

Photochemistry of $[\text{Ru}(\text{CO})_5]$ with nitrogen heterocycles

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The photochemistry of $[\text{Ru}(\text{CO})_5]$ with a series of nitrogen heterocycles has been investigated in dichloromethane solution. Photolysis with pyridine (py) leads to the highly unstable novel monosubstituted complex $[\text{Ru}(\text{CO})_4(\text{py})]$. In the case of polydentate heterocycles, photooxidation occurs. With 2,2'-bipyridine a number of complex products are generated. With 2,2':6,2''-terpyridine (terpy), $[\text{RuCl}_3(\text{terpy})]$ is formed. With 6-(2-thienyl)-2,2'-bipyridine (thbipy), $[\text{RuCl}_3(\text{thbipy})]$ is formed, this being soluble in donor solvents generating $[\text{RuCl}_3(\text{thbipy})(\text{solv})]$ (solv = solvent). The molecular structures of thbipy, $[\text{RuCl}_3(\text{thbipy})(\text{dmf})]$ (dmf = dimethylformamide) and $[\text{RuCl}_3(\text{thbipy})(\text{MeCN})]$ have been determined by single-crystal X-ray diffraction methods.

In a number of earlier papers we have reported the results of studies on the photosubstitution and photofragmentation chemistry of the trinuclear cluster $[\text{Ru}_3(\text{CO})_{12}]$ **1**.¹ These studies, as with the majority of those undertaken in the field of organometallic photochemistry, have been focused on ligand-field (LF) excitation.² The aim of our investigations here was to prepare a number of mononuclear carbonyl complexes containing nitrogen heterocycles as ligands photochemically since it has been reported that some complexes containing these ligands may well have the ability to act as efficient photosensitisers for electron-transfer processes.³ Although this aim has been partially fulfilled, the photoactivity of heterocyclic compounds themselves and their transition-metal complexes is complex and has led to unexpected results. This is illustrated clearly in the case of $[\text{Ru}(\text{bipy})_3]^{2+}$ (bipy = 2,2'-bipyridine), the photochemistry of which has received considerable attention but is still not fully understood.⁴

Work in our group has been focused on the photochemical reaction of $[\text{Ru}(\text{CO})_5]$ **2** with the heterocyclic ligands pyridine (py), bipy, 2,2':6,2''-terpyridine (terpy) and 6-(2-thienyl)-2,2'-bipyridine (thbipy). The bipy, terpy and thbipy ligands contain an α -diimine functional group which would be expected to co-ordinate to ruthenium to form $[\text{Ru}(\text{CO})_3(\alpha\text{-diimine})]$ complexes, many of which have been prepared previously by thermally mediated ligand-substitution reactions.⁵ In addition, thbipy has a thiophene ring and terpy a pyridine ring that could either co-ordinate to the metal centre or remain pendant, both bonding modes having been illustrated previously in the thermal chemistry of these ligands with transition-metal complexes.⁶

Results and Discussion

Molecular structure of 6-(2-thienyl)-2,2'-bipyridine

As a starting point to the studies, the molecular structure of 6-(2-thienyl)-2,2'-bipyridine, prepared using the general methodology of Kröhnke,⁷ was determined by X-ray crystallography from single crystals grown by slow evaporation of solvent from a methanol solution. From this structural study, together with that undertaken for terpy,⁸ the distortions of these ligands upon co-ordination to a ruthenium centre can be investigated.

The molecular structure of thbipy is shown in Fig. 1 and interatomic distances and angles in Table 1. The bonds linking the rings in the thbipy molecule are typical of C–C single

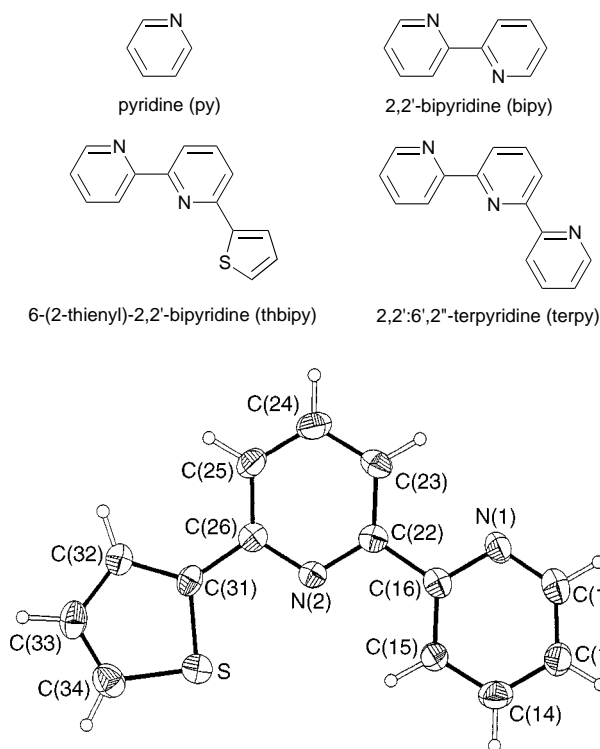


Fig. 1 Molecular structure of 6-(2-thienyl)-2,2'-bipyridine

bonds between sp^2 -hybridised carbon atoms. Within the ring systems, the C–N bond lengths vary from 1.334(6) to 1.358(5), the shortest bond lengths being observed in the N(1)–C(16)–C(22)–N(2) moiety and the longest bond between N(2) and C(26). The C–S bonds lengths are 1.713(4) [S–C(31)] and 1.700(5) Å [S–C(34)], these being in agreement with those observed in 2-(2-thienyl)pyridine,⁹ 6-phenyl-4-(2-thienyl)-pyrimidin-2(1H)-one,¹⁰ 2-(5-methyl-3-thienyl)-2,3,5,9b-tetrahydro-1H-pyrazolo[4,3-c]quinolin-3-one¹¹ and 2-(5-methyl-2-thienyl)-2,3,5,9b-tetrahydro-1H-pyrazolo[4,3-c]quinolin-3-one.¹² The angles about the C–C bonds linking the rings break down into two significantly different sets, namely those involving a heteroatom and those involving only carbon atoms. The three rings are close to being coplanar, with the angles between mean planes of the central ring and those rings containing N(1) and S being 5.1 and 4.5°, respectively.

Table 1 Bond lengths (Å) and angles (°) for thbipy

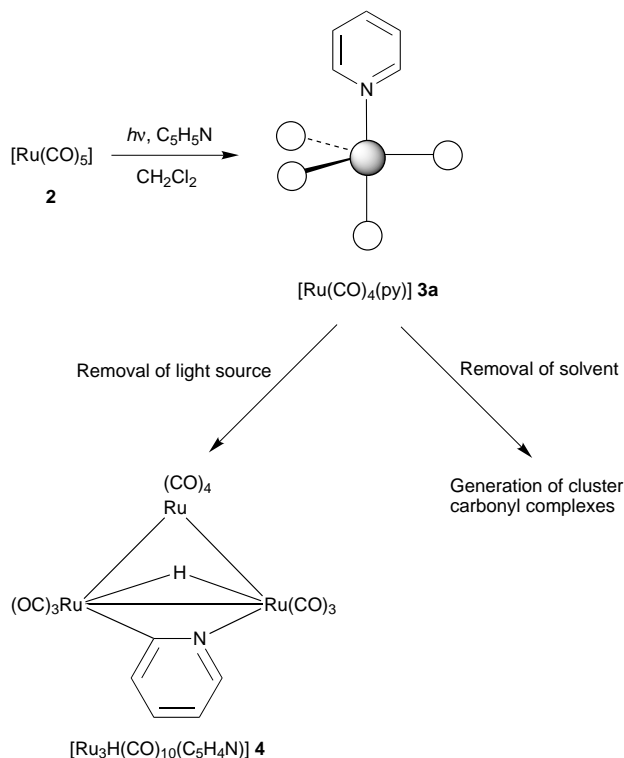
S–C(34)	1.700(5)	S–C(31)	1.713(4)
N(1)–C(12)	1.334(6)	N(1)–C(16)	1.345(5)
N(2)–C(26)	1.352(5)	N(2)–C(22)	1.358(5)
C(12)–C(13)	1.377(7)	C(13)–C(14)	1.377(6)
C(14)–C(15)	1.376(7)	C(15)–C(16)	1.391(6)
C(16)–C(22)	1.494(6)	C(22)–C(23)	1.396(6)
C(23)–C(24)	1.396(6)	C(24)–C(25)	1.390(6)
C(25)–C(26)	1.392(6)	C(26)–C(31)	1.474(5)
C(31)–C(32)	1.402(6)	C(32)–C(33)	1.433(6)
C(33)–C(34)	1.349(7)		
C(34)–S–C(31)	92.1(2)	C(12)–N(1)–C(16)	116.8(4)
C(26)–N(2)–C(22)	117.9(4)	N(1)–C(12)–C(13)	124.8(4)
C(14)–C(13)–C(12)	117.4(4)	C(15)–C(14)–C(13)	119.7(4)
C(14)–C(15)–C(16)	118.7(4)	N(1)–C(16)–C(15)	122.6(4)
N(1)–C(16)–C(22)	116.0(4)	C(15)–C(16)–C(22)	121.4(3)
N(2)–C(22)–C(23)	122.7(4)	N(2)–C(22)–C(16)	115.5(4)
C(23)–C(22)–C(16)	121.7(4)	C(22)–C(23)–C(24)	118.5(4)
C(25)–C(24)–C(23)	119.2(4)	C(24)–C(25)–C(26)	118.9(4)
N(2)–C(26)–C(25)	122.8(4)	N(2)–C(26)–C(31)	114.4(3)
C(25)–C(26)–C(31)	122.8(3)	C(32)–C(31)–C(26)	128.8(4)
C(32)–C(31)–S	111.5(3)	C(26)–C(31)–S	119.6(3)
C(31)–C(32)–C(33)	110.4(4)	C(34)–C(33)–C(32)	113.4(4)
C(33)–C(34)–S	112.5(4)		

Of interest is the *cis* arrangement of N(2) to S as opposed to the *trans* arrangement of N(1) to N(2). The reason for this may be based on a combination of crystal-packing effects, the different ring sizes of the thiophene and terminal pyridine rings and the resultant steric interactions between them and the central pyridine ring. The two pyridine rings are arranged *trans* to one another since a *cis* arrangement would place H(15) and H(23) in close proximity, this being unfavourable. In the case of the thiophene ring, this adopts a *cis* configuration with respect to the central pyridine ring due to the increased distance between H(25) and H(32) and hence the reduced repulsion between these atoms. In addition, sulfur is substantially larger than nitrogen and the repulsions between its lone pairs and that on N(2) may well be significantly lower than that between the sulfur lone pair and H(25) therefore favouring the *syn* torsion angle as opposed to the *anti* case between N(1) and N(2).

Photochemistry of [Ru(CO)₅] 2 with pyridine

Broad-band UV irradiation of a solution of [Ru(CO)₅] 2 in the presence of pyridine leads to the formation of the novel C_{3v} monosubstituted complex [Ru(CO)₄(py)] 3a as characterised by comparison of IR spectral data with those of the iron analogue.¹³ Complex 3a is highly reactive, being both solvent and light dependent. Removal of solvent leads to the formation of carbonyl complexes which are, at present, uncharacterised. Removal of the light source from a solution of 3a leads, within 30 min, to formation of the yellow-green trinuclear cluster [Ru₃H(CO)₁₀(C₅H₄N)] 4, characterised by comparison with spectral data in the literature.¹⁴ It is thought that the mechanism of this trimerisation involves sequential attack on 3a by two Ru(CO)₄ fragments, generated by loss of pyridine from 3a. This mechanism is postulated rather than a trimerisation of three Ru(CO)₄ fragments to yield [Ru₃(CO)₁₂] 1 followed by the attack of pyridine, since there is no observable reaction between pyridine and 1 at room temperature. These results are summarised in Scheme 1.

The pyridine complex 3a is remarkably unstable as compared to other monosubstituted mononuclear ruthenium carbonyl complexes such as [Ru(CO)₄(PPh₃)] or even the alkene-coordinated species [Ru(CO)₄(η²-C₂H₄)]. This may be attributed to the poor interaction between the nitrogen of the pyridine and the metal centre as compared with the good σ-donor phosphines or π-acceptor alkenes. This result demonstrates that photochemistry offers a route to highly reactive intermediates.

**Scheme 1** Photochemistry of [Ru(CO)₅] 2 with pyridine

Indeed, the instability of 3a in the absence of an irradiation source may well be the reason why this complex has not been characterised previously as a product from the thermolysis or pyrolysis of ruthenium mononuclear or cluster carbonyl complexes with pyridine.

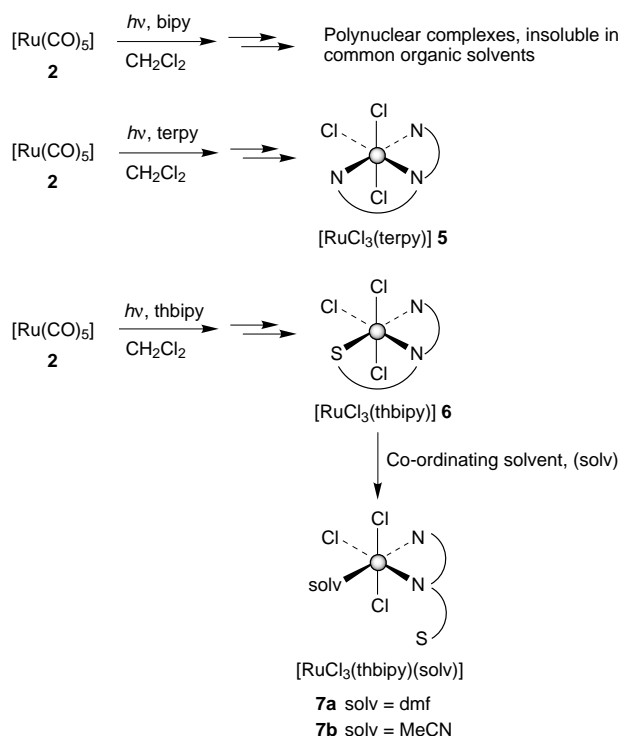
Photochemistry of [Ru(CO)₅] 2 with bipy, terpy and thbipy

The photochemistry of polydentate heterocyclic ligands with [Ru(CO)₅] 2 in chlorinated solvents is very different to that with pyridine. If a dichloromethane solution of 2 is irradiated in the presence of an excess of heterocyclic ligand there is an initial change from colourless to yellow-orange and then to purple. Over time a dark brown precipitate forms, the nature of which depends on the ligand used. With bipy and terpy the precipitate is insoluble in all common solvents. The bipy complexes are, at present, uncharacterised but they are thought, on the basis of mass spectral studies, to be polymeric in nature. The terpy complex was characterised as [RuCl₃(terpy)] 5 on the basis of comparisons of ¹H NMR data with those in the literature.¹⁵ With thbipy, again a precipitate is formed in dichloromethane, this being characterised as [RuCl₃(thbipy)] 6 by comparison with literature data.¹⁶ In this case the precipitate is soluble in co-ordinating solvents such as acetonitrile and dimethylformamide (dmf) forming the complexes [RuCl₃(thbipy)(solv)] (solv = solvent) in which the potentially tridentate ligand thbipy acts in a bidentate manner. The photochemistry of polydentate heterocycles with 2 is summarised in Scheme 2.

Of interest is the fact that, whereas the thbipy-substituted complex [RuCl₃(thbipy)] is soluble in co-ordinating solvents forming [RuCl₃(thbipy)(solv)] (solv = solvent), the analogous terpy complex [RuCl₃(terpy)] is insoluble. This may be attributed to the weaker co-ordination of the soft sulfur in thbipy to the hard ruthenium(III) centre as opposed to the case of nitrogen atoms in terpy.

Molecular structures of [RuCl₃(thbipy)(dmf)] 7a and [RuCl₃(thbipy)(MeCN)] 7b

The molecular structures of [RuCl₃(thbipy)(dmf)] 7a and [RuCl₃(thbipy)(MeCN)] 7b have been determined by X-ray crystallography from single crystals obtained by slow evapor-



Scheme 2 Photochemistry of $[\text{Ru}(\text{CO})_5]_2$ with polydentate heterocyclic ligands

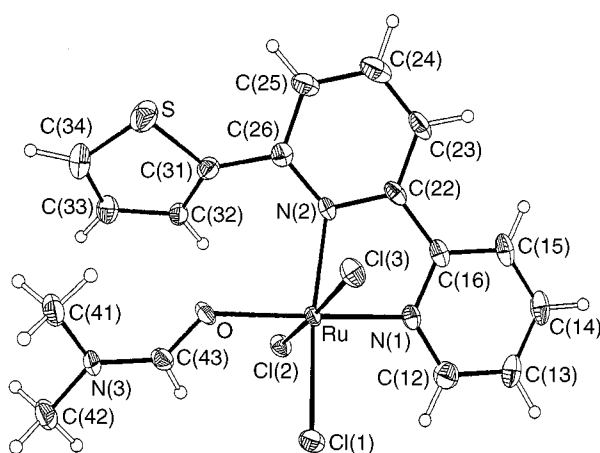


Fig. 2 Molecular structure of $[\text{RuCl}_3(\text{thbpy})(\text{dmf})] \textbf{7a}$

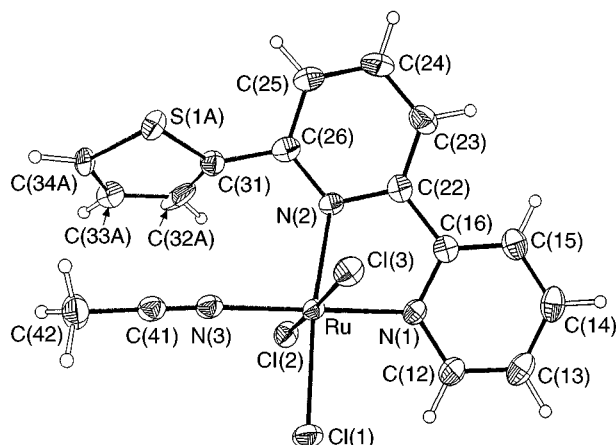


Fig. 3 Molecular structure of $[\text{RuCl}_3(\text{thbpy})(\text{MeCN})] \textbf{7b}$

ation of the donor solvent at room temperature. The molecular structures of **7a** and **7b** are shown in Figs. 2 and 3 respectively and selected geometrical parameters in Tables 2 and 3. In the

Table 2 Bond lengths (Å) and angles (°) for complex **7a**

Ru–N(1)	2.024(4)	Ru–O	2.123(4)
Ru–N(2)	2.125(4)	Ru–Cl(3)	2.3460(14)
Ru–Cl(2)	2.3524(14)	Ru–Cl(1)	2.3524(14)
N(1)–C(12)	1.340(7)	N(1)–C(16)	1.368(7)
C(12)–C(13)	1.390(9)	C(13)–C(14)	1.378(9)
C(14)–C(15)	1.365(9)	C(15)–C(16)	1.392(8)
C(16)–C(22)	1.465(8)	N(2)–C(26)	1.348(7)
N(2)–C(22)	1.370(7)	C(22)–C(23)	1.374(8)
C(23)–C(24)	1.369(9)	C(24)–C(25)	1.374(9)
C(25)–C(26)	1.387(8)	C(26)–C(31)	1.469(8)
C(31)–C(32)	1.376(8)	C(31)–S	1.730(6)
C(32)–C(33)	1.413(8)	C(33)–C(34)	1.332(9)
C(34)–S	1.712(6)	C(41)–N(3)	1.467(7)
C(42)–N(3)	1.469(8)	N(3)–C(43)	1.315(7)
C(43)–O	1.259(7)		
N(1)–Ru–O	178.3(2)	N(1)–Ru–N(2)	79.4(2)
O(1)–Ru–N(2)	99.9(2)	N(1)–Ru–Cl(3)	90.54(13)
O(1)–Ru–Cl(3)	87.81(10)	N(2)–Ru–Cl(3)	81.85(12)
N(1)–Ru–Cl(2)	88.03(13)	O–Ru–Cl(2)	93.57(10)
N(2)–Ru–Cl(2)	93.82(12)	Cl(3)–Ru–Cl(2)	175.63(5)
N(1)–Ru–Cl(1)	95.45(13)	O–Ru–Cl(1)	85.03(11)
N(2)–Ru–Cl(1)	171.69(12)	Cl–Ru–Cl(1)	91.73(5)
Cl(2)–Ru–Cl(1)	92.52(5)	C(12)–N(1)–C(16)	120.0(5)
C(12)–N(1)–Ru	124.6(4)	C(16)–N(1)–Ru	115.3(4)
N(1)–C(12)–C(13)	121.7(6)	C(14)–C(13)–C(12)	118.7(6)
C(15)–C(14)–C(13)	119.6(5)	C(14)–C(15)–C(16)	120.6(6)
N(1)–C(16)–C(15)	119.3(5)	N(2)–C(16)–C(22)	115.2(5)
C(15)–C(16)–C(22)	125.5(5)	C(26)–N(2)–C(22)	118.1(5)
C(16)–N(2)–Ru	128.5(4)	C(12)–N(2)–Ru	110.3(3)
N(2)–C(22)–C(23)	121.9(5)	N(2)–C(22)–C(16)	115.3(5)
C(23)–C(22)–C(16)	122.8(5)	C(24)–C(23)–C(22)	119.5(5)
C(23)–C(24)–C(25)	118.7(5)	C(24)–C(25)–C(26)	120.3(6)
N(2)–C(26)–C(31)	120.7(5)	N(2)–C(26)–C(31)	119.9(5)
C(25)–C(26)–C(31)	119.4(5)	C(31)–C(31)–C(26)	128.7(5)
C(32)–C(31)–S	110.4(4)	C(26)–C(31)–S	120.8(4)
C(31)–C(32)–C(33)	112.0(5)	C(34)–C(33)–C(32)	114.1(5)
C(33)–C(34)–S	111.6(5)	C(34)–S–C(31)	91.8(3)
C(43)–N(3)–C(41)	122.8(5)	C(43)–N(3)–C(42)	120.5(5)
C(41)–N(3)–C(42)	116.5(5)	O–C(43)–N(3)	123.6(5)
C(43)–O–Ru	119.6(3)		

case of **7b**, the thiophene ring is disordered about the C(26)–C(31) bond.

The molecular structures of complexes **7a** and **7b** are analogous to that of the previously characterised pyridine complex $[\text{RuCl}_3(\text{thbpy})(\text{py})] \textbf{7c}$.¹⁶ These complexes show a meridional arrangement of the chloride ligands around the ruthenium centre. The solvent (MeCN or dmf) is co-ordinated *trans* to the terminal pyridine group of the thbpy ligand, this being the site that would have been occupied by the sulfur in $[\text{RuCl}_3(\text{thbpy})] \textbf{6}$. The Ru–Cl distances observed in **7b** are similar to those in $[\text{RuCl}_3(\text{PhCN})_3]$.¹⁷ The Ru–N(2) bond, *trans* to chlorine in **7a** and **7b** at 2.125(4) and 2.102(2) Å, respectively, is significantly longer than those in $[\text{Ru}(\text{bipy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$.¹⁸ This can be attributed to steric interactions between the pendant thiophene ring and the co-ordinated dmf or acetonitrile moiety. The angle between mean planes of the central pyridine ring and the thiophene ring of the thbpy ligand is 37.0° for **7a** and 4.9° for **7b**, whilst for **7c** it is 23.8°. The wide difference in angle for the three examples is most likely due to the steric interactions between the pendant thiophene ring and the co-ordinated solvent moiety, these being greatest for the bulky dmf group and least for acetonitrile.

On bonding in a bidentate manner to Ru to form complexes **7a** and **7b**, the thbpy ligand changes from the *trans,cis* configuration adopted in free thbpy to the *cis,cis* geometry observed in the complexes. In addition, there is a need for significant distortion of the ligand in order for it to act bidentate. In order to discuss the changes in bond lengths and angles in thbpy when moving from free to co-ordinated, the convention of Churchill and co-workers⁸ can be adopted, a

Table 3 Bond lengths (Å) and angles (°) for complex **7b**

Ru–N(1)	2.034(2)	Ru–N(3)	2.052(2)
Ru–N(2)	2.102(2)	Ru–Cl(2)	2.3397(8)
Ru–Cl(3)	2.3420(8)	Ru–Cl(1)	2.3596(8)
N(3)–C(41)	1.145(4)	C(41)–C(42)	1.452(4)
N(1)–C(12)	1.344(3)	N(1)–C(16)	1.357(3)
C(12)–C(13)	1.380(4)	C(13)–C(14)	1.377(4)
C(14)–C(15)	1.384(4)	C(15)–C(16)	1.389(4)
C(16)–C(22)	1.474(4)	N(2)–C(26)	1.362(3)
N(2)–C(22)	1.372(3)	C(22)–C(23)	1.381(4)
C(23)–C(24)	1.375(4)	C(24)–C(25)	1.372(4)
C(25)–C(26)	1.392(4)	C(26)–C(31)	1.467(4)
C(31)–C(32A)	1.375(12)	C(31)–C(32B)	1.376(14)
C(31)–S(1A)	1.709(4)	C(31)–S(1B)	1.731(7)
S(1A)–C(34A)	1.765(11)	C(32A)–C(33A)	1.36(2)
C(33A)–C(34A)	1.354(8)	S(1B)–C(34B)	1.76(2)
C(32B)–C(33B)	1.36(2)	C(33B)–C(34B)	1.352(11)
N(1)–Ru–N(3)	175.65(8)	N(1)–Ru–N(2)	79.19(8)
N(3)–Ru–N(2)	101.38(9)	N(1)–Ru–Cl(2)	89.84(6)
N(3)–Ru–Cl(2)	94.43(6)	N(2)–Ru–Cl(2)	92.60(6)
N(1)–Ru–Cl(3)	88.52(6)	N(3)–Ru–Cl(3)	87.28(6)
N(2)–Ru–Cl(3)	82.93(6)	Cl(2)–Ru–Cl(3)	175.46(2)
N(1)–Ru–Cl(1)	94.85(7)	N(3)–Ru–Cl(1)	84.17(7)
N(2)–Ru–Cl(1)	172.06(6)	Cl(2)–Ru–Cl(1)	92.63(3)
Cl(3)–Ru–Cl(1)	91.73(3)	C(41)–N(3)–Ru	170.6(2)
N(3)–C(41)–C(42)	179.2(3)	C(12)–N(1)–C(16)	119.0(2)
C(12)–N(1)–Ru	125.1(2)	C(16)–N(1)–Ru	115.6(2)
N(1)–C(12)–C(13)	122.0(3)	C(14)–C(13)–C(12)	119.4(3)
C(13)–C(14)–C(15)	18.9(3)	C(14)–C(15)–C(16)	119.5(3)
N(1)–C(16)–C(15)	121.0(2)	N(1)–C(16)–C(22)	114.8(2)
C(15)–C(16)–C(22)	124.2(2)	C(26)–N(2)–C(22)	118.3(2)
C(26)–N(2)–Ru	127.9(2)	C(22)–N(2)–Ru	112.0(2)
N(2)–C(22)–C(23)	121.7(2)	N(2)–C(22)–C(16)	115.5(2)
C(23)–C(22)–C(16)	122.8(2)	C(24)–C(23)–C(22)	119.6(3)
C(25)–C(24)–C(23)	119.1(3)	C(24)–C(25)–C(26)	120.3(3)
N(2)–C(26)–C(31)	120.8(2)	N(2)–C(26)–C(31)	120.4(2)
C(25)–C(26)–C(31)	118.8(2)	C(32A)–C(31)–C(26)	130.7(6)
C(32B)–C(31)–C(26)	127.6(9)	C(32A)–C(31)–S(1A)	110.4(6)
C(26)–C(31)–S(1A)	118.7(2)	C(32B)–C(31)–S(1B)	108.4(8)
C(26)–C(31)–S(1B)	123.6(3)	C(31)–S(1A)–C(34A)	90.1(4)
C(33A)–C(32A)–C(31)	115.9(10)	C(34A)–C(33A)–C(32A)	111.6(10)
C(33A)–C(34A)–S(1A)	111.8(9)	C(31)–S(1B)–C(34B)	90.9(8)
C(33B)–C(32B)–C(31)	117.0(13)	C(34B)–C(33B)–C(32B)	112(2)
C(33B)–C(34B)–S(1B)	111(2)		

change in bond length or angle being equated to the difference between the values in the co-ordinated and free cases. When discussing the values obtained in these calculations it is important to consider the associated estimated standard deviations for each bond length and angle. From this premise, the results show that the significant distortions in bond length on co-ordination of the thbipy ligand in both **7a** and **7b** occur at the central pyridine ring and in the bond linking the two pyridine rings. Similarly, the significant distortions in bond angle in both **7a** and **7b** occur about the C–N–C bonds of the pyridine rings of the ligand and also at the 2 and 6 positions of the central and terminal pyridine rings, respectively. These observations are not unexpected since it is this bipyridyl section of the thbipy ligand that changes configuration to co-ordinate to the metal centre. This involves placing H(15) and H(23) in close proximity which is unfavourable on steric grounds. The lengthening of the bonds between the pyridine rings could then be considered as a result of both the distortion required to mollify this unfavourable steric interaction and the distortion required for co-ordination to the ruthenium centre.

General discussion of the photochemistry of [Ru(CO)₅] **2** with the heterocycles

There have been relatively few studies into the photochemistry of heterocycles with neutral metal carbonyl species and the formation of ruthenium(III) complexes from the zerovalent [Ru(CO)₅] **2** starting material is interesting from a number of

perspectives. From the results documented here it is assumed that the initial stage of the photoreaction between **2** and the heterocycles in each case is the labilisation of one of the M–CO bonds resulting in the formation of the 16-electron complex [Ru(CO)₄] which, in turn, reacts with the nitrogen-donor ligands to form a simple [Ru(CO)₄(N-donor)] complex. This is indeed known to be the case for pyridine and thus such an assumption can be made for the polydentate ligands. This supposition is strengthened by an understanding of the photochemistry of [Cr(CO)₆] with bipy where [Cr(CO)₅(bipy)] is formed upon irradiation.¹⁹ In that case, chelation then occurs to yield [Cr(CO)₄(bipy)].²⁰ From this starting point, the photochemistry of the ruthenium complexes can be discussed.

In N-heterocycle-containing transition-metal complexes there is often mixing between the π^* orbitals of the ligand and the d orbitals of the metal, this varying depending on the heterocyclic ligand and the variations in the d_π levels of the metal. This has a significant effect on the photochemical properties of these complexes since there will be a considerable difference in the charge-transfer (CT) character of the strongly allowed transition between the metal d and ligand π^* orbitals. In complexes where there is little or no mixing this transition has a strong metal-to-ligand charge-transfer (MLCT) character and is strongly solvatochromic, as illustrated in the case of [W(CO)₄(bipy)].²¹ In the case of complexes where there is significant mixing, the transition has little or no MLCT character as shown in the case of [Fe(CO)₃(HN=ICHCH=NH)].²² In addition, when considering the photochemistry of metal complexes

containing polydentate nitrogen heterocyclic ligands, it is important to bear in mind the inherent photoactivity of the ligands themselves.²³

The photochemistry of $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a** and its iron analogue $[\text{Fe}(\text{CO})_4(\text{py})]$ **3b**²⁴ is fairly unremarkable, showing similarities to that of other simple monosubstituted ruthenium complexes such as $[\text{Ru}(\text{CO})_4(\text{PPh}_3)]$ and $[\text{Ru}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_4)]$. Both **3a** and **3b** are photostable when irradiated in the absence of a substituting ligand. This means that the primary photo-product reacts back rapidly to the starting material.

For the photochemistry of complex **2** with bipy, thbipy and terpy, the derivation of a mechanistic pathway for the photo-reaction is not trivial and firm assertions cannot be made.

Conclusion

These studies have shown that the photochemistry of $[\text{Ru}(\text{CO})_5]$ **2** with nitrogen heterocycles in dichloromethane is varied and depends on the heterocycle used. Photolysis with pyridine leads to simple photosubstitution of py for a carbonyl group, this yielding the novel monosubstituted complex $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a**. This complex is unstable and, in the absence of light, reacts to form the trinuclear cluster $[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{C}_5\text{H}_4\text{N})]$ **4**.

The photochemistry of complex **2** with bipy, thbipy and terpy is very different, yielding complexes in which the ruthenium is in higher oxidation states. In the case of terpy and thbipy, photolysis with **2** leads to the formation of $[\text{RuCl}_3(\text{terpy})]$ **5** and $[\text{RuCl}_3(\text{thbipy})]$ **6** respectively. With **6**, addition of donor solvent, solv, leads to the formation of the solvent-coordinated complex $[\text{RuCl}_3(\text{thbipy})(\text{solv})]$, the potentially tridentate ligand acting in a bidentate manner with co-ordination through the two nitrogen moieties, the thiophene ring being pendant. In the case of bipy, photolysis with **2** leads to the formation of polymeric products which are uncharacterised at present.

The molecular and crystal structures of 6-(2-thienyl)-2,2'-bipyridine, $[\text{RuCl}_3(\text{thbipy})(\text{dmf})]$ **7a** and $[\text{RuCl}_3(\text{thbipy})(\text{MeCN})]$ **7b** have been determined by single-crystal X-ray diffraction studies and comparisons between co-ordinated and free thbipy made. In the free state the pyridine rings of thbipy are *trans* to one another and the thiophene and central pyridine rings *cis* to one another. Upon co-ordination, a *cis,cis* geometry is adopted and significant distortions are observed in the bipyridyl section of the thbipy ligand.

Experimental

General

Unless stated otherwise, all syntheses were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a nitrogen bubbler, reflux condenser and solid CO_2 cooling finger. A 125 W mercury-arc broad-band UV lamp was used as the irradiation source and reflectors placed around the reaction vessel to maximise efficiency. All reagents were from commercial sources and used as received unless noted otherwise. Literature methods were used to prepare the starting materials $[\text{Ru}_3(\text{CO})_{12}]$ **1**²⁵ and $[\text{Ru}(\text{CO})_5]$ **2**.²⁶

Physical measurements

Infrared spectra were recorded using a Perkin-Elmer PE 1710 Fourier-transform spectrometer, solution spectra in NaCl solution cells (path length 0.5 mm) and solid-state spectra in compressed KBr pellets. The ^1H NMR spectra were recorded using a Bruker AM400, WM250 or WP80SY Fourier-transform spectrometer and data reported using the chemical shift scale in units of ppm relative to the solvent resonance. Fast atom bombardment (FAB) mass spectra were recorded using a KRATOS

MS-50 spectrometer, with either 3-nitrobenzyl alcohol or thio-glycerol as a matrix and CsI as calibrant.

Syntheses

6-(2-Thienyl)-2,2'-bipyridine. This compound was prepared by the general method of Kröhnke^{7a} as described previously using *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide and dimethyl(3-oxo-3-thienylpropyl)ammonium chloride as starting materials.

2,2':6',2''-terpyridine. The ligand was prepared as described previously²⁷ by a modification of the Potts method²⁸ using 2-acetylpyridine and *N*-dimethoxymethyl-*N,N*-dimethylamine as starting materials.

Photolyses of dichloromethane solutions

$[\text{Ru}(\text{CO})_5]$ **2 with pyridine.** A dichloromethane solution of $[\text{Ru}(\text{CO})_5]$ **2** (30 mg in 150 cm^3) containing an excess of pyridine (1 cm^3) was irradiated using the broad-band UV source, the reaction mixture being maintained at low temperature by means of the solid CO_2 cooling finger. The reaction was deemed complete when there was no further change in the IR spectrum (1 h). On the basis of vibrational analysis and comparison with literature data for the iron complex¹³ it was proposed that the colourless monosubstituted mononuclear complex $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a** was formed. Yield: quantitative by IR. IR(CH_2Cl_2): $\nu(\text{CO})$ 2052s, 1982s and 1943vs cm^{-1} . Removal of solvent from a dichloromethane solution of **3a** yields a number of products which are, at present, uncharacterised.

Effect of prolonged removal of the irradiation source on $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a.** When the irradiation source was removed from a dichloromethane solution of $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a** over the period of 30 min the yellow-green cluster $[\text{Ru}_3\text{H}(\text{CO})_{10}(\text{C}_5\text{H}_4\text{N})]$ **4** was generated as characterised by comparison of IR and ^1H NMR spectral data with those in the literature.¹⁴ IR(CH_2Cl_2): $\nu(\text{CO})$ 2099m, 2061vs, 2050vs, 2024s, 2015vs, 2008m (sh), 1999s and 1984w. ^1H NMR (CDCl_3): δ 8.13 (dd, 1 H), 7.48 (m, 2 H), 6.83 (td, 1 H) and -14.37 (d, 1 H).

Prolonged photolysis of $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a.** Irradiation of a dichloromethane solution of $[\text{Ru}(\text{CO})_4(\text{py})]$ **3a** for 2 h using the broad-band UV source resulted in no change in the IR spectrum of the reaction mixture thereby confirming that **3a** is photostable when irradiated in the absence of a substituting ligand.

$[\text{Ru}(\text{CO})_5]$ **2 with bipyridine.** A dichloromethane solution of $[\text{Ru}(\text{CO})_5]$ **2** (30 mg in 150 cm^3) containing an excess of bipyridine (30 mg) was irradiated using the broad-band UV source, the reaction mixture being maintained at low temperature by means of the solid CO_2 cooling finger. A change from colourless to orange and then to deep purple was observed and then, over about 30 min, a brown precipitate formed, insoluble in common organic solvents. The reaction products are, as yet, uncharacterised. A mass spectrum of the product mixture showed a number of peaks all above m/z 800 indicative of polynuclear products.

$[\text{Ru}(\text{CO})_5]$ **2 with 2,2':6',2''-terpyridine.** A dichloromethane solution of $[\text{Ru}(\text{CO})_5]$ **2** (30 mg in 150 cm^3) containing an excess of terpy (50 mg) was irradiated using the broad-band UV source, the reaction mixture being maintained at low temperature by means of the solid CO_2 cooling finger. A change from colourless to yellow and then to deep purple was observed and then, over about 30 min, a brown precipitate formed, characterised as $[\text{RuCl}_3(\text{terpy})]$ **5** by comparison of spectroscopic data with those in the literature.¹⁵ Yield: 75%. ^1H NMR (CD_3CN): δ 8.5 (m), 8.2 (m), 7.76 (m), 7.64 (m), 7.43 (m) and 7.35 (m).

Table 4 Crystal data and structure refinement parameters for thbipy, [RuCl₃(thbipy)(dmf)] **7a** and [RuCl₃(thbipy)(MeCN)] **7b**

	thbipy	7a	7b
Molecular formula	C ₁₄ H ₁₀ N ₂ S	C ₁₇ H ₁₇ Cl ₃ N ₃ ORuS	C ₁₆ H ₁₃ Cl ₃ N ₃ RuS
<i>M</i>	238.30	518.82	486.77
Crystal habit	Pale yellow needles	Black blocks	Brown blocks
Crystal size/mm	0.35 × 0.31 × 0.22	0.26 × 0.25 × 0.22	0.37 × 0.34 × 0.33
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	10.478(2)	8.853(2)	25.459(5)
<i>b</i> /Å	16.550(3)	14.578(3)	9.041(2)
<i>c</i> /Å	6.8570(10)	15.095(3)	15.795(3)
β/°	—	90.08(3)	102.01(3)
<i>U</i> /Å ³	1189.1(4)	1948.1(7)	3699.6(13)
<i>Z</i>	4	4	8
<i>D_c</i> /Mg m ³	1.331	1.769	1.748
<i>F</i> (000)	496	1036	1928
μ/mm ^{−1}	0.248	1.335	1.396
Maximum, minimum transmission	—	0.279, 0.269	0.313, 0.282
2θ Data collection range/°	7.52–44.98	7.08–50	7.28–50
Index ranges	−11 ≤ <i>h</i> ≤ 11, −17 ≤ <i>k</i> ≤ 17, −7 ≤ <i>l</i> ≤ 7	−9 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 16	−27 ≤ <i>h</i> ≤ 0, −10 ≤ <i>k</i> ≤ 0, −16 ≤ <i>l</i> ≤ 17
Reflections measured	1712	2965	2474
Independent reflections (<i>R_{int}</i>)	1559 (0.0269)	2552 (0.0188)	2411 (0.006)
Parameters, restraints	154, 1	237, 0	250, 22
<i>wR</i> 2 (all data)	0.1332	0.1544	0.0812
<i>x</i> , <i>y</i>	0.0794, 0.7174	0.120, 0.4375	0.0223, 6.1748
<i>R</i> 1[<i>I</i> > 2σ(<i>I</i>)]	0.0383	0.0326	0.0193
Observed reflections	1441	2328	2201
Goodness of fit on <i>F</i> ² (all data)	1.172	1.176	1.142
Maximum shift/σ	0.017	0.002	−0.001
Peak, hole in final difference map/e Å ^{−3}	0.225, −0.239	0.776, −1.525	0.902, −0.329
Absolute structure parameter	−0.02 (16)	—	—

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where *x* and *y* are constants adjusted by the program. Goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

[Ru(CO)₅] 2 with 6-(2-thienyl)-2,2'-bipyridine. A dichloromethane solution of [Ru(CO)₅] **2** (30 mg in 150 cm³) containing on excess of thbipy (50 mg) was irradiated using the broadband UV source, the reaction mixture being maintained at low temperature by means of the solid CO₂ cooling finger. A change from colourless to yellow and then to deep purple was observed and then, over about 30 min, a brown precipitate formed, characterised as [RuCl₃(thbipy)] **6** by comparison of spectroscopic data with those in the literature.¹⁶ Yield: 66%. IR (KBr): 1595s, 1551m, 1459s, 1442m, 1292m, 812m, 782s, 720m, 712m, 341m and 310s cm^{−1}. FAB mass spectrum: *m/z* 409 {[RuCl₂(thbipy)]⁺}, 374 {[RuCl(thbipy)]⁺} and 339 {[Ru(thbipy)]⁺}.

Solvation of [RuCl₃(thbipy)] **6**

In dimethylformamide. A sample of [RuCl₃(thbipy)] **6** was dissolved in dmf and the brown solvate characterised spectroscopically as [RuCl₃(thbipy)(dmf)] **7a** by comparison with literature data.¹⁶ IR (KBr): 1629s, 1605m, 1557m, 1452s, 1427m, 1377m, 770s, 734m and 324m cm^{−1}. FAB mass spectrum: *m/z* 410 {[RuCl₂(thbipy)]⁺}, 374 {[RuCl(thbipy)]⁺} and 340 {[Ru(thbipy)]⁺}.

In acetonitrile. A sample of [RuCl₃(thbipy)] **6** was dissolved in acetonitrile and the brown solvate characterised spectroscopically as [RuCl₃(thbipy)(MeCN)] **7b**. IR (KBr): 1609s, 1580m, 1522m, 1445s, 1330m, 774s, 715m, 320m and 319w cm^{−1}. ¹H NMR (CD₃CN): δ 8.5 (m), 8.2 (m), 7.76 (m), 7.64 (m), 7.43 (m), 7.35 (m) and 2.6 (s). FAB mass spectrum: *m/z* 450 {[RuCl₂(thbipy)(MeCN)]⁺}, 410 {[RuCl₂(thbipy)]⁺}, 373 {[RuCl(thbipy)]⁺} and 341 {[Ru(thbipy)]⁺}.

X-Ray crystallography

Structural determinations were undertaken on single crystals of

thbipy, [RuCl₃(thbipy)(dmf)] **7a** and [RuCl₃(thbipy)(MeCN)] **7b** using X-ray diffraction. All measurements were made at −120 °C with Mo-Kα radiation (λ = 0.710 73 Å) in the ω-θ scan mode on a Stoe-Siemens AED diffractometer equipped with a graphite monochromator. Crystal data and data acquisition details are summarised in Table 4. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections (20 < 2θ < 22.5°). Semiempirical absorption corrections based on ψ-scan data were applied for **7a** and **7b**.^{29,30}

The structures was solved by direct methods (SHELXTL PLUS)³¹ followed by Fourier-difference synthesis and refined by full-matrix least squares on *F*² (SHELXL 93).³² All non-hydrogen atoms were treated anisotropically and the hydrogen atoms placed in idealised positions and allowed to ride on the relevant carbon atoms. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. The absolute structure parameter for thbipy was determined by the method of Flack.³³

The thiophene ring in [RuCl₃(thbipy)(MeCN)] **7b** is disordered over two orientations about the C(26)–C(31) bond with relative occupancies 0.69 and 0.31 and was refined with appropriate restraints on the coordinates and thermal parameters. Those atoms of the major contribution are annotated with the suffix A and those from the minor contribution with the suffix B.

CCDC reference number 186/610.

Acknowledgements

Financial support granted by the EPSRC, Girton College Cambridge and Ciba Geigy is gratefully acknowledged. Ruthenium chloride was generously loaned by Johnson

Matthey plc. The authors thank G. P. Shields for valuable crystallographic assistance.

References

- 1 A. J. Edwards, N. E. Leadbeater, J. Lewis and P.R. Raithby, *J. Organomet. Chem.*, 1995, **512**, 13; N. E. Leadbeater, *J. Chem. Soc., Dalton Trans.*, 1995, 2923; N. E. Leadbeater, J. Lewis and P. R. Raithby, *J. Organomet. Chem.*, in the press.
- 2 G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979.
- 3 M. S. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998; J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952; A. Vogler and H. Kunkely, *Inorg. Chim. Acta.*, 1980, **35**, L265; *Inorg. Chem.*, 1987, **26**, 1819.
- 4 K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992.
- 5 D. J. Stufkens, *Coord. Chem. Rev.*, 1990, **104**, 39.
- 6 E. C. Constable, R. P. G. Henney, P. R. Raithby and L. R. Sousa, *J. Chem. Soc., Dalton Trans.*, 1992, 2251; P. A. Anderson, F. R. Keene, E. Horn and E. R. T. Tiekink, *Appl. Organomet. Chem.*, 1990, **4**, 523; T. J. Giordano and P. G. Rasmussen, *Inorg. Chem.*, 1975, **14**, 1628; E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, H. J. Pain, V. Sik, M. B. Hursthouse and M. A. Mazid, *J. Chem. Soc., Dalton Trans.*, 1993, 597; G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas and A. H. White, *Aust. J. Chem.*, 1984, **37**, 929; F. Neve, M. Ghedini and A. Crispini, *J. Organomet. Chem.*, 1994, **466**, 259.
- 7 (a) F. Kröhnke, *Synthesis*, 1976, 1; (b) E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443.
- 8 C. A. Bessel, R. F. See, D. L. Jameson, M. R. Churchill and K. J. Takeuchi, *J. Chem. Soc., Dalton Trans.*, 1992, 3223.
- 9 R. Ghosh and S. H. Simonsen, *Acta Crystallogr., Sect. C*, 1993, **49**, 1031.
- 10 A. J. Tennon, N. Ebby, E. Degny, R. Viani and H. Bodot, *Acta Crystallogr., Sect. C*, 1988, **44**, 95.
- 11 H. Nakai, *Acta Crystallogr., Sect. C*, 1990, **46**, 1951.
- 12 M. Shiro, *Acta Crystallogr., Sect. C*, 1990, **46**, 1152.
- 13 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 3438.
- 14 G. A. Foulds, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1985, **296**, 147.
- 15 E. C. Constable, A. M. W. Cargill-Thompson, M. A. M. Daniels and D. A. Tocher, *New J. Chem.*, 1992, **16**, 855.
- 16 E. C. Constable, R. P. G. Henney and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 2335.
- 17 C. M. Duff, G. A. Heath and A. C. Willis, *Acta Crystallogr., Sect. C*, 1990, **46**, 2320.
- 18 D. S. Egglestone, K. A. Goldsby, D. J. Hodgson and T. J. Meyer, *Inorg. Chem.*, 1985, **24**, 4573.
- 19 S. Oishi, *Organometallics*, 1988, **7**, 1237.
- 20 K. Kalyanasundaram, *J. Phys. Chem.*, 1988, **92**, 2219.
- 21 R. W. Balk, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta*, 1979, **34**, 267; R. W. Balk, Th. L. Snoeck, D. J. Stufkens and A. Oskam, *Inorg. Chem.*, 1980, **19**, 3015.
- 22 H. K. van Dijk, D. J. Stufkens and A. Oskam, *J. Am. Chem. Soc.*, 1989, **111**, 541; M. W. Kokkes, D. J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1984, 1005; *J. Mol. Struct.*, 1984, **114**, 61; *J. Chem. Soc., Dalton Trans.*, 1983, 439.
- 23 Y. Kondo and A. H. Maki, *J. Phys. Chem.*, 1968, **72**, 3215; B. A. Bandyopadhyay and A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, 1977, 663; R. D. Saini, S. Dhanya and P. K. Bhattacharya, *J. Photochem. Photobiol. A*, 1988, **43**, 91.
- 24 G. Boxhoorn, M. B. Cerfontain, D. J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1980, 1336.
- 25 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.
- 26 R. Huq, A. J. Poë and S. Chawla, *Inorg. Chim. Acta*, 1980, **38**, 121.
- 27 D. L. Jameson and L. E. Guise, *Tetrahedron Lett.*, 1991, **32**, 1999.
- 28 K. T. Potts, M. J. Cipullo, P. Ralli, G. Thodoridis and P. Winslow, *Org. Synth.*, 1985, **64**, 189.
- 29 TEXSAN, Version 1.7-1, Molecular Structure Corporation, The Woodlands, TX, 1985, 1992, 1995.
- 30 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- 31 G. M. Sheldrick, SHELXL PLUS, program for solving, refining and displaying crystal structures from diffraction data, University of Göttingen, 1990.
- 32 G. M. Sheldrick, SHELXL 93, program for crystal structure refinement, University of Göttingen, 1993.
- 33 H. D. Flack, *Acta Crystallogr., Sect. C*, 1983, **39**, 876.

Received 10th March 1997; Paper 7/01651D