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Oxidative addition reactions of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 2-imine-substituted derivatives of furan, thiophene, selenophene and pyrrole

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Abstract

The reactions of 2-methylaldimine-furan, -thiophene, -selenophene, -pyrrole ($\text{C}_4\text{H}_3\text{X}\cdot\text{CH}=\text{NMe}-2$) with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ have been studied to examine the possibility that initial imine coordination at one metal centre might induce reactivity of the heterocyclic ring at another metal centre. There are some products in which this has not occurred, that is where oxidative addition has involved solely the imine group to give $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{XC}=\text{NMe})(\text{CO})_{10}]$ ($\text{X} = \text{O}, \text{S}, \text{Se}$). Other products are derived by C–H bond cleavage at the 3-position of the heterocyclic ring, namely $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_2\text{XCH}=\text{NMe})(\text{CO})_{10}]$ ($\text{X} = \text{O}$) and $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_2\text{XCH}=\text{NMe})(\text{CO})_9]$ ($\text{X} = \text{O}, \text{NH}$); the crystal structure is reported for the compound with $\text{X} = \text{NH}$. Only for the pyrrole derivative did metallation also occur at the 1-position to give an isomeric product involving coordination of the nitrogen atom of the heterocyclic ring. Some related chemistry for other imine compounds is also described, including the crystal structure of $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_3\text{N}\text{-C}_4\text{H}_6\text{N})(\text{CO})_9]$, derived from 2-pyrrolylpyrrole, in which both the imine and the pyrrolyl nitrogen atom are coordinated.

Introduction

Aldimines ($\text{RCH}=\text{NR}'$) react with triosmium clusters with C–H bond cleavage to give the μ -iminyl systems $[\text{Os}_3(\mu\text{-H})(\mu\text{-RC}=\text{NR}')] [1,2]$ in a reaction related to the formation of 2-pyridyl complexes from pyridine [3]. Such iminyl compounds are also formed by C–H and C–N cleavages in tertiary and secondary amines or by insertion of isonitriles RNC into metal–hydrogen bonds of $[\text{Os}_3\text{H}_2(\text{CO})_{10}] [4]$. For

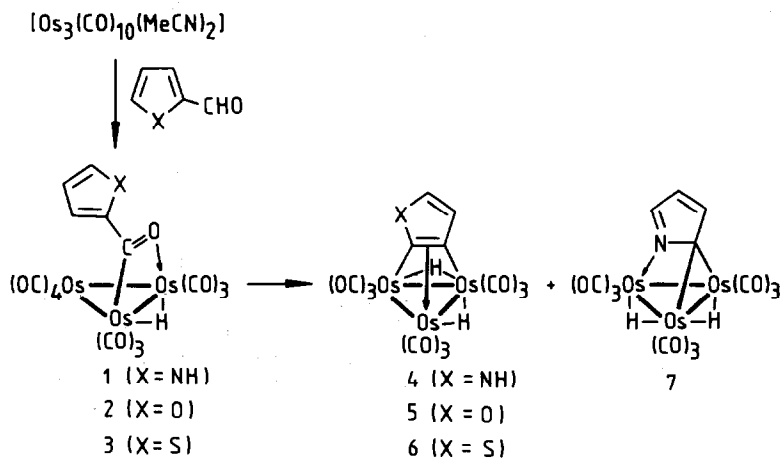
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X = NH, O, S, Se

Fig. 1. Heterocyclic ligands used in this work to react with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$.

example, we have shown that traces of $[\text{Os}_3(\mu\text{-H})(\mu\text{-PhC=NMe})(\text{CO})_{10}]$ are formed in the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with dimethylbenzylamine at high temperatures [2], and recently it has been shown that the iminyl complex $[\text{Os}_3(\mu\text{-H})(\mu\text{-C=NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{CO})_{10}]$ is one of the products formed from $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ and piperidine [5]. Work has also been carried out on the reactions of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with the 5-membered heterocycles $\text{C}_5\text{H}_4\text{X}$ (X = NH, O, S, Se, Te): pyrrole [6], furan [7,8], thiophene, selenophene, and tellurophene [8,9]; such reactions lead to cleavage of a C-H bond at a site adjacent to the heteroatom for X = NH, O and S, or to cleavage of a C-X bond for X = Se or Te. In the light of these observations we thought it of interest of combine these functionalities by using 2-iminyl-substituted pyrrole, -furan, -thiophene and -selenophene (Fig. 1). We hoped that the initial coordination of the imine nitrogen atom, expected to be the most favourable donor site, at one metal centre would facilitate subsequent reaction of the heterocyclic ring at another metal centre or centres. This might be related in some way to some chemistry we have developed for 2-formyl substituted heterocycles, shown in Scheme 1; initial oxidative addition of the formyl group to give the acyl complexes **1** to **3** allowed the subsequent thermal decarbonylation to give the μ_3 -heterocyclic systems **4** to **7**. We expected the oxidative addition step for the imine to correspond to that for the formyl, but without the possibility of subsequent decarbonylation.



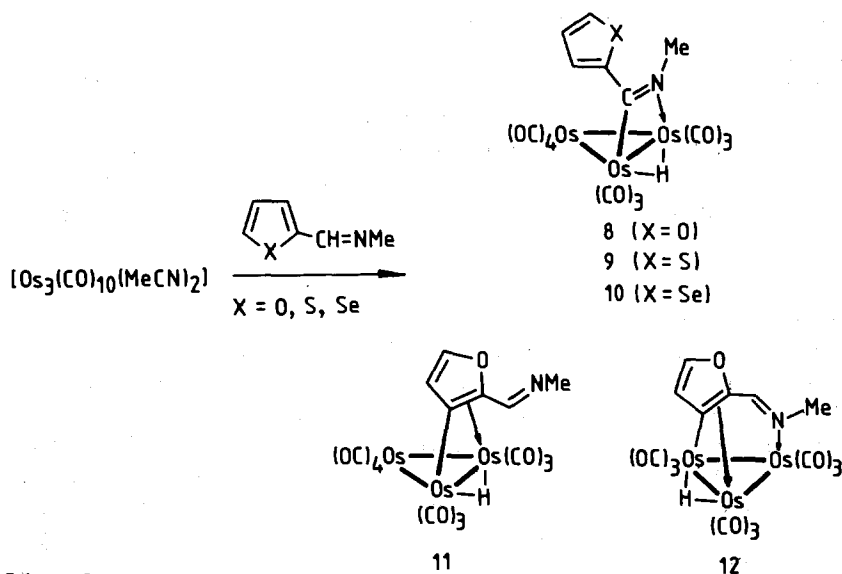
Scheme 1.

Results and discussion

Reactions of the group 16 heterocycles

The furyl-, thienyl-, and selenophenyl-aldimines ($C_4H_3XCH=NMe$, $X = O, S, Se$) all react with $[Os_3(CO)_{10}(MeCN)_2]$ at room temperature in dichloromethane to give iminyl oxidative addition products in which the aldimine C–H bond has been cleaved. The heterocyclic ligand plays a spectator role, and the products, $[Os_3(\mu-H)(\mu-C_4H_3XC=NMe)(CO)_{10}]$ **8** ($X = O$) (23%), **9** ($X = S$) (45%), **10** ($X = Se$) (50%), are closely related to a similar derivative of $PhCH=NMe$ [1]. The IR and 1H NMR spectra show the expected correspondence with those of $[Os_3(\mu-H)(\mu-PhC=NMe)(CO)_{10}]$ of known structure [1], confirming that the structures of **8** to **10** are correctly represented in Scheme 2.

In the case of the furyl aldimine only, two other products were obtained in which the heterocyclic ring has been activated, namely $[Os_3(\mu-H)(\mu-C_4H_2XCH=NMe)(CO)_{10}]$ (**11**, 17%), and its decarbonylated derivative, $[Os_3(\mu-H)(\mu_3-C_4H_2XCH=NMe)(CO)_9]$ (**12**, 35%). The 1H NMR spectra show that C–H bond cleavage has occurred at the 3-position in both of these compounds. At present we can only suggest reasonable structures for these compounds based on their spectra and analogies with known compounds. Compound **11** is closely related spectroscopically to the 2-furyl compound $[Os_3(\mu-H)(\mu,\eta^2-C_4H_3O)(CO)_{10}]$ [7], and these two compounds probably have very similar structures except that metallation has occurred at the 3-position in the case of cluster **11**. We therefore believe that **11** has a free aldimine group (its NMR spectrum is similar to that in the free ligand), and contains a μ,η^2 -furyl type system as shown, rather than being a η^1 -furyl with a coordinated aldimine ligand.



Scheme 2.

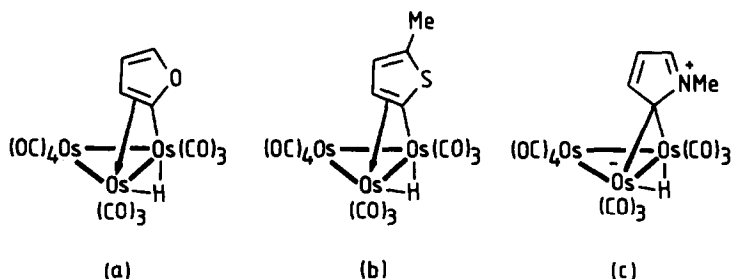


Fig. 2. Structures adopted by the compounds $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_2\text{RX})(\text{CO})_{10}]$; η^2 -coordination adopted for (a) $\text{R} = \text{H}$, $\text{X} = \text{O}$ and for (b) $\text{R} = \text{Me}$, $\text{X} = \text{S}$ but η^1 -coordination adopted for (c) $\text{R} = \text{H}$, $\text{X} = \text{NMe}$.

The structure of **12** is also based on spectroscopic evidence and analogy. The compound clearly has a μ_3 -organic ligand bridging three $\text{Os}(\text{CO})_3$ units and the imine is coordinated, and we propose the bonding mode shown in Scheme 2. This is based largely on the structure that we have established for the corresponding pyrrole compound **13** (see later). Previously we compared the structures of the related pyrrolyl [8], furyl [7], and thienyl [8] complexes, which are shown in Fig. 2. The NMe compound has a vertical μ, η^1 -pyrrolyl bridge whereas the furyl and thienyl ligands are μ, η^2 -bonded. The greater π -donor ability of a NMe group than of O or S groups is related to this difference in structure. Hence we propose a η^2 -mode for the heterocyclic bridge in **12**, in contrast to the η^1 -mode found in compound **13**. We cannot readily account for the differences between the furan and the thiophene and selenophene systems containing 2-iminyl groups. The stereochemistry of the imine $\text{C}=\text{N}$ bond is *cis* in compounds **8** to **10** but *trans* in **12**. It is most likely that the ligand is coordinated to the cluster initially through the imine nitrogen atom in all cases, and it is possible that relative proportions of metallation at the aldimine CH group or the heterocyclic ring depend upon the *cis-trans* isomer distribution in the coordinated state prior to C–H bond cleavage. However, this is unlikely to account for the total absence of ring metallation when $\text{X} = \text{S}$ or Se, so we believe that the furan ring may be intrinsically much more easily metallated than the other rings. It is noteworthy that direct reaction of selenophene with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ leads to cleavage of the Se–C rather than the C–H bond [9]. Metallation at the site δ to a donor atom of a ligand normally occurs, with formation of a 5-membered chelate ring, at a single metal atom, and it is unusual for δ metallation to occur to form a 6-membered ring involving two metal atoms.

Reactions of pyrrolylimines

We studied the reactions of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with the two pyrrole derivatives shown in Fig. 1, and found that both give a mixture of green and orange-red isomers. Room temperature reaction of the aldimine $\text{C}_5\text{H}_3\text{NHCH}=\text{NMe}$ in dichloromethane gives the green product $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-NHCHCHCCCH}=\text{NMe})(\text{CO})_9]$ (**13**, 60%), whereas reaction in refluxing cyclohexane gives none of this and only the orange-red isomer $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-NCHCHCHCCH}=\text{NMe})(\text{CO})_9]$ (**14**, 50%). We were surprised that orange-red **14** was not formed upon heating of the green isomer **13** in cyclohexane or at even higher temperatures. No decar-

Table 1. IR and ^1H NMR data for the new compounds.

Compound	$\nu(\text{CO})^a$ (cm^{-1})	$\delta(^1\text{H})^b$	
[Os ₃ H ^w ($\overline{\text{OCH}^x\text{CH}^y\text{CH}^z\text{C}}-\text{C}=\text{NMe}(\text{CO})_{10}$)] (8)	2109m, 2062vs,	7.76 (dd,x)	J_{xy} 1.8
	2051s, 2022vs,	6.73 (dd,z)	J_{xz} 0.5
	2005vs, 1992s,	6.63 (m,y)	J_{yz} 3.6
	1976m.	3.64 (s,Me) -14.96 (s,w)	
[Os ₃ H ^w ($\overline{\text{SCH}^x\text{CH}^y\text{CH}^z\text{C}}-\text{C}=\text{NMe}(\text{CO})_{10}$)] (9)	2105m, 2062vs,	7.55 (d,x)	J_{xy} 4.8
	2051s, 2023vs,	7.18 (m,y,z) ^c	J_{xz} 1.3
	2006vs, 1991s,	3.51 (s,Me)	J_{yz} 3.7
	1978m.	-14.94 (s,w)	
[Os ₃ H ^w ($\overline{\text{SeCH}^x\text{CH}^y\text{CH}^z\text{C}}-\text{C}=\text{NMe}(\text{CO})_{10}$)] (10)	2104m, 2063vs,	8.27 (dd,x)	J_{xy} 5.5
	2051s, 2023vs,	7.32 (dd,y)	J_{xz} 1.1
	2005vs, 1991s,	7.11 (dd,z)	J_{yz} 3.9
	1977m.	3.59 (s,Me) -14.96 (s,w)	
[Os ₃ H ^w ($\overline{\text{OCH}^x\text{CH}^y\text{CC}}-\text{CH}^z=\text{NMe}(\text{CO})_{10}$)] (11)	2103m, 2061vs,	8.44 (m,z)	J_{xy} 1.6
	2051s, 2020vs,	7.76 (d,x)	J_{yz} 0.7
	2008vs, 1991s,	6.91 (m,y)	$J_{z\text{Me}}$ 1.1
	1973m.	4.15 (d,Me) -15.01 (s,w)	
[Os ₃ H ^w ($\overline{\text{OCH}^x\text{CH}^y\text{CC}}-\text{CH}^z=\text{NMe}(\text{CO})_9$)] (12)	2090m, 2059s,	9.42 (m,br,z)	$J_{xy} = 1.9$
	2043vs, 2011s,	7.45 (d,x)	$J_{z\text{Me}} = 1.4$
	1990s, 1973w,	7.18 (d,y)	$J_{wz} = 0.6$
	1966w.	3.72 (d,Me) -15.43 (d,w)	
[Os ₃ H ^w ($\overline{\text{NHCH}^x\text{CH}^y\text{CC}}-\text{CH}^z=\text{NMe}(\text{CO})_9$)] (13)	2073m, 2042vs,	9.65 (s,br,NH)	J_{xy} 2.2
	2015s, 1982s,	8.16 (m,br,z)	$J_{x\text{Me}}$ 1.1
	1950m ^d .	7.43 (d,x)	
		7.09 (d,y)	
		3.95 (d,Me) -11.92 (s,w)	
[Os ₃ H ^v ($\overline{\text{NCH}^x\text{CH}^y\text{CH}^z\text{C}}-\text{CH}^w=\text{NMe}(\text{CO})_9$)] (14)	2082m, 2052vs,	7.67 (m,x)	J_{xy} 1.9
	2026s, 1995vs,	7.34 (m,w)	J_{xz} 1.0
	1982s, 1964m,	6.82 (dd,z)	J_{yz} 3.9
	1951m.	6.24 (dd,y)	$J_{x\text{Me}}$ 1.0
		3.85 (d,Me) -14.43 (s,v)	
[Os ₃ H ^v ($\overline{\text{NHCH}^w\text{CH}^u\text{CC}}-\text{CCH}_2^x\text{CH}_2^y\text{CH}_2^z\text{N}(\text{CO})_9$)] (15)	2071m, 2040vs,	9.34 (br,NH)	J_{uv} 2.6
	2014s, 1980s,	7.36 (dd,w)	$J_{v\text{NH}}$ 0.3
	1949m ^d .	7.07 (dd,v)	$J_{w\text{NH}}$ 0.5
		3.91 (tt,x)	J_{xy} 7.5
		2.88 (tt,z)	J_{yz} 8.3
		2.15 (m,y)	J_{yz} 1.7
	-11.92 (s,u)		
[Os ₃ H ^v ($\overline{\text{NCH}^u\text{CH}^v\text{CH}^w\text{C}}-\text{CCH}_2^x\text{CH}_2^y\text{CH}_2^z\text{N}(\text{CO})_9$)] (16)	2082m, 2052vs,	7.33 (dd,u)	J_{uv} 1.0
	2026s, 1995vs,	7.08 (dd,v)	J_{uw} 3.5
	1982m, 1964m,	6.19 (dd,w)	J_{vw} 2.6
	1950m.	4.36 (tt,x)	J_{xy} 7.4
		3.17 (tt,z)	J_{yz} 8.6
		1.92 (m,y)	J_{xz} 1.7
		-11.71 (s,t)	

^a Recorded in cyclohexane. ^b Recorded at 300 MHz, J in Hz. Solvents: CD_2Cl_2 for compounds 8, 9, 10, 13, 14, 15 and 16; CD_3COCD_3 for compounds 11 and 12. ^c AB portion of an ABX pattern.

^d Recorded in CH_2Cl_2 .

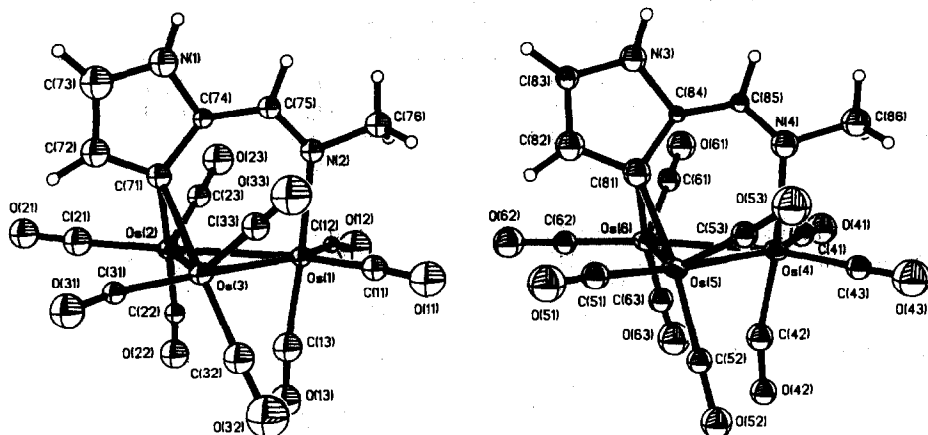


Fig. 3. Molecular structures for the two independent molecules in the crystals for $[\text{Os}_3(\mu\text{-H})\mu\text{-C}_4\text{H}_2\text{NHCH}=\text{NMe}(\text{CO})_9]$ (13).

Table 2

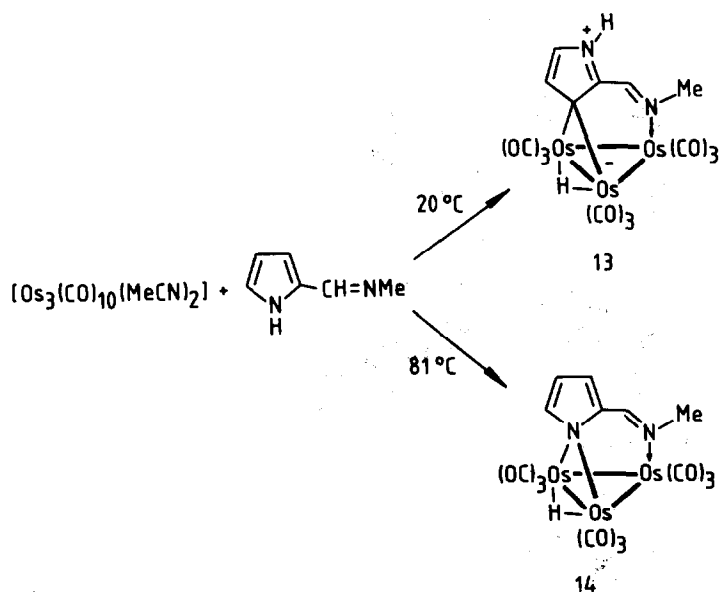
Selected bond lengths (Å) and angles (°) for $[\text{Os}_3(\mu\text{-H})\mu\text{-NHCHCHCCCH}=\text{NMe}(\text{CO})_9]$ (13)

Molecule 1		Molecule 2	
Os(1)–Os(2)	2.809(3)	Os(4)–Os(5)	2.805(3)
Os(2)–Os(3)	2.769(3)	Os(5)–Os(6)	2.766(3)
Os(1)–Os(3)	2.815(3)	Os(4)–Os(6)	2.810(3)
Os(1)–N(2)	2.16(4)	Os(4)–N(4)	2.19(4)
Os(2)–C(71)	2.24(4)	Os(5)–C(81)	2.21(5)
Os(3)–C(71)	2.28(4)	Os(6)–C(81)	2.25(5)
N(1)–C(73)	1.36(8)	N(3)–C(83)	1.33(6)
N(1)–C(74)	1.35(6)	N(3)–C(84)	1.42(5)
C(71)–C(72)	1.34(7)	C(81)–C(82)	1.42(8)
C(72)–C(73)	1.36(8)	C(82)–C(83)	1.34(7)
C(74)–C(75)	1.35(6)	C(84)–C(85)	1.31(6)
C(75)–N(2)	1.33(6)	C(85)–N(4)	1.27(6)
C(76)–N(2)	1.45(6)	C(86)–N(4)	1.55(7)
Os(1)–Os(2)–Os(3)	60.6(1)	Os(4)–Os(5)–Os(6)	60.6(1)
Os(1)–Os(3)–Os(2)	60.4(1)	Os(4)–Os(6)–Os(5)	60.4(1)
Os(2)–Os(1)–Os(3)	59.0(1)	Os(5)–Os(4)–Os(6)	59.0(1)
Os(2)–C(71)–Os(3)	76(1)	Os(5)–C(81)–Os(6)	77(1)
Os(1)–Os(2)–C(71)	84(1)	Os(4)–Os(5)–C(81)	84(1)
Os(1)–Os(3)–C(71)	84(1)	Os(4)–Os(6)–C(81)	83(1)
Os(2)–Os(3)–C(71)	52(1)	Os(5)–Os(6)–C(81)	51(1)
Os(3)–Os(2)–C(71)	53(1)	Os(6)–Os(5)–C(81)	52(1)
Os(2)–Os(1)–N(2)	94(1)	Os(5)–Os(4)–N(4)	92(1)
Os(3)–Os(1)–N(2)	96(1)	Os(6)–Os(4)–N(4)	93(1)
Os(3)–C(71)–C(74)	117(3)	Os(6)–C(81)–C(84)	117(3)
Os(2)–C(71)–C(74)	118(3)	Os(5)–C(81)–C(84)	122(3)
C(71)–C(74)–C(75)	137(4)	C(81)–C(84)–C(85)	135(4)
C(74)–C(75)–N(2)	127(4)	C(84)–C(85)–N(4)	128(4)
C(75)–N(2)–C(76)	115(4)	C(85)–N(4)–C(86)	121(4)
C(75)–N(2)–Os(1)	127(3)	C(85)–N(4)–Os(4)	130(3)
C(76)–N(2)–Os(1)	117(3)	C(86)–N(4)–Os(4)	109(3)

bonyls were formed in these reactions; no iminyl species related to compounds **8** to **10** is formed. This indicates that oxidative additions with C–H cleavage in the heterocyclics C_4H_4X are probably favoured in the order: $X = NH \gg O > S, Se$. Probably different transient decacarbonyl compounds are formed depending upon the solvent and temperature, and these lead independently to **13** or **14**, so that compound **13** is not a precursor of compound **14**.

Compounds **13** and **14** were initially characterised spectroscopically. Each gives three 1H NMR signals for the heterocyclic rings (Table 1) and, since one of these signals is quite broad for compound **13**, we assign it to an NH group. All three signals are sharp for compound **14** and assignable to CH groups, so that metallation must have occurred at the pyrrole NH group in this case. Only in the case of the green isomer **13** were we able to obtain crystals suitable for an X-ray structural study.

Compounds **15** and **16** are a corresponding pair of green and orange-red isomers, similarly derived from the related bicyclic ligand in which the imine is part of a 5-membered heterocycle (Fig. 1). In this case crystals of the orange-red isomer were suitable for crystal structure determination, so we were able to obtain a structure of each isomeric type. Crystals of compound **13** contain two independent but very similar molecules in the unit cell, which are shown in Fig. 3; selected bond lengths and angles are in Table 2. The following discussion refers to molecule 1. The imine is shown to be coordinated and the heterocyclic ring is metallated adjacent to the imine substituent. The ring is shown bonded through atom C(71) in molecule 1 to the two metal atoms, Os(2) and Os(3). However, the quality of the structure determination is not sufficiently high to discriminate between C and N atoms. Hence the arrangement with a carbon rather than a nitrogen atom coordinated is based on 1H NMR rather than diffraction evidence; a NH group is



Scheme 3.



Fig. 4. Components of the bonding in alkylidene bridges.

identified spectroscopically (see above). The organic ligand is essentially planar; indeed there is an approximate molecular mirror plane through the ligand and through Os(1). The four-atom bridge across the metal atoms is an unusual feature in a trimetallic cluster. It requires six-membered rings involving the ligand and two metal atoms, which seems to be an unfavourable situation and to involve large angles within the rings. Thus for molecule 1 the angles Os(3)C(71)C(74), C(71)C(74)C(75), C(74)C(75)N(2), and C(75)N(2)Os(1) are 117(3), 137(4), 127(4), and 127(3)°, respectively. Since the ligand is planar there is no puckering which would allow these angles to be reduced. The hydride ligand was not located directly from the diffraction results, but it was judged to lie along the Os(2)–Os(3) edge approximately at the intersection of the C(23)Os(3) and C(33)Os(3) vectors. This is consistent with the positions of the other ligands in the molecule.

Compound 13 is represented in Scheme 3 as a zwitterion, with a spiro carbon atom bonded to osmium. This representation requires a negative charge at the metal atoms, and this receives some support from the rather lower $\nu(\text{CO})$ frequencies for 13 compared with those for 12 or 14. Even though the spiro carbon atom

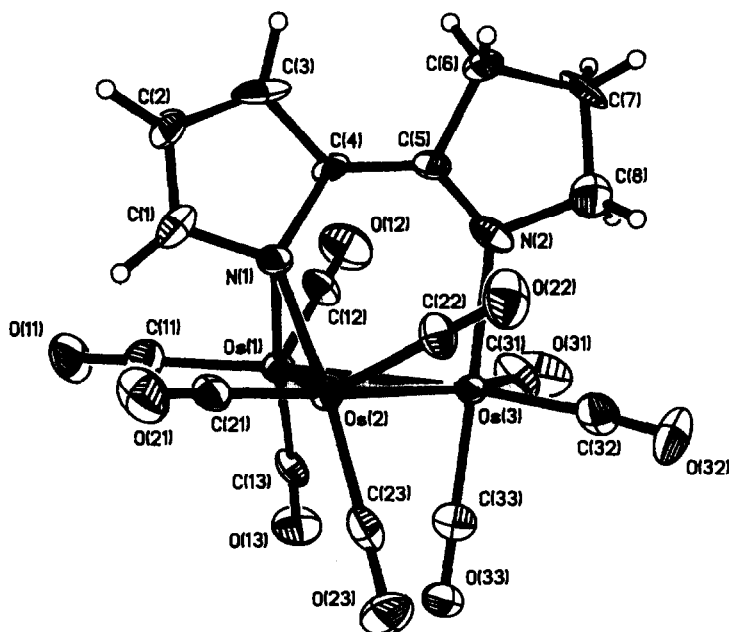


Fig. 5. Molecular structure of $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_3\text{NC}_4\text{H}_6\text{N})(\text{CO})_9]$ (16).

Table 3

Selected bond lengths (Å) and angles (°) for $[\text{Os}_3(\mu\text{-H})(\mu\text{-NCHCHCHCCCH}_2\text{CH}_2\text{CH}_2\text{N})(\text{CO})_9]$ (**16**)

Os(1)–Os(2)	2.803(1)	C(2)–C(3)	1.36(4)
Os(2)–Os(3)	2.795(1)	C(3)–C(4)	1.40(3)
Os(1)–Os(3)	2.806(1)	C(4)–C(5)	1.38(3)
Os(3)–N(2)	2.17(2)	C(5)–C(6)	1.51(3)
Os(1)–N(1)	2.20(2)	C(6)–C(7)	1.51(4)
Os(2)–N(1)	2.20(2)	C(7)–C(8)	1.47(4)
N(1)–C(1)	1.41(3)	N(2)–C(5)	1.30(3)
C(1)–C(2)	1.31(3)	N(2)–C(8)	1.47(3)
Os(1)–Os(2)–Os(3)	60.2(1)	Os(1)–Os(3)–N(2)	92.5(5)
Os(1)–Os(3)–Os(2)	60.1(1)	Os(2)–Os(3)–N(2)	89.7(4)
Os(2)–Os(1)–Os(3)	59.8(1)	Os(1)–N(1)–C(1)	113(1)
Os(1)–N(1)–Os(2)	79.2(5)	Os(1)–N(1)–C(4)	122(1)
Os(3)–Os(1)–N(1)	83.1(4)	Os(2)–N(1)–C(4)	124(1)
Os(3)–Os(2)–N(1)	83.2(4)	N(1)–C(4)–C(5)	124(2)
Os(1)–Os(2)–N(1)	50.3(4)	C(4)–C(5)–N(2)	130(2)
Os(2)–Os(1)–N(1)	50.5(4)	Os(3)–N(2)–C(5)	132(1)

bridging two osmium atoms might imply a lack of aromaticity in the heterocycle, the normal view of alkylidene bridges with σ and π components, as in Fig. 4, does not require this. The aromaticity need not be substantially disrupted even though the Os-bonded carbon is four-coordinate, and the charge separation is probably much less than implied by the representation in Scheme 3. Compounds **13** and **15** are both green, and spectroscopically similar, and the ^1H NMR spectra of both contain broad NH signals; they must be structurally very similar.

Likewise the orange-red compounds **14** and **16** must be structurally similar. The molecular structure of **16** determined by X-ray diffraction is shown in Fig. 5, and selected bond lengths and angles are given in Table 3. Superficially the structures

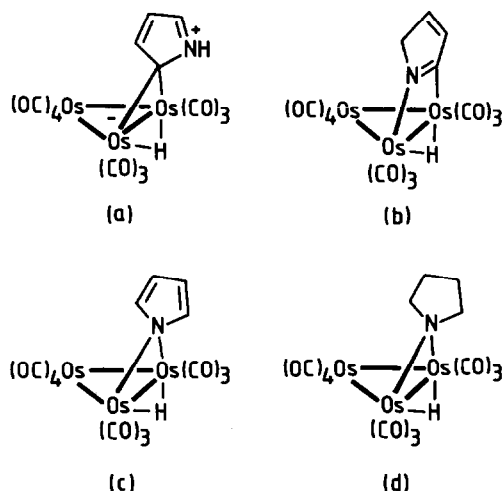


Fig. 6. Modes of double-bridging heterocyclic ligands X in compounds of the type $[\text{Os}_3(\mu\text{-H})(\mu\text{-XX})(\text{CO})_{10}]$ that have either been established (a, b and d) or predicted (c).

shown in Figs. 3 and 5 are very similar, and again we have had to decide where to place the nitrogen atom in the heterocyclic ring N(1)C(1)C(2)C(3)C(4) on the basis of ^1H NMR data (Table 1). There are no structural differences between the structures of **13** and **16** that could be used to identify these unambiguously as C-bonded and N-bonded species, respectively. The hydride ligand in **16** is in the same corresponding position as that in **13**; it lies close to the intersection of the C(12)Os(1) and C(22)Os(2) vectors along the Os(1)–Os(2) edge.

Compound **16** contains a N-bonded pyrrolyl bridge, which suggests the possibility of a new isomer of $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_4\text{N})(\text{CO})_{10}]$. We represent the synthesis and crystal structures of the isomeric compounds **a** and **b** in Fig. 6; the X-ray structure of the N-methyl form of **a** has been determined [8]. We had no evidence for the N-bonded form **c**, but forms **a** and **c** are related in the same way as isomers **13** and **14**, and so the isomeric form **c** is a feasible synthetic target. The N-bonded form of the pyrrolidinyll complex **d** is also known [5].

Experimental

The cluster $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ was prepared as previously described [10]. The methylaldimine derivatives of pyrrole, furan, thiophene and selenophene ($2\text{-C}_4\text{H}_3\text{XCH}=\text{NMe}$, X = NH, O, S, Se) were made by a modification of a method described by Emmert *et al.* for the pyrrole analogue [11], and 2,2'-(1'-pyrrolinyl)pyrrole by the method described by Rapoport and Bordner [12]. TLC was carried out on SiO_2 with light petroleum (b.p. 40–60°C) as eluant unless otherwise stated.

Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with the furyl-imine, $2\text{-C}_4\text{H}_3\text{OCH}=\text{NMe}$

A solution of the bis-acetonitrile compound (0.100 g) and the aldimine (0.010 g, 1 mol/mol Os_3) in dichloromethane (25 cm^3) was stirred at room temperature under nitrogen for 3.5 h. After removal of solvent under reduced pressure the yellow residue was subjected to TLC to give three main yellow bands, each of which gave a single spectroscopically-pure product on extraction and work-up. These products were characterised as $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{OC}=\text{NMe})(\text{CO})_{10}]$ (**8**) (0.020 g, 23%), $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_2\text{OCH}=\text{NMe})(\text{CO})_{10}]$ (**11**) (0.014 g, 17%) and $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_2\text{O-CH}=\text{NMe})(\text{CO})_9]$ (**12**) (0.030 g, 35%), all obtained as yellow solids.

Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with the thienyl-imine, $2\text{-C}_4\text{H}_3\text{SCH}=\text{NMe}$

A solution of the bis-acetonitrile cluster (0.150 g) and the aldimine (0.020 g, 1 mol/mol Os_3) in dichloromethane (30 cm^3) was stirred under nitrogen at room temperature for 3 h. Removal of the solvent and TLC work-up gave one main band, which yielded $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{S-C}=\text{NMe})(\text{CO})_{10}]$ (**9**) as an air-stable yellow solid (0.056 g, 45%).

Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with the selenophenyl-imine, $2\text{-C}_4\text{H}_3\text{SeCH}=\text{NMe}$

A solution of the bis-acetonitrile (0.092 g) and the aldimine (0.017 g, 1 mol/mol Os_3) in dichloromethane (20 cm^3) was stirred at room temperature under nitrogen for 2 h. After removal of the solvent the orange-yellow residue was subjected to TLC to give one main band, from which an orange solid was obtained: $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{SeC}=\text{NMe})(\text{CO})_{10}]$ (**10**) (0.042 g, 50%).

Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with the pyrrolyl-imine, $2\text{-C}_4\text{H}_3\text{NHCH}=\text{NMe}$

(a) A solution of the bis-acetonitrile compound (0.080 g) and the aldimine (0.019 g, 2 mol/mol Os_3) in dichloromethane (40 cm^3) was stirred at room temperature under nitrogen for 2 h. Removal of the solvent and TLC (eluant: light petroleum/diethyl ether (1/1 v/v)) gave one main green band, which yielded $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_2\text{NHCH}=\text{NMe})(\text{CO})_9]$ (**13**) as deep green crystals (0.045 g, 60%). Crystals suitable for single-crystal structure determination were obtained by slow evaporation of a hexane solution.

(b) A stirred solution of the bis-acetonitrile compound (0.070 g) and the aldimine (0.010 g, 1 mol/mol Os_3) in cyclohexane (30 cm^3) was refluxed under nitrogen for 20 min. TLC work-up gave one main band, which yielded an isomer of cluster **13** above: $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_3\text{NCH}=\text{NMe})(\text{CO})_9]$ (**14**) as orange-red crystals.

Table 4

Crystal data and details of intensity measurements, structure solution and refinement for $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_2\text{NHCH}=\text{NMe})(\text{CO})_9]$ (**13**) and $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_4\text{H}_3\text{NC}_4\text{H}_6\text{N})(\text{CO})_9]$ (**16**)^a

	Compound 13	Compound 16
Formula	$\text{C}_{15}\text{H}_8\text{N}_2\text{O}_9\text{Os}_3$	$\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_9\text{Os}_3$
M (g mol^{-1})	930.85	956.89
Colour	green	red
Crystal size (mm^3)	$0.45 \times 0.30 \times 0.55$	$0.36 \times 0.30 \times 0.10$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (\AA)	14.004(3)	14.034(3)
b (\AA)	19.943(5)	10.661(4)
c (\AA)	14.028(4)	14.144(5)
β ($^\circ$)	97.59(2)	91.66(2)
V (\AA^3)	3884(2)	2115(1)
Z	8	4
D_c (g cm^{-3})	3.18	3.00
μ (Mo- K_α) (cm^{-1})	196.5	180.6
$F(000)$	3296	1704
No. orientation reflns; 2θ range ($^\circ$)	30; 12 to 26	35; 4 to 30
Total data	7296	4056
Unique data	6780	3673
Reflns used	3132	2989
Rejection criterion	$I_o \leq 5\sigma(I_o)$	$I_o \leq 1.5\sigma(I_o)$
Parameters refined	263	280
R^b	0.0777	0.0615
R_w^c	0.0785	0.0558
g^d	0.0004	0.0005
Max. shift/e.s.d. in final refinement	0.003	< 0.001
Largest residual peak ($\text{e}\text{\AA}^{-3}$)	2.71	2.60

^a Data common to both compounds: Mo radiation ($\lambda = 0.71073$ \AA); Nicolet R3m/v diffractometer, intensity data were collected in the $\omega-2\theta$ scan mode at 23°C in the range $5 \leq 2\theta \leq 50$ and were corrected for decay based on intensities of three check reflections, for Lorentz and polarization effects, and for absorption by azimuthal scan method; direct methods structure solution. ^b $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. ^c $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. ^d $w = [\sigma^2(F_o) + g(F_o^2)]^{-1}$.

Table 5. Fractional atomic coordinates ($\times 10^4$) for $[\text{Os}_3(\mu\text{-HX})\mu\text{-NHCHCHCCCH=NMe}(\text{CO})_9]$ (13).

Atom	x	y	z
Os(1)	6913(2)	409(1)	3073(1)
Os(2)	6980(1)	346(1)	1082(1)
Os(3)	8684(2)	354(1)	2333(1)
Os(4)	8231(2)	2133(1)	7044(1)
Os(5)	8173(2)	2199(1)	9033(1)
Os(6)	6468(2)	2109(1)	7795(1)
N(1)	7943(29)	-1620(21)	1573(30)
N(2)	6749(26)	-661(18)	3217(26)
C(71)	7980(32)	-518(22)	1458(32)
C(72)	8436(37)	-787(25)	770(38)
C(73)	8460(43)	-1464(29)	852(42)
C(74)	7642(29)	-1059(19)	1982(28)
C(75)	7200(30)	-1134(21)	2776(31)
C(76)	6311(34)	-891(23)	4041(33)
N(3)	6939(27)	4120(19)	8550(28)
N(4)	8209(30)	3227(20)	6907(30)
C(81)	7105(36)	2998(25)	8637(37)
C(82)	6555(38)	3274(26)	9324(39)
C(83)	6403(31)	3935(20)	9217(31)
C(84)	7324(26)	3561(18)	8105(25)
C(85)	7804(27)	3662(19)	7379(27)
C(86)	8780(39)	3437(27)	6079(39)
C(11)	7443(33)	439(22)	4310(33)
O(11)	7777(30)	493(21)	5132(30)
C(12)	5543(26)	454(17)	3053(25)
O(12)	4733(33)	589(23)	3148(34)
C(13)	7135(39)	1333(27)	2913(39)
O(13)	6977(27)	1922(19)	2806(27)
C(21)	7157(40)	262(26)	-250(40)
O(21)	7220(26)	177(18)	-1072(28)
C(22)	6353(30)	1140(20)	854(29)
O(22)	5993(27)	1659(18)	647(26)
C(23)	5833(35)	-99(23)	1075(33)
O(23)	5158(30)	-442(21)	1124(30)
C(31)	9789(30)	393(20)	1644(29)
O(31)	10527(27)	460(18)	1388(27)
C(32)	9095(39)	1094(27)	2997(39)
O(32)	9220(36)	1613(26)	3413(36)
C(33)	9217(33)	-171(22)	3334(33)
O(33)	9597(32)	-496(23)	3956(32)
C(41)	7681(34)	2082(22)	5771(35)
O(41)	7410(30)	2017(21)	4959(31)
C(42)	8117(36)	1199(25)	7212(37)
O(42)	8295(23)	638(16)	7305(23)
C(43)	9587(34)	2117(22)	6982(33)
O(43)	10339(35)	2084(23)	6848(35)
C(51)	8071(34)	2289(23)	10363(35)
O(51)	8082(30)	2332(20)	11178(31)
C(52)	8846(32)	1415(22)	9289(31)
O(52)	9318(25)	908(17)	9482(26)
C(53)	9304(33)	2669(22)	9003(32)
O(53)	10000(32)	3024(21)	8972(32)
C(61)	5924(33)	2608(22)	6740(33)
O(61)	5585(27)	2896(19)	6105(28)
C(62)	5473(33)	2047(22)	8396(33)
O(62)	4648(29)	1985(20)	8728(29)
C(63)	6133(37)	1295(24)	7107(36)
O(63)	6060(31)	789(22)	6741(33)

tals (0.034 g, 50%). Cluster **13** is not a precursor of **14**, since solutions of **13** in refluxing cyclohexane (or n-octane) do not give any of cluster **14**.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with the pyrrolinyl pyrrole, 2- $C_4H_3NHC_4H_6N$

(a) A solution of the bis-acetonitrile cluster (0.110 g) and the bicyclic heterocycle (0.032 g, 2 mol/mol Os_3) in dichloromethane (40 cm³) was stirred at room temperature under nitrogen for 4 h. Removal of the solvent and TLC (eluant: light petroleum/diethyl ether (1/1 v/v)) gave one main green band which yielded $[Os_3(\mu-H)(\mu_3-C_4H_2NHC_4H_6N)(CO)_9]$ (**15**) as green crystals (0.063 g, 56%).

(b) A solution of the bis-acetonitrile cluster (0.090 g) and the bicyclic heterocycle (0.013 g, 1 mol/mol Os_3) in refluxing cyclohexane (30 cm³) for 1 h, after TLC work-up, did not give any of complex **15** but only a single product isomeric with this: $[Os_3(\mu-H)(\mu_3-C_4H_3NC_4H_6N)(CO)_9]$ (**16**) obtained as orange-red crystals (0.044 g, 48%). Crystals suitable for single-crystal structure determination were obtained by slow evaporation of a hexane solution.

Table 6

Fractional atomic coordinates ($\times 10^4$) for $[Os_3(\mu-H)(\mu_3-NCHCHCHCCCH_2CH_2CH_2N)(CO)_9]$ (**16**)

Atom	x	y	z
Os(1)	-1212(1)	1402(1)	7850(1)
Os(2)	461(1)	1758(1)	8948(1)
Os(3)	550(1)	1640(1)	6978(1)
N(1)	-718(11)	3067(14)	8634(10)
C(1)	-1286(15)	3348(21)	9411(16)
C(2)	-1511(17)	4536(22)	9464(16)
C(3)	-1105(18)	5124(20)	8725(19)
C(4)	-597(14)	4272(18)	8177(15)
C(5)	6(15)	4467(17)	7439(14)
C(6)	182(15)	5802(20)	7134(17)
C(7)	728(22)	5651(20)	6233(17)
C(8)	991(21)	4315(26)	6190(20)
N(2)	435(12)	3664(15)	6909(12)
C(11)	-2340(16)	1170(25)	8592(16)
O(11)	-3057(12)	987(19)	8919(14)
C(12)	-1752(17)	2276(21)	6792(16)
O(12)	-2075(15)	2716(18)	6142(14)
C(13)	-1389(14)	-173(19)	7232(14)
O(13)	-1505(13)	-1114(15)	6906(13)
C(21)	331(16)	1876(18)	10292(14)
O(21)	339(15)	1941(17)	11104(11)
C(22)	1496(15)	2848(21)	8781(15)
O(22)	2119(12)	3495(17)	8715(12)
C(23)	1283(15)	395(22)	9101(15)
O(23)	1767(11)	-458(16)	9208(12)
C(31)	92(19)	1511(23)	5688(14)
O(31)	-184(19)	1383(19)	4959(15)
C(32)	1900(18)	1768(23)	6759(16)
O(32)	2681(12)	1763(19)	6638(13)
C(33)	682(15)	-111(21)	7083(15)
O(33)	775(12)	-1158(15)	7178(11)

Single-crystal structure determinations for the clusters 13 and 16

Crystals of the green compound **13** and the orange-red compound **16**, each obtained by evaporation of hexane solutions, were mounted at room temperature in air on glass fibres which were fixed to goniometers on a Nicolet R3v/m diffractometer. Crystal data and details for the collection of intensity data, structure solution, and refinement are given in Table 4. Unit cells were determined by auto-indexing and least-squares fitting of 30 and 35 orientation reflections selected from rotation photographs for **13** and **16**, respectively.

Structures were solved by direct methods. Compounds **13** did not give very good crystals and the structure was refined to $R = 0.0777$ using 3132 intensity data with $I_o > 5\sigma(I_o)$ for a model with 263 parameters by alternating cycles of full-matrix least-squares and difference Fourier synthesis. There are two independent Os_3 clusters in the unit cell and, in view of the limited quality and quantity of data, only the Os atoms were refined anisotropically. H-atoms (except that bonded to Os) were included in idealised positions (C–H 0.96, N–H 0.90 Å, $U_{iso} = 0.08 \text{ \AA}^2$) and constrained to ride on the respective C and N atoms. The quality of the refinement was insufficient to confirm that the pyrrole ring was C- rather than N-bonded to osmium. Atoms N(1) and C(71) in one molecule, N(3) and C(81) in the other, were positioned on the basis of NMR data. Reversal of these C and N atoms made little difference to the refinement but would be inconsistent with the spectra. Atomic coordinates are in Table 5.

Compound **16** gave rather better data, which led to a value of R of 0.0615 using 2989 intensity data with $I_o > 3\sigma(I_o)$ for a model with 280 parameters. All non-hydrogen atoms were refined anisotropically* and H-atoms were included in the model as for **13**. Atomic coordinates are listed in Table 6.

All calculations were carried out on a MicroVax II computer running SHELXTL PLUS [13]. Full lists of bond lengths and angles, thermal parameters, and F_o/F_c values for compounds **13** and **16** may be obtained from the authors.

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