3(CO)_{12}$ and azoarenes (under nitrogen)

$Ru_3(CO)_{12}$ (mg (mmol))	$C_6H_4RN{=}NC_6H_4R'$			Solvent (ml)	Conditions (°C, h)	Separation technique	Products	Yield (%)
	R	R′	mg (mmol)					
500 (0.78)	H	H	285 (1.56)	n-octane (80)	127, 4	Column	$Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**4**) $Ru(C_6H_4N{=}NC_6H_5)_2(CO)_2$ (**8**)	20 3.8
500 (0.78)	H	H	143 (0.78)	n-octane (70)	127, 4	Column	$Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**4**) $Ru(C_6H_4N{=}NC_6H_5)_2(CO)_2$ (**8**)	16.1 3.2
300 (0.47)	H	H	171 (0.94)	toluene (50)	110, 6	Column	$Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**4**) $Ru(C_6H_4N{=}NC_6H_5)_2(CO)_2$ (**8**)	15.8 2.0
300 (0.47)	3-Me	3-Me	198 (0.94)	n-octane (50)	127, 4	TLC	$Ru_3(\mu_3\text{-}NC_6H_4Me\text{-}3)_2(CO)_9$ (**13**) $Ru(C_6H_3MeN{=}NC_6H_4Me\text{-}3)_2(CO)_2$ (**14**)	19.7 7.7
300 (0.47)	3-Me	3-Me	198 (0.94)	n-octane (50)	127, 18	TLC	$Ru_3(\mu_3\text{-}NC_6H_4Me\text{-}3)_2(CO)_9$ (**13**) $Ru(C_6H_3MeN{=}NC_6H_4Me\text{-}3)_2(CO)_2$ (**14**)	10.0 2.2
500 (0.78)	H	3-Me	155 (0.79)	n-octane (70)	127, 2$\frac{1}{2}$	TLC	$Ru(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4Me\text{-}3)(CO)_9$ (**9**)	12.8
500 (0.78)	H	3-CF_3	391 (1.56)	n-octane (80)	127, 18	TLC	$Ru(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4CF_3\text{-}3)(CO)_9$ (**10**)	9.6
300 (0.47)	H	3-F	190 (0.94)	n-octane (60)	127, 18	TLC	$Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ (**11**)	11.3
500 (0.78)	H	4-F	313 (1.56)	n-octane (70)	127, 2$\frac{1}{2}$	TLC	$Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}4)(CO)_9$ (**12**)	11.0

Table 2

Selected bond distances (Å) and angles (°) for complexes $Ru_3(\mu_3\text{-}NAr)(\mu_3\text{-}NAr')(CO)_7(L)(L')$ [a]

Ar =	Ph	Ph	Ph		Ph	Ph	
Ar′ =	Ph	C_6H_4F-3	Ph		Ph	Ph	
(L)(L′) =	$(CO)_2$	$(CO)_2$	$(CO)(PPh_3)$		$(CO)(CNC_6H_3Me_2$-2,6)	(dppm)	
			molecule a	molecule b		molecule a	molecule b
Ru(1)–Ru(2)	2.710(1)	2.702(1)	2.717(1)	2.718(1)	2.708(1)	2.680(1)	2.699(1)
Ru(2)–Ru(3)	2.626(1)	2.615(1)	2.596(1)	2.619(1)	2.620(1)	2.664(1)	2.663(1)
Ru(1)...Ru(3)	3.290(1)	3.291(1)	3.370(1)	3.354(1)	3.284(1)	3.320(1)	3.321(1)
Ru(1)–N(1)	2.110(4)	2.051(4)	2.208(8)	2.044(9)	2.064(4)	2.100(5)	2.101(6)
Ru(1)–N(2)	2.129(6)	2.057(4)	2.097(6)	2.036(7)	2.067(4)	2.058(5)	2.077(5)
Ru(2)–N(1)	2.052(4)	2.127(4)	2.128(9)	2.152(10)	2.137(4)	2.117(6)	2.130(6)
Ru(2)–N(2)	2.061(4)	2.131(4)	2.145(7)	2.135(8)	2.119(4)	2.166(5)	2.120(6)
Ru(3)–N(1)	2.080(4)	2.098(4)	2.041(8)	2.110(8)	2.074(4)	2.081(5)	2.084(6)
Ru(3)–N(2)	2.079(4)	2.082(4)	2.071(7)	2.141(7)	2.073(4)	2.085(6)	2.071(6)
Ru(1)–L[a]	1.876(6)	1.886(5)	2.318(3)	2.327(3)	2.000(6)	2.335(2)	2.304(2)
Ru(1)–L′	1.914(7)	1.917(7)	1.910(13)	1.978(17)	1.928(8)	2.310(2)	2.340(2)
Ru(1)...C	2.983(7)	2.975(5)	2.951(11)	3.049(12)	2.899(7)	2.967(9)	2.936(11)
N(1)...N(2)	2.405(11)	2.424(6)	2.448(10)	2.394(10)	2.421(5)	2.423(5)	2.422(6)
Ru(1)–Ru(2)–Ru(3)	76.1(1)	76.5(1)	78.7(1)	77.9(1)	76.1(1)	76.8(1)	77.0(1)
N(1)–Ru(1)–N(2)	69.1(2)	72.3(3)	69.2(3)	71.8(3)	71.8(2)	71.3(2)	70.9(2)
N(1)–Ru(2)–N(2)	71.5(2)	69.4(1)	69.9(3)	67.9(3)	69.3(2)	68.9(2)	69.5(2)
N(1)–Ru(3)–N(2)	70.6(2)	70.9(2)	73.0(3)	68.6(3)	71.4(2)	71.1(2)	71.3(2)
Ru(2)–Ru(1)–L	143.1(2)	141.0(2)	151.0(1)	153.0(1)	111.9(2)	139.1(1)	139.0(1)
Ru(2)–Ru(3)–L′	148.6(2)	150.7(2)	154.5(3)	152.2(4)	147.4(2)	141.6(1)	141.1(1)
N(1)–Ru(1)–L	101.8(2)	98.0(2)	106.8(2)	109.1(3)	162.7(2)	95.5(2)	94.2(2)
N(2)–Ru(1)–L	101.8(2)	101.8(2)	108.9(2)	109.0(2)	95.3(2)	99.2(2)	102.7(2)
N(1)–Ru(3)–L′	103.4(2)	106.1(2)	106.1(4)	109.5(5)	103.7(3)	97.7(2)	96.1(2)
N(2)–Ru(3)–L′	105.2(3)	105.1(2)	110.5(4)	103.6(4)	102.4(2)	100.3(2)	100.8(2)
Ru(2)–C(3)–O(3)	172.8(6)	171.5(6)	167.1(9)	171.8(13)	174.6(6)	171.1(8)	171.2(9)

[a] where L = L′ = CO for $Ru_3(NPh)_2(CO)_9$ [9], $Ru_3(NPh)(NC_6H_4F\text{-}3)(CO)_9$; L = P, L′ = CO for $Ru_3(NPh)_2(CO)_8(PPh_3)$, L = C, L′ = CO for $Ru_3(NPh)_2(CO)_8$(CN-xy); L = L′ = P for $Ru_3(NPh)_2(CO)_8$(dppm) [20].

fication) were obtained. The complex $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_9$ (**2**) was not detected.

(b) Other azoarenes

Reactions between several azoarenes and $Ru_3(CO)_{12}$ were carried out under the conditions summarised in Table 1. The following complexes were identified: (i) $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4Me\text{-}3)(CO)_9$ (**9**), m.p. 144 °C. (Found: C, 35.19; H, 1.66; N, 3.75%; *M*, 753. $C_{22}H_{12}N_2O_9Ru_3$ calcd.: C, 35.16; H, 1.61; N, 3.73%; *M*, 753.) IR (cyclohexane): ν(CO) 2098w, 2077vs, 2053vs, 2027vs, 2020vs, 2016vs, 1995s, 1984m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.27 (s, 3H, Me), 6.6-7.25 (m, 9H, Ph + C_6H_4).

(ii) $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4CF_3\text{-}3)(CO)_9$ (**10**), m.p. 89 °C. (Found: C, 32.92; H, 1.17; N, 3.46%; *M*, 807. $C_{22}H_9F_3N_2O_9Ru_3$ calcd.: C, 32.80; H, 1.13; N, 3.48%; *M*, 807.) IR (cyclohexane): ν(CO) 2099w, 2078vs, 2054vs, 2028vs, 2020vs, 2018vs, 1997s, 1986m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 6.75–7.35 (m, Ph + C_6H_4).

(iii) $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ (**11**), m.p. 150 °C (dec). (Found: C, 33.29; H, 1.20; N, 3.70%; *M*, 757. $C_{21}H_9FN_2O_9Ru_3$ calcd. C, 33.39; H, 1.20; N, 3.71%; *M*, 757.) IR (cyclohexane): ν(CO) 2100w, 2080vs, 2056vs, 2028vs, 2021vs, 2018vs, 1997s, 1987m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 6.63–7.4 (m, Ph + C_6H_4).

(iv) $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}4)(CO)_9$ (**12**), m.p. 92 °C. (Found: C, 33.12; H, 1.28; N, 3.65%; *M*, 757. $C_{21}H_9FN_2O_9Ru_3$ calcd.: C, 33.39; H, 1.20; N, 3.71%; *M*, 757.) IR (cyclohexane): ν(CO) 2100w, 2079vs, 2055vs, 2028vs, 2022vs, 2017vs, 1996s, 1986m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 6.65–7.4 (m, Ph + C_6H_4).

(v) $Ru_3(\mu\text{-}NC_6H_4Me\text{-}3)_2(CO)_9$ (**13**), m.p. 160 °C (dec). (Found: C, 35.97; H, 1.84; N, 3.64%; *M*, 767. $C_{23}H_{14}N_2O_9Ru_3$ calcd. C, 36.08; H, 1.84; N, 3.66%; *M*, 767.) IR (cyclohexane): ν(CO) 2098w, 2076vs, 2052vs, 2024vs, 2018vs, 2014vs, 1994s, 1983m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.26 (s, 6H, Me), 6.6–7.25 (m, 8H, C_6H_4). From the reaction with 3-azotoluene, the mononuclear cyclometallated complex $\overline{Ru(C_6H_3MeN{=}N}C_6H_4Me\text{-}3)_2(CO)_2$ was also obtained (2.2–7.7%) m.p. 163 °C (dec). IR (cyclohexane): ν(CO) 2033vs, 1983vs cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 8.1–6.3 (m, 14H, Ph), 2.5–2.1 (m, 12H, CH_3).

*Reactions of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (**4**)*

(a) With 2,6-dimethylphenyl isocyanide. A solution of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and 2,6-dimethylphenyl isocyanide (9 mg, 0.068 mmol) in tetrahydrofuran (10 ml) was treated with six drops of sodium diphenylketyl solution (ca. 0.025 *M* $Na^+[Ph_2CO]^-$ in tetrahydrofuran). After stirring for five minutes, monitoring by TLC showed unreacted **4** remained. Addition of more initiator (six drops), was followed by stirring for five minutes longer, and evaporation in vacuo. A dichloromethane extract of the residue was chromatographed (preparative TLC on silica gel, 1/9 acetone/light petroleum eluant). The complex $Ru_3(\mu_3\text{-}NPh)_2\text{-}(CO)_8(CNxy)$ (**15**) (23 mg, 40%) was isolated from the second and major band (of six) ($R_f = 0.60$) as a red-orange powder, m.p. 125–128 °C (dec) (from $CHCl_3/MeOH$). (Found: C, 40.89; H, 2.51; N, 4.83. $C_{29}H_{19}N_3O_8Ru$ calcd.: C, 41.43; H, 2.28; N, 5.00%). IR (cyclohexane): ν(CN) 2156m(br); ν(CO) 2086m, 2078s, 2061m, 2045vs, 2038s, 2018(sh), 2011vs, 1996s, 1984s, 1975m, 1969m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.15 (s, 6H, CH_3); 6.86–7.10 (m, 13H, Ph + $C_6H_3Me_2$). FAB mass spectrum: 841, $[M^+]$, 12; 813, $[M-CO]^+$, 67; 785, $[M-2CO]^+$, 100; 757.

$[M-3CO]^+$, 9; 745, ?, 9; 729, $[M-4CO]^+$, 31; 701, $[M-5CO]^+$, 16; 673, $[M-6CO]^+$, 47; 645, $[M-7CO]^+$, 34; 632, ?, 21; 616, $[M-8CO-H]^+$, 37.

(b) With PPh_3. As in (a) above, $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and PPh_3 (18 mg, 0.069 mmol) afforded $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(PPh_3)$ (**16**) as an orange powder from dichloromethane/methanol (34 mg, 52%), m.p. 135–138 °C (dec). (Found: C, 46.36; H, 2.87; N, 2.75%. $C_{38}H_{25}N_2O_8PRu_3$ calcd.: C, 46.97; H, 2.59; N, 2.88%). IR (cyclohexane): $\nu(CO)$ 2075s, 2045vs, 2026vs, 2009vs, 1991m, 1981vs, 1973vs cm^{-1}. ^1H NMR: δ ($CDCl_3$) 6.5–7.5 (m, Ph). EI and FAB mass spectra (m/z, assignment, relative intensity values for FAB spectrum in brackets); 973, $[M]^+$, 26 (5); 945, $[M-CO]^+$, 76 (39); 917, $[M-2CO]^+$, 13 (0); 889, $[M-3CO]^+$, 21 (11); 861, $[M-4CO]^+$, 100 (100); 833, $[M-5CO]$, 21 (8); 821, ?, - (6); 805, $[M-6CO]^+$, 82 (38); 777, $[M-7CO]^+$, 47 (25); 763, ?, - (22); 749, $[M-8CO]^+$, 87 (88); 262, $[PPh_3]^+$, 2630.

(c) With $P(OMe)_3$. Similarly, $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and $P(OMe)_3$ (1 ml of a 0.068 *M* solution in tetrahydrofuran, 0.068 mmol), afforded $Ru_3(\mu_3\text{-}NPh)_2(CO)_8\{P(OMe)_3\}$ (**17**), isolated by TLC chromatography (silica; 1/9 acetone/light petroleum eluant) as the third of five bands eluted ($R_f = 0.30$), as red crystals from light petroleum (7 mg, 12%), m.p. 138–141 °C (dec). (Found: C, 33.06; H, 2.35; N, 3.35. $C_{23}H_{19}N_2O_{11}PRu_3$ calcd.: C, 33.14; H, 2.30; N, 3.36%). IR (cyclohexane): 2078s, 2047vs, 2038m, 2032s, 2009vs, 1981s, 1973m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.49 (d, J(HP) 12.2Hz, 9H, Me); 6.77–7.12, (m, 10H, Ph). FAB mass spectrum: 835, $[M]^+$, 22; 807, $[M-CO]^+$, 100; 779, $[M-2CO]^+$, 84; 751, $[M-3CO]^+$, 16; 723, $[M-4CO]^+$, 44; 695, $[M-5CO]^+$, 25; 667, $[M-6CO]^+$, 25; 636*, $[M-6CO-OMe]^+$, 22; 608, $[M-7CO-OMe]^+$, 31: 578, $[M-7CO-20Me]^+$, 22. Unreacted $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (11 mg, 22%) was recovered by chromatography as the fastest moving band ($R_f = 0.80$).

(d) With 1,2-bis(diphenylphosphino)acetylene (dppa). The binuclear complex $\{Ru_3(\mu_3\text{-}NPh)_2(CO)_8\}_2(\mu\text{-}dppa)$ (**18**) (20 mg, 31%) was obtained similarly from $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and dppa (14 mg, 0.036 mmol). It was isolated by TLC (silica gel; 1/9 acetone/light petroleum eluant) in the fourth and major red-orange band of seven bands eluted ($R_f = 0.25$), which was rechromatographed as above and afforded three bands; the fastest moving and major component was identified as the product above after crystallisation from dichloromethane/methanol, m.p. 135–137 °C (dec) (Found: C, 43.49; H, 2.27; N, 3.06%. $C_{66}H_{40}N_4O_{16}P_2Ru_6$ calcd.: C, 43.71; H, 3.09; N, 2.22%). IR (cyclohexane): $\nu(CO)$ 2077s, 2059w, 2047vs, 2032s, 2012vs, 1995w, 1979s (br) cm^{-1}. ^1H NMR: δ ($CDCl_3$) 6.34–7.65 (m, Ph). FAB mass spectrum: 1816, $[M]^+$, 8; 1732, $[M-3CO]^+$, 10; 1648, $[M-6CO]^+$, 17; 1620 $[M-7CO]^+$, 8; 1592, $[M-8CO]^+$, 12; 1564, $[M-9CO]^+$, 15; 1536, $[M-10CO]^+$, 11; 1508, $[M-11CO]^+$, 10; 1480, $[M-12CO]^+$, 5; 1452, $[M-13CO]^+$, 9; 1424, $[M-14CO]^+$, 11; 1396, $[M-15CO]^+$, 8; 1368 $[M-16CO]^+$, 8; 998, $[M-16CO-2PPh_2]^+$, 34; 937, ?, 100; 881, ?, 68.

(e) With bis(diphenylphosphino)methane (dppm). A similar reaction between $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and dppm (26 mg, 0.068 mmol) gave a product separated (preparative TLC, 1/9 acetone/light petroleum) into unreacted dppm, recovered $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (24 mg, 48%; $R_f = 0.80$) and a red-orange band ($R_f = 0.20$) crystallised (CH_2Cl_2/ethanol/hexane) as a red powder, and identified as $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}dppm)(CO)_7$ (**19**) (27 mg, 37%), m.p. 190–193 °C (dec). (Found: C, 49.55; H, 3.21; N, 2.56. $C_{44}H_{32}N_2O_7P_2Ru_3$ calcd. C, 49.58; H,

3.03; N, 2.63%.) IR (cyclohexane): ν(CO) 2057(sh), 2053vs, 2022vs, 2003s, 1994s, 1970s, 1950m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.33 (t, J(HP) 11.4Hz, 2H, CH_2); 6.4–7.4 (m, 30H, Ph). FAB mass spectrum: 1067, $[M]^+$, 21; 1039 $[M-CO]^+$, 38; 1011, $[M-2CO]^+$, 67; 955, $[M-4CO]^+$, 50; 927, $[M-5CO]^+$, 13; 917, –, 13; 899, $[M-6CO]^+$, 100; 871, $[M-7CO]^+$, 42; 822, $[M-6CO-Ph]^+$, 13; 794, $[M-7CO-Ph]^+$, 33; 780, $[M-7CO-NPh]^+$, 25.

(f) With 1,2-bis(diphenylphosphino)ethane (dppe). The reaction between $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (50 mg, 0.068 mmol) and dppe (28 mg, 0.07 mmol) gave $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-dppe})(CO)_7 \cdot 0.5CH_2Cl_2$ (**20**) (5 mg, 7%) from the second of three bands (silica gel, 1/4 acetone/light petroleum) as red crystals m.p. 188–190 °C (dec.) from CH_2Cl_2/MeOH. (Found: C, 50.05; H, 3.17; N, 2.59. $C_{45}H_{34}N_2O_7P_2Ru_3 \cdot 0.5CH_2Cl_2$ calcd. C, 48.69; H, 3.14; N, 2.50%.) IR (cyclohexane): ν(CO) 2056(sh), 2052vs, 2022vs, 2006s, 1991s, 1970s, 1950m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.79 (m, 4H, PCH_2); 5.29 (s, 1H, CH_2Cl_2); 7.59–7.63 (m, 30H, Ph). FAB mass spectrum: 1080, $[M-H]^+$, 18; 1052, $[M-CO-H]^+$, 16; 1024*, $[M-2CO-H]^+$, 4; 984*, ?, 4; 969 $[M-4CO]^+$, 62; 941, $[M-5CO]^+$, 6; 928*, $[M-PPh_2+H]^+$, 18; 913*, $[M-6CO]^+$, 100; 885, $[M-7CO]^+$, 10.

Crystallography

Intensity data for **11**, **15** and **16** were measured at room-temperature on an Enraf–Nonius CAD4F diffractometer with the use of the $\omega:2\theta$ scan technique and

Table 3

Crystal data for complexes **11**, **15** and **16**

Compound	**11**	**15**	**16**
Formula	$C_{21}H_9FN_2O_9Ru_3$	$C_{29}H_{19}N_3O_8Ru_3$	$C_{38}H_{25}N_2O_8PRu_3 \cdot 0.5CHCl_3$
Formula wt	755.5	840.7	1031.5
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	Pc
	variant (C_{2h}^5, No 14)	variant (C_{2h}^5, No 14)	(C_s^2, No 7)
a, Å	11.496(2)	11.933(2)	17.507(3)
b, Å	14.020(2)	18.952(2)	11.657(2)
c, Å	15.735(2)	14.370(4)	19.518(4)
β, deg	99.43(1)	100.29(2)	100.41(2)
V, Å^3	2501.8	3197.6	3917.7
D_m, g cm^{-3}	2.02	1.76	1.70
Z	4	4	4
D_x, g cm^{-3}	2.006	1.746	1.749
F(000)	1448	1640	2028
μ(Mo-K_α), cm^{-1}	17.78	13.95	12.79
Transmission factors	0.3506–0.7035	0.4818–0.7677	0.5492–0.8667
Reflections measured	4345	5659	7348
θ range, deg	$1 \leq \theta \leq 25$	$1 \leq \theta \leq 22.5$	$1 \leq \theta \leq 22.5$
Unique reflections	4008	4974	6582
Observed reflections with $I \geq 2.5\sigma(I)$	3653	3903	5291
R	0.037	0.041	0.039
g	0.005	0.006	0.003
R_w	0.048	0.046	0.047
ρ_{max}, e Å^{-3}	0.89	0.74	0.94

graphite-monochromatized Mo-K_α radiation, λ 0.71073 Å. No decomposition of the crystals occurred during their respective data collections. Corrections were routinely applied for Lorentz and polarization effects and for absorption [36]. Crystal data for the three compounds are listed in Table 3.

The structures were solved by direct-methods [36] and refined by a full-matrix least-squares procedure for **11** and **16**. For **15** two cluster molecules, as well as a $CHCl_3$ molecule, comprise the asymmetric unit and hence the large number of refinable parameters required the use of blocked-matrix least-squares method. Anisotropic thermal parameters were introduced for all non-hydrogen atoms in **11**. A difference map calculated at this stage revealed that the fluorine atom of the

Table 4

Fractional atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for other atoms) for $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$ (**11**)

Atom	*x*	*y*	*z*
Ru(1)	85297(3)	16558(3)	8082(2)
Ru(2)	92875(3)	34824(3)	9436(2)
Ru(3)	97822(3)	28406(3)	25218(2)
F(1)	5134(9)	2256(10)	3339(7)
F(1′)	13689(10)	472(10)	2295(7)
N(1)	10126(3)	2183(2)	1392(3)
N(2)	8207(3)	2689(3)	1668(2)
C(1)	6909(5)	1480(4)	262(3)
O(1)	5951(3)	1358(4)	−27(3)
C(2)	9064(4)	999(4)	−144(3)
O(2)	9336(4)	628(3)	−721(3)
C(3)	8519(4)	536(4)	1471(4)
O(3)	8578(5)	−108(4)	1917(3)
C(4)	8585(8)	3407(4)	−252(5)
O(4)	8218(8)	3477(4)	−957(3)
C(5)	10756(6)	4048(4)	802(5)
O(5)	11655(6)	4328(4)	778(5)
C(6)	8653(8)	4686(4)	1153(4)
O(6)	8153(7)	5373(4)	1301(5)
C(7)	9768(6)	1838(5)	3349(4)
O(7)	9748(6)	1276(5)	3869(3)
C(8)	9269(4)	3834(4)	3202(3)
O(8)	8975(4)	4442(3)	3594(3)
C(9)	11374(5)	3207(4)	2934(3)
O(9)	12309(4)	3431(3)	3166(3)
C(10)	11237(4)	1818(3)	1248(3)
C(11)	11569(5)	1903(5)	459(4)
C(12)	12648(6)	1542(5)	311(5)
C(13)	13388(7)	1032(5)	953(6)
C(14)	12979(5)	898(5)	1719(5)
C(15)	11933(5)	1280(4)	1890(4)
C(16)	7050(5)	2876(4)	1799(4)
C(17)	6672(5)	2529(5)	2535(4)
C(18)	5503(7)	2665(6)	2639(6)
C(19)	4717(6)	3151(7)	2050(7)
C(20)	5121(6)	3549(6)	1360(7)
C(21)	6258(6)	3393(5)	1200(4)

meta-group substituted phenylimido group was disordered. The nature of the disorder was such that the fluorine atom was partly located on both carbon atoms C(14) and C(18). The occupancy factors of the fluorine atoms F(1) and F(1′), i.e. x and $1 - x$, were refined and at the convergence of the refinement $x = 0.67(1)$. Hydrogen atom positions were determined from a difference map but were not

Table 5

Fractional atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for other atoms) for $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)$ (**15**)

Atom	x	y	z
Ru(1)	41720(3)	41720(2)	31421(3)
Ru(2)	22299(4)	34120(2)	26865(3)
Ru(3)	17382(4)	46199(3)	18228(3)
N(1)	2523(3)	4462(2)	3216(3)
N(2)	3170(4)	3999(2)	1833(3)
N(3)	6257(4)	3346(3)	2646(3)
C(1)	4820(5)	4155(3)	4480(4)
O(1)	5179(5)	4128(3)	5247(3)
C(2)	4844(5)	5021(4)	2925(4)
O(2)	5208(6)	5550(3)	2752(4)
C(3)	3256(6)	2802(4)	3498(5)
O(3)	3806(5)	2397(3)	3956(5)
C(4)	888(6)	3278(4)	3240(5)
O(4)	95(5)	3242(3)	3551(4)
C(5)	1729(6)	2717(5)	1732(6)
O(5)	1443(6)	2323(4)	1150(6)
C(6)	332(6)	4946(4)	2128(5)
O(6)	−504(4)	5140(4)	2313(4)
C(7)	1013(6)	4368(5)	571(5)
O(7)	571(6)	4180(4)	−156(4)
C(8)	2263(6)	5540(4)	1523(6)
O(8)	2600(7)	6066(3)	1353(6)
C(9)	2053(4)	5507(2)	4029(3)
C(10)	1778(4)	5840(2)	4825(3)
C(11)	1684(4)	5445(2)	5626(3)
C(12)	1864(4)	4718(2)	5633(3)
C(13)	2139(4)	4385(2)	4837(3)
C(14)	2233(4)	4780(2)	4035(3)
C(15)	4058(3)	3100(2)	977(2)
C(16)	4591(3)	2912(2)	225(2)
C(17)	4716(3)	3410(2)	−465(2)
C(18)	4308(3)	4094(2)	−402(2)
C(19)	3774(3)	4282(2)	350(2)
C(20)	3649(3)	3785(2)	1040(2)
C(21)	5526(5)	3647(3)	2859(3)
C(22)	7597(5)	3307(4)	1595(5)
C(23)	8387(7)	2915(6)	1210(6)
C(24)	8612(7)	2210(6)	1505(7)
C(25)	8082(7)	1907(5)	2167(8)
C(26)	7292(6)	2272(4)	2578(5)
C(27)	7088(4)	2981(3)	2269(4)
C(28)	7306(8)	4042(5)	1315(6)
C(29)	6727(8)	1956(6)	3320(8)

Table 6

Fractional atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for other atoms) for $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(PPh_3)$ (**16**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1A)	30625(–)	72279(6)	56891(–)	Ru(3B)	83148(5)	84926(7)	4808(5)
Ru(2A)	30152(5)	77167(7)	43209(5)	P(1B)	7479(2)	7183(2)	−1693(2)
Ru(3A)	16759(5)	84866(6)	45056(5)	N(1B)	7227(5)	8726(8)	−173(6)
P(1A)	2479(2)	7157(2)	6664(2)	N(2B)	7783(4)	6884(6)	149(4)
N(1A)	2139(5)	6909(7)	4778(5)	C(1B)	6044(7)	7776(10)	−1268(7)
N(2A)	2738(4)	8757(5)	5149(4)	O(1B)	5462(5)	8050(8)	−1663(5)
C(1A)	3475(5)	5770(7)	5834(5)	C(2B)	6628(8)	5650(12)	−875(7)
O(1A)	3793(5)	4876(7)	5958(5)	O(2B)	6331(6)	4792(7)	−904(6)
C(2A)	3953(7)	7805(7)	6276(6)	C(3B)	6008(7)	6887(13)	475(7)
O(2A)	4471(5)	8209(7)	6610(6)	O(3B)	5413(6)	6523(9)	323(5)
C(3A)	3974(7)	6923(7)	4569(5)	C(4B)	7274(6)	6916(10)	1554(6)
O(3A)	4534(4)	6338(6)	4597(5)	O(4B)	7436(5)	6539(9)	2075(5)
C(4A)	3394(8)	8949(12)	3905(7)	C(5B)	6542(7)	8961(10)	1156(8)
O(4A)	3647(7)	9724(7)	3555(6)	O(5B)	6328(7)	9716(9)	1347(5)
C(5A)	2741(8)	7000(11)	3475(9)	C(6B)	8374(7)	9962(10)	936(6)
O(5A)	2516(7)	6482(9)	2941(6)	O(6B)	8384(6)	10880(8)	1201(6)
C(6A)	848(7)	8684(10)	5012(6)	C(7B)	9001(6)	7942(8)	1310(6)
O(6A)	317(6)	8767(10)	5226(6)	O(7B)	9348(6)	7652(8)	1835(6)
C(7A)	1001(8)	8029(11)	3715(8)	C(8B)	9151(8)	8640(10)	−74(9)
O(7A)	565(5)	7737(7)	3225(4)	O(8B)	9734(6)	8700(10)	−293(6)
C(8A)	1563(7)	10046(10)	4141(7)	C(9B)	6932(4)	9846(6)	−363(5)
O(8A)	1458(7)	10828(7)	3853(6)	C(10B)	6145(4)	10040(6)	−369(5)
C(9A)	1804(3)	5808(5)	4611(4)	C(11B)	5831(4)	11131(6)	−520(5)
C(10A)	2249(3)	4854(5)	4502(4)	C(12B)	6306(4)	12028(6)	−665(5)
C(11A)	1890(3)	3798(5)	4332(4)	C(13B)	7093(4)	11833(6)	−659(5)
C(12A)	1086(3)	3696(5)	4269(4)	C(14B)	7406(4)	10742(6)	−508(5)
C(13A)	642(3)	4650(5)	4378(4)	C(15B)	8143(3)	5800(5)	392(4)
C(14A)	1001(3)	5706(5)	4548(4)	C(16B)	7689(3)	4896(5)	561(4)
C(15A)	3138(3)	9844(4)	5322(4)	C(17B)	8024(3)	3824(5)	732(4)
C(16A)	3936(3)	9973(4)	5355(4)	C(18B)	8814(3)	3657(5)	734(4)
C(17A)	4283(3)	11042(4)	5508(4)	C(19B)	9268(3)	4560(5)	565(4)
C(18A)	3833(3)	11982(4)	5628(4)	C(20B)	8933(3)	5632(5)	394(4)
C(19A)	3035(3)	11853(4)	5596(4)	C(21B)	8102(5)	8406(6)	−1786(6)
C(20A)	2688(3)	10783(4)	5443(4)	C(22B)	8897(5)	8393(6)	−1792(6)
C(21A)	1811(5)	6118(6)	6769(4)	C(23B)	9280(5)	9408(6)	−1901(6)
C(22A)	1459(5)	6133(6)	7355(4)	C(24B)	8868(5)	10436(6)	−2004(6)
C(23A)	966(5)	5240(6)	7470(4)	C(25B)	8072(5)	10449(6)	−1999(6)
C(24A)	826(5)	4332(6)	6998(4)	C(26B)	7689(5)	9434(6)	−1890(6)
C(25A)	1178(5)	4317(6)	6412(4)	C(27B)	6874(5)	6972(5)	−2517(4)
C(26A)	1671(5)	5210(6)	6297(4)	C(28B)	6858(5)	7752(5)	−3061(4)
C(27A)	3225(5)	6927(6)	7505(4)	C(29B)	6376(5)	7555(5)	−3701(4)
C(28A)	3686(5)	5945(6)	7546(4)	C(30B)	5909(5)	6577(5)	−3797(4)
C(29A)	4146(3)	5633(6)	8179(4)	C(31B)	5925(5)	5796(5)	−3253(4)
C(30A)	4145(5)	6304(6)	8771(4)	C(32B)	6407(5)	5994(5)	−2613(4)
C(31A)	3684(5)	7287(6)	8729(4)	C(33B)	8169(4)	5954(6)	−1748(3)
C(32A)	3224(5)	7598(6)	8097(4)	C(34B)	8278(4)	5086(6)	−1248(3)
C(33A)	2089(4)	8597(5)	6813(5)	C(35B)	8728(4)	4129(6)	−1338(3)
C(34A)	1292(4)	8721(5)	6789(5)	C(36B)	9070(4)	4041(6)	−1928(3)
C(35A)	982(4)	9798(5)	6888(5)	C(37B)	8962(4)	4908(6)	−2428(3)
C(36A)	1470(4)	10751(5)	7012(5)	C(38B)	8511(4)	5865(6)	−2338(3)
C(37A)	2266(4)	10627(5)	7036(5)	C(39)	5123(11)	8131(8)	2668(15)
C(38A)	2576(4)	9550(5)	6936(5)	Cl(1)	4321(10)	7286(14)	2606(13)
Ru(1B)	69370(5)	72175(7)	−6891(5)	Cl(2)	4973(9)	9417(5)	2450(8)
Ru(2B)	69678(5)	77114(7)	6765(5)	Cl(3)	5825(6)	7353(7)	2452(5)

refined. In the refinement of **15**, the phenyl groups of the imido ligands were constrained as hexagonal rigid groups, remaining non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen-atoms were included in the model at their calculated positions. Final refinement details for the three compounds are given in Table 3.

The crystal structure of **16** was originally solved and refined in the centrosymmetric space group $P2/c$, in which the (disordered) solvent molecule is required to be on a crystallographic two-fold axis. In order to satisfy stoichiometric and symmetry requirements of the $CHCl_3$ molecules the lower symmetry space group Pc was chosen, which enabled refinement to proceed smoothly. The low residual ($R = 0.039$) suggests this choice of the space group to be satisfactory. The phenyl groups bonded to the P atoms were refined as hexagonal rigid groups and remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the model due to the already large number of parameters included in the calculation. The absolute configuration of **16** was not determined as there were no significant differences in Friedel pairs included in the data set.

The scattering factors for neutral Ru were those from the International Tables [37] and were corrected for f' and f''. Values for the remaining atoms were those incorporated in SHELX76 [36].

Fractional atomic coordinates for **11**, **15** and **16** are listed in Tables 4–6, selected bond distances and angles for these, and related compounds, are given in Table 2; the numbering schemes used are shown in Figs. 1–3. Listings of thermal parameters, interatomic bond distances and angles, hydrogen atom parameters, and structure factors for compounds **11**, **15** and **16** are available on request from the authors.

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