DALTON

Reaction of $[Ru_5C(CO)_{15}]$ and $[Ru_6C(CO)_{17}]$ with 1,10-phenanthroline and 2,2′-bipyridyl†

Gideon Freeman,[a] **Scott L. Ingham,**[a] **Brian F. G. Johnson,***[b] **Mary McPartlin**[c] **and Ian J. Scowen**[c]

[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*
[c] *School of Applied Chemistry, University of North London, Holloway Road, London, UK N7 8DB*

Reaction of the cluster $[Ru_5C(CO)_{15}]$ **1** with the bidentate nitrogen heterocycles 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) in the presence of 1.1 and 2.2 molar equivalents of Me_3NO led to a facile metal–metal bond cleavage and a structural change in the cluster to yield the bridged butterfly products $[Ru_5C(CO)_{14}(phen)]$ and $[Ru_5C(CO)_{14}(bipy)]$ respectively as the major products, and the orthometallated derivatives $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{12}H_7N_2)]$ and $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)]$ as the minor product as revealed by spectroscopy and X-ray crystallography.

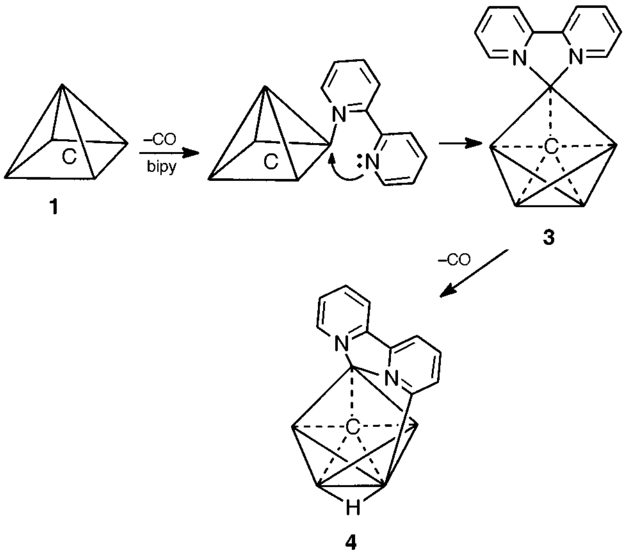
In the course of our studies on the synthesis and reactivity of the square-based-pyramidal ruthenium carbidocarbonyl cluster $[Ru_5C(CO)_{15}]$ **1** we have shown that the cluster readily accepts electron pairs and undergoes facile metal–metal bond cleavage to form 76-electron, bridged butterfly cluster adducts, *e.g.* in its reaction with MeCN[1] or the halides Br^-, Cl^- or I^-.[2] We have also discovered that a second pertinent feature of the cluster's reactivity is its ability to undergo substitution reactions, *e.g.* reaction with 1.1 equivalents of PPh_3 gives the 74-electron *closo*-$[Ru_5C(CO)_{14}(PPh_3)]$ cluster, which is proposed to form *via* a bridged butterfly adduct intermediate.[3] Attack of the phosphine occurs at the basal ruthenium atom, the site of lowest connectivity, and in the presence of an excess of phosphine the compound reacts further to produce the disubstituted cluster $[Ru_5C(CO)_{13}(PPh_3)_2]$. Both of these species have been confirmed by X-ray crystallographic studies and show the expected square-based-pyramidal structure.[3] The bulk of the PPh_3 groups is sufficient to cause the diphosphine derivative to show co-ordination of the ligands at diagonally opposite basal sites, whilst the bidentate $Ph_2P(CH_2)_2PPh_2$ chelates to a single basal ruthenium atom only.[3]

In this paper we report our findings on the reactivity of $[Ru_5C(CO)_{15}]$ with the bidentate nitrogen heterocycles 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) in the presence of Me_3NO, and compare this reactivity with that of the $[Ru_6C(CO)_{17}]$ cluster.

Results and Discussion

The addition of 2,2′-bipyridyl to a dichloromethane solution of $[Ru_5C(CO)_{15}]$ **1**, cooled to −78 °C, was followed by the dropwise addition of 2.2 molar equivalents of Me_3NO to initiate the loss of two carbonyls and cause a similar disubstitution reaction as observed for $[M_4(\mu\text{-}H)_4(CO)_{12}]$ (M = Ru or Os).[4]

Compound **1** is known to substitute typically at only the basal ruthenium atom sites, although apical substitution has been suggested for a benzene derivative.[5] Hence it was predicted that direct substitution of two carbonyls would lead to the formation of $[Ru_5C(CO)_{13}(bipy)]$ **2**, showing a basal connectivity of the ligand to a single Ru atom. The reaction was instead found to afford the orange-red bridged butterfly cluster $[Ru_5C(CO)_{14}(bipy)]$ **3** as the major product, and the yellow orthometallated derivative $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)]$ **4** as a minor one (Scheme 1). One possible mechanistic explanation of this chemistry is that this reaction proceeds *via* the initial generation of the hypothetical monohapto intermediate $[Ru_5C(CO)_{14}(bipy\text{-}N)]$, which then undergoes adduct formation to yield $[Ru_5C(CO)_{14}(bipy)]$ **3**. Further reaction of this species with Me_3NO then results in the subsequent loss of a second carbonyl ligand and the formation of the orthometallated product **4**.



Scheme 1 Formation of $[Ru_5C(CO)_{14}(bipy)]$ **3** and $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)]$ **4** *via* the hypothetical intermediate $[Ru_5C(CO)_{14}(bipy\text{-}N)]$

The molecular formula of compound **3** was initially established by spectroscopy. Its IR spectrum indicated the presence of only terminal carbonyl ligands and the compound was formulated as $[Ru_5C(CO)_{14}(bipy)]$ on the basis of its mass spectrum. Further elemental analysis and single-crystal X-ray diffraction studies confirmed this formulation. The cluster produced is clearly not the expected $[Ru_5C(CO)_{13}(bipy)]$ compound **2**. Instead only one carbonyl has been lost and a 76-electron bridged butterfly adduct formed by the addition of the second nitrogen lone pair to the basal ruthenium atom, as shown by the crystal structure (Fig. 1). Dutton[6] had previously suggested the

---

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

Table 1 Selected bond lengths (Å) and angles (°) for $[Ru_5C(CO)_{14}(bipy)]$

Ru(1)–Ru(2)	2.9174(9)	Ru(1)–N(2)	2.124(5)
Ru(1)–Ru(3)	2.9041(11)	Ru(1)–C	2.110(6)
Ru(2)–Ru(4)	2.8699(12)	Ru(2)–C	1.958(6)
Ru(2)–Ru(5)	2.8390(10)	Ru(3)–C	1.990(6)
Ru(3)–Ru(4)	2.9173(10)	Ru(4)–C	2.083(6)
Ru(3)–Ru(5)	2.8690(11)	Ru(5)–C	2.150(6)
Ru(4)–Ru(5)	2.7212(9)	C–O	1.14 (mean)
Ru(1)–N(1)	2.161(6)		
N(1)–Ru(1)–N(2)	76.2(2)	N(2)–Ru(1)–Ru(2)	95.11(4)
N(1)–Ru(1)–Ru(3)	100.67(13)		

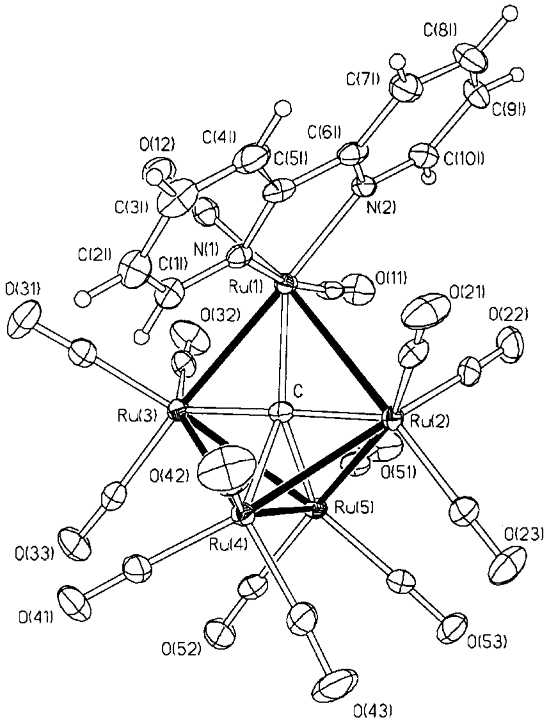


Fig. 1 Thermal ellipsoid plot at 50% probability depicting the molecular structure of $[Ru_5C(CO)_{14}(bipy)]$ **3** at 150 K

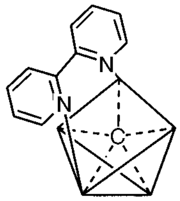


Fig. 2 Suggested structure of Dutton's $[Ru_5C(CO)_{14}(bipy)]$ isomer

formation of an isomer of cluster **3** (Fig. 2) from the reaction between $[Ru_5C(CO)_{15}]$ and 2,2′-bipyridyl in refluxing dichloromethane, by analogy with the previously incorrectly postulated edge-bridging structure proposed for $[Ru_3(CO)_{10}(bipy)]$.[7] It is uncertain what the exact nature of this product was, yet by comparison of the ^1H NMR data it is apparent that it cannot be either of the products **3** or **4** discussed herein. Furthermore, the air-sensitive character of Dutton's product rules it out as both the species formed in this work are air stable.

The solid-state molecular structure of $[Ru_5C(CO)_{14}(bipy)]$ **3** is given in Fig. 1, and selected structural parameters are listed in Table 1. The metal framework geometry is best described as an approximately bridged butterfly structure. The ligand is bound in a bidentate manner to this apical ruthenium atom, which shows further co-ordination to Ru(2) and Ru(3), the central carbide and two terminal carbonyl ligands. The remaining ruthenium atoms are each bound to three terminal carbonyl ligands. There is little variation seen between the carbonyl bond lengths which range from 1.127(8) to 1.157(8) Å. The five-co-ordinate carbide atom is asymmetrically bound, showing shorter Ru–C distances between the wing-tip atoms Ru(2), Ru(3) than the bridging atoms Ru(4), Ru(5) as observed previously for $[Ru_5C(CO)_{14}(\mu\text{-}AuPPh_3)(\mu\text{-}Br)]$[8] and $[Ru_5(\mu\text{-}H)C(CO)_{14}(SEt)]$.[9] The bipyridyl ligand is also asymmetrically co-ordinated to the cluster with Ru–N bond lengths of 2.161(6) and 2.124(5) Å, and is tilted somewhat to minimise steric hindrance.

The ^1H HMR spectrum of compound **3** shows seven resonances of relative integral 1 : 1 : 1 : 2 : 1 : 1 : 1 for the ring protons (H^1–H^4, H^7–H^{10}), indicating that the magnetic environments of the analogous protons of the two rings have become inequivalent. This inequivalence arises from the protons of one of the two aryl rings being brought into closer proximity with carbonyl ligands than the other. The high-frequency resonance at δ 9.45 is characteristic of an α-proton adjacent to nitrogen: H^1 or H^{10} but it cannot be unambiguously stated which. The other α-proton must give rise to an equivalent resonance with a similar structure and therefore lies hidden amongst the multiplet at *ca.* δ 8.55. The two remaining resonances showing only one large ^3J coupling are therefore assigned to H^4 and H^7. The ddd resonance at *ca.* δ 8.3 shows two large three-bond couplings (8.7 and 7.65 Hz) and must therefore be attributed to one of the protons H^3 and H^8 rather than H^2 and H^9 which are expected to show a characteristically smaller coupling to the α-proton in addition to the large coupling to H^3/H^8. Its equivalent partner must give rise to the resonance which is partially obscured in the multiplet at *ca.* δ 8.5. The remaining ddd resonances at δ 8.02 and 7.74 are therefore assigned to H^2 and H^9 which show a very similar intensity and structural pattern as expected. These assignments were confirmed by a ^1H COSY (correlation spectroscopy) experiment.

The minor yellow reaction product **4** was formulated initially as $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)]$ by a consideration of the spectroscopic evidence. Its ^1H NMR spectrum showed the presence of a hydride resonance at δ −21.42, implying that orthometallation of bipy had occurred. This was confirmed by a single crystal X-ray diffraction analysis (Fig. 3). The structure perhaps shows that orthometallation of bipy occurs in preference to reformation of the metal–metal bond presumably as a result of the steric hindrance which might be encountered in attempting to bring Ru(1) and Ru(5) close enough to bond. The structure shows a bridged butterfly Ru_5 cluster unit in accordance with the 76 electron count. Notably, the cluster core is analogous to that established by Conole[10] for the related bis(pyridine) cluster $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_5H_4N)(py)]$. The bridged butterfly core in each arises from cleavage of one metal–metal bond of the parent cluster $[Ru_5C(CO)_{15}]$ and in **4**, Ru(2) and Ru(4) are 3.5439(11) Å apart. The deprotonated 2,2′-bipyridyl ligand spans this opening chelating Ru(2) through both of its nitrogens and binding to Ru(4) through the carbon [C(1)] of one ring, the proton having migrated to an edge-bridging site between Ru(3) and Ru(4). The position of the proton was located directly from a Fourier-difference map and corresponds with a void in the carbonyl distribution along the Ru(3)–Ru(4) edge in computed space-filling models. The central carbide atom is asymmetrically bonded to all five metal atoms, showing longer bonds to metals of the bridged hinge [Ru(2), Ru(3) and Ru(4)] than to those at the wing-tips [Ru(1) and Ru(5)]. All thirteen carbonyls are terminally bonded in agreement with the IR data and show C–O bond lengths in the range 1.128(11)–1.157(10) Å (mean 1.14 Å). Three carbonyl ligands are co-ordinated to each of Ru(1), Ru(3) and Ru(5) while the metal atoms bonded to the orthometallated bipy ligand [Ru(2) and Ru(4)] are each additionally co-ordinated to two carbonyl ligands.

Table 2 Selected bond lengths (Å) and angles (°) of [$Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)$] **4**

Ru(1)–Ru(2)	2.9009(10)	Ru(4)–C(1)	2.053(9)
Ru(1)–Ru(3)	2.8460(10)	Ru(1)–C	1.971(8)
Ru(1)–Ru(4)	2.8676(11)	Ru(2)–C	2.060(8)
Ru(2)–Ru(5)	2.8826(11)	Ru(3)–C	2.096(8)
Ru(3)–Ru(4)	2.8959(11)	Ru(4)–C	2.046(8)
Ru(3)–Ru(5)	2.8785(11)	Ru(5)–C	2.006(8)
Ru(4)–Ru(5)	2.8115(10)	Ru(3)–H(1)	1.5765(8)
Ru(2)–N(1)	2.125(7)	Ru(4)–H(1)	2.0672(8)
Ru(2)–N(2)	2.138(7)	C–O	1.14 (mean)
N(1)–Ru(2)–N(2)	76.2(3)	C(1)–N(1)–Ru(2)	123.1(6)
N(1)–C(1)–Ru(4)	118.7(6)		

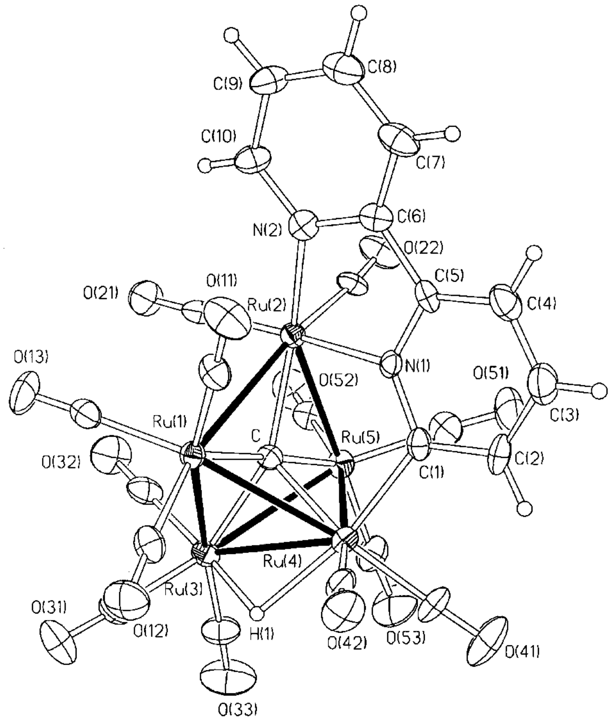


Fig. 3 Thermal ellipsoid plot at 30% probability depicting the molecular structure of [$Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)$] **4** at 298 K

Owing to the somewhat unexpected favoured removal of only one carbonyl ligand in the presence of 2.2 equivalents of Me_3NO, the reaction was repeated using 1.1 equivalents of Me_3NO to establish whether cluster **3**, [$Ru_5C(CO)_{14}$(bipy)], would still be formed, but in relatively higher yield. This was indeed found to be the case, and cluster decomposition levels were consequently greatly reduced. The favoured removal of only one carbonyl ligand, whether 1.1 or 2.2 equivalents of Me_3NO were used, is in direct contrast to the reactivity of the [$Ru_4(\mu\text{-}H)_4(CO)_{12}$] cluster which showed the removal of two carbonyl ligands under analogous conditions.[4]

Reaction of [$Ru_5C(CO)_{15}$] with 1,10-phenanthroline

The reaction between [$Ru_5C(CO)_{15}$] **1** and 1,10-phenanthroline was carried out in an analogous manner to that reported for the bipyridyl ligand. Initially 2.2 equivalents of Me_3NO were used to activate the cluster, and a dark brown solution was produced upon warming the solution from −78 °C to room temperature. Product separation by TLC using hexane–dichloromethane (1 : 1 v/v) as eluent isolated one main orange-red product which was identified as [$Ru_5C(CO)_{14}$(phen)] **5**, and a second yellow species in lower yield, characterised as [$Ru_5(\mu\text{-}H)C(CO)_{13}(C_{12}H_7N_2)$] **6**, analogous to the 2,2′-bipyridyl derivatives.

Table 3 Selected bond lengths (Å) and angles (°) of [$Ru_5(CO)_{14}$(phen)] **5**

Ru(1)–Ru(2)	2.8950(14)	Ru(1)–N(2)	2.130(5)
Ru(1)–Ru(4)	2.906(2)	Ru(1)–C	2.114(6)
Ru(2)–Ru(3)	2.8514(13)	Ru(2)–C	1.975(5)
Ru(2)–Ru(5)	2.930(2)	Ru(3)–C	2.144(6)
Ru(3)–Ru(4)	2.8469(12)	Ru(4)–C	1.973(5)
Ru(3)–Ru(5)	2.7136(12)	Ru(5)–C	2.085(6)
Ru(4)–Ru(5)	2.893(2)	C–O	1.14 (mean)
Ru(1)–N(1)	2.166(5)		
N(1)–Ru(1)–N(2)	77.3(2)	N(2)–Ru(1)–Ru(4)	95.14(3)
N(1)–Ru(1)–Ru(2)	98.33(13)		

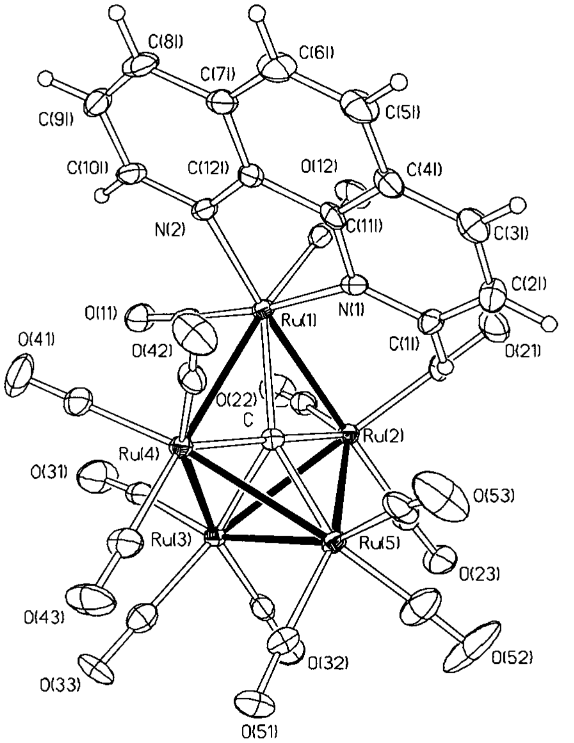


Fig. 4 Thermal ellipsoid plot at 50% probability depicting the molecular structure of [$Ru_5C(CO)_{14}$(phen)] **5** at 150 K

The IR carbonyl pattern of compound **5** being almost identical to that of the bipyridyl derivative [$Ru_5C(CO)_{14}$(bipy)] **3**, implied the formulation [$Ru_5C(CO)_{14}$(phen)]. This was confirmed by further spectroscopy and an X-ray diffraction study on a single crystal grown from a solution of hexane–dichloromethane. Its mass spectrum showed the molecular ion at *m/z* 1091 (calc. 1089), further confirming the preliminary identification of the cluster. Its molecular structure is presented in Fig. 4. The familiar bridged butterfly skeleton of metal atoms is observed, which shows an outer shell of fourteen terminal carbonyls, of which three are bound to each of the wing-tip and the basal rutheniums Ru(2), Ru(4) and Ru(3), Ru(5) respectively. The remaining two carbonyl ligands are bound to the apical ruthenium Ru(1), which also shows co-ordination to the phenanthroline ligand in a bidentate manner, with a bite angle of 77.3(2)°. The five ruthenium atoms are bound to the central carbido atom, and show an average Ru–C bond length of 1.974 Å to the wing-tip atoms, and an average bond length of 2.114 Å to the hinge atoms, which is comparable to the Ru–C distance to the apical ruthenium. The exposure of the carbido atom is therefore intermediate between that fully enclosed in [$Ru_6C(CO)_{17}$] **7**[11] and that semi-exposed in [$Ru_5C(CO)_{15}$] **1**.[2,3]

The ^1H NMR spectrum of [$Ru_5C(CO)_{14}$(phen)] exhibits six resonances all of relative intensity one except for the multiplet

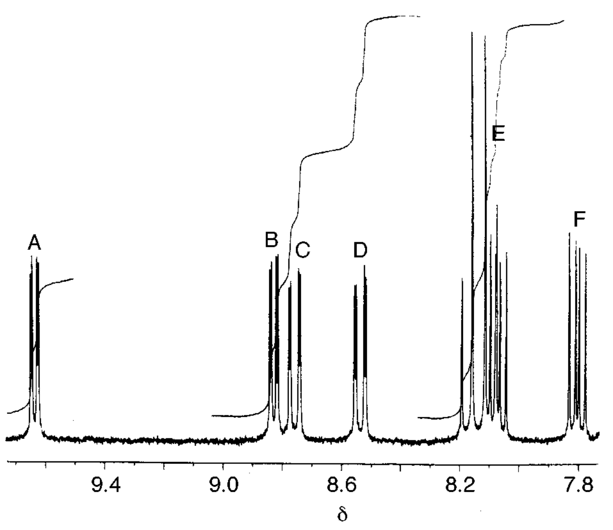
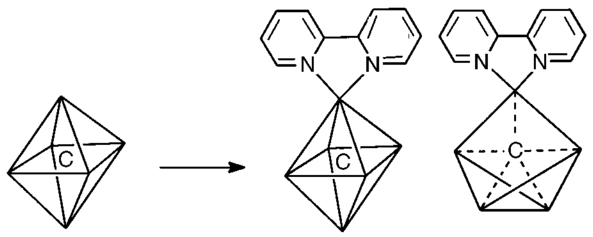


Fig. 5 The ^{1}H NMR spectrum of $[Ru_5C(CO)_{14}(phen)]$ **5** run in $(CD_3)_2CO$

at δ 8.04–8.19 which has a relative intensity of three (Fig. 5). The resonances have been labelled **A**–**F** for ease of reference. It is apparent from our earlier discussions that the doublet of doublets resonance **A** at high frequency (δ 9.64) results from an α-proton, either proton H^1 or H^{10}, although it is not possible to state unambiguously which. From the magnitude of the coupling constants (8.22, 1.32 Hz), resonance **C** at δ 8.76 can be attributed to either proton H^3 or H^8. Furthermore, either H^2 or H^9 is responsible for the resonance in amongst the 'multiplet' at δ 8.06, showing one relatively large ^3J coupling of 8.18 Hz to proton H^3 or H^8 and a characteristically smaller one to the α-proton of 5.28 Hz. Consequently these resonances result from a set of protons residing on one of the pyridine rings of the phenanthroline ligand. From similar considerations resonances **B** and **F** are assigned to the α- and β-protons respectively of the other pyridine ring. Thus, only the multiplet between δ 8.04 and 8.19 remains to be assigned and is obviously the result of the overlap between the resonances of H^5, H^6 and either H^3 or H^8. Expansion of the multiplet allowed the doublet of doublets resonance arising from either H^3 or H^8 to be more readily identified. The exact nature of the remaining resonance was not obvious and hence a further nuclear Overhauser effect (NOE) experiment was carried out. A 3.9% enhancement of resonance **E** at *ca.* δ 8.1, attributed to H^5 and H^6, was observed, and appeared as a triplet rather than a doublet, therefore coupling to both H^5 and H^8 must be occurring. Resonance **F** (H^2/H^9) showed a greater enhancement of 12.6%, which is as expected since this proton lies closer in space to H^3/H^8 than H^5/H^6. Thus the multiplet shows a closely overlapping set of triplets for H^5 and H^6 which explains the apparent 1:3:3:1 ratio of the resonance. Therefore, these protons are not only coupled to each other but also to H^3 and H^8 respectively.

From the carbonyl IR spectrum of the minor reaction product **6** it was evident that an analogous species to the orthometallated bipyridyl product **4** had been formed. Its formulation as $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{12}H_7N_2)]$ was further corroborated by the mass spectrum which showed a strong molecular ion peak at *m/z* 1061 (calc. 1061) followed by the stepwise loss of several carbonyls. Attempts to grow crystals suitable for X-ray diffraction have proven unsuccessful.

The reaction between $[Ru_5C(CO)_{15}]$ **1** and phenanthroline was repeated using only 1.1 equivalent of Me_3NO to see whether this affected the resulting products. It was found that, as observed previously with the bipyridyl ligand, the same products are formed and the relative yield of $[Ru_5C(CO)_{14}(phen)]$ **5** was increased whilst the yield of the orthometallated derivative **6** was reduced.



7 **8** **3**

Scheme 2 Reaction of $[Ru_6C(CO)_{17}]$ **7** with 2,2′-bipyridyl at −78 °C in the presence of 2.2 equivalents of Me_3NO to form $[Ru_5C(CO)_{14}(bipy)]$ **3** and $[Ru_6C(CO)_{15}(bipy)]$ **8**

Photolysis of $[Ru_5C(CO)_{14}(bipy)]$ and $[Ru_5C(CO)_{14}(phen)]$

The clusters $[Ru_5C(CO)_{14}(bipy)]$ **3** and $[Ru_5C(CO)_{14}(phen)]$ **5** were irradiated both in solution and also as samples embedded in a thin poly(methyl methacrylate) film. The aim of the photolysis reaction was to attempt to remove a carbonyl ligand from the cluster and cause the subsequent bond formation to yield a square-based pyramidal cluster. However, it was observed that after 8 h of irradiation of the film there was no apparent change as monitored by IR spectroscopy. Likewise irradiation in solution proved unsuccessful resulting in product decomposition only. It is suggested that the square-based-pyramidal compound is not formed as a result of the steric hindrance which would be incurred in attempting to bring the two relevant metal atoms close enough to bond.

Reaction of $[Ru_6C(CO)_{17}]$ with 2,2′-bipyridyl and 1,10-phenanthroline

The reaction between $[Ru_6C(CO)_{17}]$ **7** and the 2,2′-bipyridyl or 1,10-phenanthroline ligand was carried out using 2.2 equivalents of Me_3NO at −78 °C in an analogous manner to that described previously for the $[Ru_5C(CO)_{15}]$ cluster. The resulting dark red-brown solution was separated by TLC using hexane–dichloromethane (1:1 v/v) as eluent. It was found to be necessary to allow the solvent front to run to almost the top of the plate to permit the gradual separation of the two very closely spaced bands, which were orange-yellow and deep red and were present in approximately similar quantities. The IR carbonyl spectrum of the orange band was found to be identical to that recorded for the cluster $[Ru_5C(CO)_{14}(bipy)]$ **3**, although this was only realised in hindsight because its formation was unexpected. The confirmation of its identity was completed by (*a*) mass spectrometry, which showed the parent ion peak at *m/z* 1065 (calc. 1065) and (*b*) by X-ray diffraction which showed an isomorphous crystal structure to that of $[Ru_5C(CO)_{14}(bipy)]$ **3**.

Thus it would appear that the $[Ru_6C(CO)_{17}]$ cluster has undergone an unexpected degradative elimination reaction under mild conditions, with the resultant loss of an $Ru(CO)_3$ unit. This is in stark contrast to the forcing conditions required to convert the $[Ru_6C(CO)_{17}]$ cluster into $[Ru_5C(CO)_{15}]$ in the autoclave reaction (90 °C, 70 atm CO, 3.5 h).

The second product isolated from the reaction mixture was a red cluster whose IR spectrum clearly showed the presence of terminal carbonyls and possibly a bridging carbonyl, although this feature was somewhat weak and broad. From the IR pattern and its colour it was immediately apparent that the product was not the orthometallated cluster $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)]$ **4**. It was instead assigned as the expected product $[Ru_6C(CO)_{15}(bipy)]$ **8** (Scheme 2) on the basis of its mass spectrum. The sample was found to be somewhat unstable and decomposed over time to an insoluble black solid.

A similar reaction was observed between 1,10-phenanthroline and $[Ru_6C(CO)_{17}]$, from which two products were chromatographically separated. On the basis of the IR carbonyl pattern the identity of the orange-yellow product was inferred as [Ru$_5$C(CO)$_{14}$(phen)] **5**, and this was backed up by the ^{1}H NMR spectrum. The mass spectrum showed the molecular ion peak at *m/z* 1092 (calc. 1089) followed by the subsequent loss of carbonyl ligands. Single crystals were grown, and although a full refinement of the structure was not performed sufficient refinement was carried out to confirm that they were isostructural to [Ru$_5$C(CO)$_{14}$(phen)] crystals grown previously. The similarity in the IR spectrum of the second red product **9**, to the previously determined derivative [Ru$_6$C(CO)$_{15}$(bipy)] **8**, implied that an analogous species had been formed which was formulated as [Ru$_6$C(CO)$_{15}$(phen)] **9**. Its ^{1}H NMR spectrum confirmed the presence of phen but was somewhat weak owing to the cluster's instability.

Conclusion

Our research into the reactivity of the [Ru$_5$C(CO)$_{15}$] and [Ru$_6$C(CO)$_{17}$] clusters with bidentate nitrogen heterocycles (L–L) has given rise to some rather interesting chemistry. It has been shown that both clusters undergo facile bond cleavage under mild reaction conditions to produce the bridged butterfly cluster [Ru$_5$C(CO)$_{14}$(L–L)]. For [Ru$_6$C(CO)$_{17}$] this requires in addition the elimination of a metal carbonyl fragment. Also, NMR studies showed that the ligands' proton environments become inequivalent on co-ordination to the Ru$_5$C(CO)$_{14}$ unit. This has been rationalised by the change in the magnetic environments of the two 'pyridine' ring protons due to differences in their proximity to the carbonyl ligands of the cluster. Although the relative yield of this product was found to be much greater from the reaction with the [Ru$_5$C(CO)$_{15}$] cluster **1** the secondary product of the reactions was however found to differ. In the preparation involving cluster **1** the products were characterised as the orthometallated bridged butterfly derivatives [Ru$_5$(μ-H)C(CO)$_{13}$(L–L′)] (L–L′ = ligand − H), which were apparently favoured to the alternative square-based-pyramidal (74 e) [Ru$_5$C(CO)$_{13}$(L–L)] cluster because of the steric crowding which would result between the heterocycle and the carbonyl ligands. The cluster [Ru$_6$C(CO)$_{17}$] **7** was found to form the expected product [Ru$_6$C(CO)$_{15}$(L–L)] on the basis of spectroscopic results, and was proposed to have the ligand bound to the apical ruthenium atom. It was however found to decompose readily.

Experimental

Synthesis and characterisation

All separations were achieved chromatographically on silica, on the open bench without any precautions to exclude air. Thin-layer chromatography (TLC) was carried out using glass plates (20 × 20 cm) coated with a 0.25 cm layer of silica gel 60 F$_{254}$, which were supplied by Merck. Column chromatography was carried out using a 50 cm long glass column with an internal diameter of 3 cm, fitted with a solvent reservoir (100 cm^3), and a facility for pressurisation; 60 mesh silica was used to pack the column, and the eluents used for both column and thin-layer chromatography were mixed from standard grade laboratory solvents. Infrared spectra were recorded in dichloromethane in NaCl cells (0.5 mm path length) supplied by Specac Ltd., using a Perkin-Elmer Series 1600 Fourier-transform instrument. Fast atom bombardment mass spectra were obtained on a Kratos MS50TC spectrometer which was run in positive mode. Samples were run as a matrix in *m*-nitrobenzyl alcohol. Proton NMR spectra were recorded on Bruker WH 200 or 250 MHz Fourier-transform instruments. All spectra described herein were recorded in deuteriated solvents, and were referenced to an internal tetramethylsilane standard.

Trimethylamine *N*-oxide dihydrate (Me$_3$NO·2H$_2$O), from Aldrich, was carefully dried by first refluxing the sample (15 g) in benzene (250 cm^3) for 24 h, to remove the water of crystallisation *via* a Dean and Stark distillation. The benzene was then decanted and the sample dried under vacuum on a Schlenk line, and sublimed prior to use. Addition of Me$_3$NO to the reaction solutions was carried out under an atmosphere of dry nitrogen, although no strict precautions were taken completely to exclude air from the reaction systems. Dichloromethane was dried using CaH$_2$ and freshly distilled prior to reaction. All other reagents were used as supplied without further purification. 2.2′-Bipyridyl and 1,10-phenanthroline were obtained from Aldrich Chemicals.

[Ru$_6$C(CO)$_{17}$] 7. A stirred Burghoff autoclave fitted with a poly(tetrafluoroethylene) sleeve (250 cm^3) was used to prepare the cluster starting materials. The autoclave was first flushed three times with ethylene before a heptane solution of [Ru$_3$(CO)$_{12}$] (1 g in 150 cm^3) was pressurised to 30 atm with C$_2$H$_4$ and heated for 3.5 h at 145 °C to yield dark red crystals of [Ru$_6$C(CO)$_{17}$] on cooling.

[Ru$_5$C(CO)$_{15}$] 1. The autoclave was first flushed three times with CO before heptane solution of [Ru$_6$C(CO)$_{17}$] (1 g in 50 cm^3) was pressurised to 70 atm and heated for 3.5 h at 90 °C to yield the dark red cluster [Ru$_5$C(CO)$_{15}$] which precipitated on cooling. A large amount of the cluster remained in solution and should be evaporated *in vacuo* followed by washing with boiling hexane.

Reactions of [Ru$_5$C(CO)$_{15}$] 1

With 2,2′-bipyridyl. Compound **1** (88 mg) was dissolved in dichloromethane (50 cm^3) and cooled to −78 °C before the addition of an excess of 2,2′-bipyridyl (44 mg in 10 cm^3 CH$_2$Cl$_2$). A solution of Me$_3$NO (15.4 mg, 2.1 molar equivalents) in dichloromethane (25 cm^3) was added dropwise over a period of 20 min, before being allowed to warm to room temperature gradually. The solution became dark red-brown, was reduced *in vacuo* and the residue separated by column chromatography. Initially hexane–dichloromethane (7 : 3) was used as the eluent with a gradient elution to remove first the yellow cluster [Ru$_5$(μ-H)C(CO)$_{13}$(C$_{10}$H$_7$N$_2$)] **4** (3% yield) and then the major red cluster [Ru$_5$C(CO)$_{14}$(bipy)] **3** (8% yield) which were identified from both spectroscopic and X-ray crystallographic data. Single crystals of compound **3** were grown from hexane–dichloromethane at 5 °C, and **4** was crystallised from a solution of chloroform–hexane at −20 °C. Spectroscopic data for compound **3**: IR (CH$_2$Cl$_2$) ν(CO) 2074m, 2040s, 2032s, 2013m (sh), 2008s, 1981m and 1960m/w (br) cm^{-1}; ^{1}H NMR [(CD$_3$)$_2$CO] δ 9.45 (ddd, 1 H, *J* = 0.75, 1.46, 5.68), 8.91 (ddd, 1 H, *J* = 0.76, 1.35, 8.43), 8.75 (d, 1 H, *J* = 0.73, 1.3, 8.45), 8.56–8.48 (m, 2 H), 8.33 (ddd, 1 H, *J* = 1.60, 7.65, 8.70), 8.02 (ddd, 1 H, *J* = 1.40, 5.72, 7.62) and 7.74 (ddd, 1 H, *J* = 1.34, 5.64, 7.65 Hz); *m/z* 1068 calc.: 1065, M^+) [Found (Calc. for C$_{25}$H$_8$N$_2$O$_{14}$Ru$_5$·CH$_2$Cl$_2$) C, 27.1 (27.15); H, 0.85 (0.55); N, 2.45 (2.30)%]. Spectroscopic data for compound **4**: IR (CH$_2$Cl$_2$) ν(CO) 2085m, 2046s, 2028s, 2007w, 1992 (sh), 1987w/m and 1944w (br) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.14 (ddd, 1 H, *J* = 0.81, 1.51, 5.61), 8.03 (m, 2 H), 7.49 (m, 2 H), 7.23 (dd, 1 H, *J* = *ca*. 7.54, 1.26, resonance partially obscured by CHCl$_3$ solvent peak) and 7.01 (t, 1H, *J* = 7.76 Hz).

With 1,10-phenanthroline. Compound **1** (97 mg) was dissolved in dichloromethane (75 cm^3), and cooled to −78 °C before the addition of an excess of 1,10-phenanthroline (72 mg in 10 cm^3 CH$_2$Cl$_2$). A solution of Me$_3$NO (17.5 mg, 2.2 mol equivalents in 25 cm^3 dichloromethane) was then added dropwise over a period of 20 min. The reactants were stirred for 20 min whilst warming to room temperature, producing a dark red-brown solution. Removal of the solvent under reduced pressure followed by TLC separation using hexane–dichloromethane (1:1) as eluent allowed two major products to be isolated and characterised. The red cluster $[Ru_5C(CO)_{14}(phen)]$ **5** was formed in relatively higher yields (7%) than the yellow cluster $[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{12}H_7N_2)]$ **6** (2%). Spectroscopic data for compound **5**: IR (CH_2Cl_2) ν(CO) 2085vw, 2074m, 2040s, 2032s, 2013m (sh), 2008s, 1981m and 1961m/w (br) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 9.64 (1 H, dd, $J = 5.33, 1.33$), 8.83 (1 H, dd, $J = 5.25, 1.46$), 8.76 (dd, 1 H, $J = 8.22, 1.32$), 8.54 (1 H, dd, $J = 8.25, 1.44$), 8.13 (dd, 2 H, $J = 8.25, 1.44$), 8.06 (dd, 2 H, $J = 8.18, 5.28$), 7.80 (dd, 1 H, $J = 5.24, 8.21$ Hz) and −21.42 (s, 1 H); *m/z* 1091 (Calc.: 1089, M^+). Spectroscopic data for compound **6**: IR (CH_2Cl_2) ν(CO) 2085m, 2047s, 2042 (sh), 2029s, 2010w, 1993 (sh), 1986m and 1945w cm^{-1}; *m/z* 1061 (Calc.: 1061, M^+).

Reactions of $[Ru_6C(CO)_{17}]$ 7

With 2,2′-bipyridyl. To a dichloromethane solution (150 cm^3) of compound **7** (122 mg) cooled to −78 °C was added an excess of 2,2′-bipyridyl (60 mg in 10 cm^3 CH_2Cl_2) and Me_3NO (18.7 mg, 2.2 equivalents in 25 cm^3 CH_2Cl_2) added steadily dropwise over 20 min. The solution was then allowed slowly to warm to room temperature and was left to stir for 10 min on reaching this temperature. Removal of solvent *in vacuo* and subsequent product separation by TLC using hexane–dichloromethane (1:1) as eluent led to the isolation of two major products: $[Ru_5(CO)_{14}(bipy)]$ **3** (5% yield) and $[Ru_6C(CO)_{15}(bipy)]$ **8** (7% yield), which were characterised spectroscopically. In addition, single crystals of **3** were grown from a pentane–ethyl acetate solution at 5 °C, and their composition confirmed by their unit-cell dimensions. Spectroscopic data for compound **8**: IR (CH_2Cl_2) ν(CO) 2070m/w, 2018s, 1978m/w and 1826vw (br) cm^{-1}; *m/z* 1165 (Calc.: 1166, M^+).

With 1,10-phenanthroline. Compound **7** (74 mg) was dissolved in dichloromethane (50 cm^3) with rapid stirring over 10 min and cooled to −78 °C before the addition of an excess of 1,10-phenanthroline in dichloromethane (204 mg in 5 cm^3). A Me_3NO solution (2.2 molar equivalents; 11 mg in 15 cm^3 CH_2Cl_2) was then dripped into the reaction mixture over 20 min and then left to stir for 10 min. The solution became a deeper red on gradually warming to room temperature. Reduction of the solvent volume followed by TLC using hexane–dichloromethane (1:1) as eluent allowed the successful separation of two major products which were characterised spectroscopically as $[Ru_5C(CO)_{14}(phen)]$ **5** (4% yield) and $[Ru_6C(CO)_{15}(phen)]$ **9** (6% yield). In addition the identification of cluster **5** was confirmed from the successful growth of single crystals from a hexane–dichloromethane solution at 5 °C, and the determination of their unit-cell dimensions. Spectroscopic data for compound **9**: IR (CH_2Cl_2) ν(CO) 2071m/w, 2018m and 1979m/w cm^{-1}; ^1H NMR ($CDCl_3$) 8.52 (dd, 2 H), 8.44 (dd, 2 H), 7.98 (s, 2 H) and 7.70 (q, 2 H). Owing to decomposition of the cluster in solution over time, the resonances in the NMR spectrum were too weak to determine all couplings precisely.

Crystallography

Diffraction data for clusters **3** and **5** were collected on a Stoë Stadi four-circle diffractometer with an Oxford Cryosystems device for low-temperature data collection.[12] Data for cluster **4** were collected on a Siemens P4 diffractometer at ambient temperature (298 K). All computations were carried out with SHELXL 93[13] and SHELXTL PC.[14]

$[Ru_5C(CO)_{14}(bipy)]$ 3, prepared from $[Ru_5C(CO)_{15}]$ 1 and 2,2′-bipyridyl. $C_{25}H_8N_2O_{14}Ru_5{\cdot}CH_2Cl_2$, M 1150.61, crystal size 0.85 × 0.45 × 0.20 mm, monoclinic, space group $P2_1/c$, $a = 10.615(3)$, $b = 17.967(5)$, $c = 17.696(6)$ Å, $\beta = 100.63(3)°$, $U = 3317(2)$ Å^3, $Z = 4$, $F(000) = 2184$, $D_c = 2.304$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, 150(2) K, 2θ = 5.1–50.0°, measured reflections 6083, semiempirical absorption correction using ψ scans ($T_{max} = 0.340$, $T_{min} = 0.214$), unique observed reflections $[I > 2\sigma(I)]$ 4796, all H atoms in idealised positions and refined using a riding model, refined parameters 442, weight $w^{-1} = [\sigma^2(F_o^2) + (0.0606P)^2 + 10.6866P]$ where $P = (F_o^2 + 2F_c^2)/3$, goodness of fit on F^2 1.270, final $R1 = 0.0333$, $wR2 = 0.1048$ $[I > 2\sigma(I)]$, $R1 = 0.0365$, $wR2 = 0.1071$ (all data). Anisotropic thermal motion was assumed for all non-hydrogen atoms. The dichloromethane solvent molecule was modelled as full occupancy of an ordered site. A final Fourier-difference electron-density synthesis revealed maximum and minimum residual electron-density peaks of 1.99 and −1.391 e Å^{-3}, which were located in close proximity to ruthenium atoms.

$[Ru_5(\mu\text{-}H)C(CO)_{13}(C_{10}H_7N_2)]$ 4. $C_{24}H_8N_2O_{13}Ru_5$, M 1037.67, crystal size 0.56 × 0.10 × 0.10 mm, monoclinic, space group $P2_1/n$, $a = 10.297(2)$, $b = 17.162(2)$, $c = 16.803(2)$ Å, $\beta = 92.76(2)°$, $U = 2965.8(7)$ Å^3, $Z = 4$, $F(000) = 1960$, $D_c = 2.324$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, 298 K, 2θ = 3.4–50.0°, measured reflections 6591, unique observed reflections $[I > 2\sigma(I)]$ 3592, refined parameters 398, goodness of fit on F^2 1.132, final $R1 = 0.0436$, $wR2 = 0.0718$ $[I > 2\sigma(I)]$, $R1 = 0.0852$, $wR2 = 0.0964$ (all data). A final Fourier-difference electron-density synthesis revealed maximum and minimum residual electron density peaks of 0.573 and −0.657 e Å^{-3}, which were located in close proximity to ruthenium atoms.

$[Ru_5C(CO)_{14}(phen)]$ 5, prepared from $[Ru_5C(CO)_{15}]$ 1 and 1,10-phenanthroline. $C_{27}H_8N_2O_{14}Ru_5{\cdot}0.5CH_2Cl_2$, M 1132.17, crystal size 0.15 × 0.12 × 0.06 mm, triclinic, space group $P\bar{1}$, $a = 9.087(4)$, $b = 13.005(5)$, $c = 15.597(7)$ Å, $\alpha = 105.48(3)$, $\beta = 92.96(3)$, $\gamma = 104.53(3)°$, $U = 1705.6(13)$ Å^3, $Z = 2$, $F(000) = 1074$, $D_c = 2.205$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, 150(2) K, 2θ = 5.10–50.08°, measured reflections 6406, semiempirical absorption correction using ψ scans ($T_{max} = 0.813$, $T_{min} = 0.766$), unique observed reflections $[I > 2\sigma(I)]$ 6007, all H atoms in idealised positions and refined using a riding model, refined parameters 455, weight $w^{-1} = [\sigma^2(F_o^2) + (0.0384P)^2 + 11.1677P]$ where $P = F_o^2 + 2F_c^2)/3$, goodness of fit on F^2 1.062, final $R1 = 0.0338$, $wR2 = 0.0844$ $[I > 2\sigma(I)]$, $R1 = 0.0415$, $wR2 = 0.0907$ (all data). Anisotropic thermal motion was assumed for all non-hydrogen atoms. The dichloromethane solvent molecule was modelled as half occupancy of an ordered site, with the C−Cl bond lengths fixed at 1.70 Å. A final Fourier-difference electron-density synthesis revealed maximum and minimum residual electron-density peaks of 1.532 and −1.005 e Å^{-3}, located in close proximity to ruthenium atoms.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/515.

Acknowledgements

G. F. thanks the University of Edinburgh for grant funding. I. J. S. and M.McP. thank the EPSRC for financial support. The authors express their thanks to Drs. A. J. Blake and S. Parsons for the crystallographic data collection on compounds **3** and **5**.

References

1 B. F. G. Johnson, J. Lewis, J. N. Nicholls, I. A. Oxton, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1982, 289.
2 D. H. Farrar, P. F. Jackson, B. F. G. Johnson, J. Lewis and J. N. Nicholls, *J. Chem. Soc., Chem. Commun.*, 1981, 415.
3 B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, P. R. Raithby,

M. J. Rosales, M. McPartlin and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 277.
4 G. Freeman, Ph.D. Thesis, University of Edinburgh, 1995.
5 D. Braga, F. Grepioni, P. Sabatino, P. J. Dyson, B. F. G. Johnson, J. Lewis, P. J. Bailey, P. R. Raithby and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1993, 985.
6 T. Dutton, Ph.D. Thesis, University of Cambridge, 1989.
7 B. F. G. Johnson, J. Lewis and G. A. Foulds, *J. Organomet. Chem.*, 1985, **294**, 123.
8 B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga and K. H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 1983, 787.
9 A. G. Cowie, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1983, 2311.
10 G. Conole, Ph.D. Thesis, The Polytechnic of North London, 1990.
11 A. Sirigu, M. Bianchi and E. Benedetti, *Chem. Commun.*, 1969, 596.
12 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
13 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinement, University of Göttingen, 1993.
14 G. M. Sheldrick, SHELXTL PC, University of Göttingen and Siemens Analytical X-ray Instruments, Madison, WI, 1990.

Received 24*th December* 1996; *Paper* 6/08623C