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Photochemistry of $[Ru_3(CO)_{12}]$ with nitrogen heterocycles

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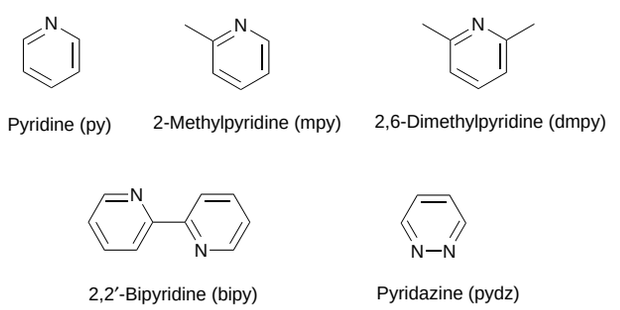
The photochemistry of $[M_3(CO)_{12}]$ (M = Ru **1a** or Os **1b**) with nitrogen heterocycles has been studied. In all cases photolysis leads to photosubstitution products, the heterocycles inhibiting the photofragmentation pathway. With pyridine (py) **1a** formed the orthometallated complex $[Ru_3H(CO)_{10}(C_5H_4N)]$ **2a**. With osmium, the simple substitution product $[Os_3(CO)_{11}(py)]$ **3b** can be isolated. With 2-methylpyridine (mpy) $[Ru_3H(CO)_{10}(2\text{-}MeC_5H_3N)]$ **5a** and $[Os_3(CO)_{11}(mpy)]$ **6b** were formed from **1a** and **1b** respectively. With 2,6-dimethylpyridine no net photoreaction was observed. Photolysis of **1a** and **1b** with 2,2′-bipyridine led to the formation of $[M_3(CO)_{10}(bipy)]$ (M = Ru **7a** and Os **7b**). The molecular structure of **7b** has been obtained by single-crystal X-ray diffraction studies. Photolysis of **1a** and **1b** with pyridazine (pydz) led to the substituted products $[M_3(CO)_{10}(pydz)]$ (M = Ru **8a** or Os **8b**).

The reaction chemistry of cluster carbonyl complexes with nitrogen heterocyclic ligands has received little attention as compared to that of other ligands such as phosphines.[1] This may be attributed in part to the harsh reaction conditions frequently required which often result in cluster degradation or the formation of complex products.[2] Our research into the photochemistry of binary carbonyls has led us to investigate the photochemistry of ruthenium and osmium complexes with a number of ligand systems.[3,4] Photochemistry offers a simple, and often highly selective, route to organometallic compounds, overcoming large enthalpy barriers. As a consequence, it is often possible to prepare complexes that are otherwise inaccessible by conventional thermochemical routes.[3–5] The work documented here focuses on the photochemistry of $[Ru_3(CO)_{12}]$ **1a** and $[Os_3(CO)_{12}]$ **1b** with pyridine (py), 2-methylpyridine (mpy), 2,6-dimethylpyridine (dmpy), 2,2′-bipyridine (bipy) and pyridazine (pydz). The aim of our investigations was to prepare photochemically a number of trinuclear carbonyl complexes containing nitrogen heterocycles as ligands as it has been reported that such compounds may well have the ability to act as efficient catalysts for key industrial synthetic transformations.[6]



Results and Discussion

Photoreactions with pyridine

Broad-band UV photolysis of a dichloromethane solution of $[Ru_3(CO)_{12}]$ **1a** in the presence of an excess of pyridine leads initially to the formation of the orthometallated complex $[Ru_3H(CO)_{10}(C_5H_4N)]$ **2a** in 85% yield as characterised by comparison of spectral data (Table 1) with those in the literature.[7] The reaction most probably proceeds *via* the formation of the intermediate $[Ru_3(CO)_{11}(py)]$ **3a**, generated by photosubstitution of a carbonyl group by pyridine. Infrared monitoring of the reaction shows the formation of small amounts of $[Ru(CO)_4(py)]$ as characterised by comparison with data (Table 1) from our previous investigations.[8] This complex was formed in only very small amounts and, on removal of the irradiation source, reacts to yield **2a**. The complex **2a** is photostable in the absence of a reactant.

The formation of trinuclear products from the photolysis is of some interest. In general, our research has shown that photolysis of complex **1a** with a two-electron donor ligand in dichloromethane leads predominantly to photofragmentation products.[3] This is illustrated in the photolysis of **1a** with triphenylphosphine or acrylonitrile which generates the mononuclear products $[Ru(CO)_4(PPh_3)]$ and $[Ru(CO)_4(\eta^2\text{-}H_2C{=}CHCN)]$ respectively.[3,9] In the case of pyridine, since substitution is the predominant photopathway, the ligand itself acts as a photofragmentation inhibitor. The term inhibitor is used rather than quencher because to class pyridine as a photofragmentation quencher would not be strictly correct as it has been shown not to adhere perfectly to Stern–Volmer kinetic behaviour.[10] To demonstrate the photofragmentation-inhibiting behaviour of pyridine, a dichloromethane solution of **1a** containing acrylonitrile was irradiated after doping with a small volume of pyridine. Generation of mononuclear products was suppressed and, after 5 h, analysis of the photolysis mixture showed there to be 95% unchanged starting material, the remainder being **2a**, formed as expected in the course of the photolysis.

The formation of complex **2a** from **1a** is a relatively inefficient process, the photoreactions taking some considerable time. To explain this the mechanism for photosubstitution needs to be considered. By using matrix-isolation and flash-photolysis techniques previous workers have generated key intermediates involved in the photosubstitution pathway of **1a**.[10,11] The primary photoreaction is the dissociation of CO to form $[Ru_3(CO)_{11}]$ **4a** which is trapped by solvent (solv) to generate the solvated species $[Ru_3(CO)_{11}(solv)]$. Therefore, the photosubstitution mechanism is favoured when donor solvents are used, in this case pyridine. However, the photogenerated intermediate $[Ru_3(CO)_{11}]$ **4a** shows a significant reaction selectivity.[10] This is illustrated by the observation that its reaction with photoejected CO is eight times faster than with added PPh_3.[11] Therefore, in the case of an added ligand, L, photosubstitution of CO by L is in competition with recombination of **4a** with photoejected CO. This may be contrasted to the case of the

Table 1 Infrared and ^{1}H NMR spectral data for complexes prepared in this study

Compound	IR [a]	^{1}H NMR [b]	Mass [c], *m/z*
1a $[Ru_3(CO)_{12}]$	2059vs, 2027s, 2007m		—
1b $[Os_3(CO)_{12}]$	2068s, 2035s, 2014m, 2002m		—
2a $[Ru_3H(CO)_{10}(C_5H_4N)]$	2099m, 2061s, 2050vs, 2024s, 2015vs, 1999s, 1984w	8.10dd, 7.45m, 6.89m, −14.33s	662
3b $[Os_3(CO)_{11}(py)]$	2104w, 2051s, 2035vs, 2018m, 2004vs, 1998 (sh), 1960w	8.42m, 7.53m, 7.32m	*d*
5a $[Ru_3H(C)_{10}(2\text{-}MeC_5H_3N)]$	2099m, 2060s, 2048vs, 2024s, 2013vs, 1996s, 1980w	7.15m, 6.79m, 2.55s, −14.06m	676
6b $[Os_3(CO)_{11}(mpy)]$	2105w, 2047s, 2030vs, 2022m, 2002vs, 1994 (sh), 1964w	8.65m, 7.42m, 2.63s	*d*
7a $[Ru_3(CO)_{10}(bipy)]$	2075s, 2030vs, 1995 (sh), 1990s, 1970m, 1944w, 1740w (br)	9.62d, 8.35m, 8.12m, 7.81m	*d*
7b $[Os_3(CO)_{10}(bipy)]$	2084m, 2032s, 2002s, 1989s, 1973s, 1953m, 1901m	9.62d, 8.93m, 8.31m, 7.81m	1492
8a $[Ru_3(CO)_{10}(pydz)]$	2082m, 2056s, 2034vs, 2016s, 2007vs, 1977 (sh), 1815w (br)	8.57t, 8.38t, 7.51t, 7.24t	663
8b $[Os_3(CO)_{10}(pydz)]$	2082m, 2054s, 2030vs, 2020s, 2005s, 1975w	*e*	*d*
9b $[Os_3H(CO)_{10}(C_4H_3N_2)]$	2104w, 2068s, 2058s, 2027s, 2010s, 1992m, 1980m, 1966w	8.28m, 6.97m, 6.85m, −14.45s	936

[a] In CH_2Cl_2 unless stated otherwise. [b] In $CDCl_3$ unless stated otherwise. [c] Based on ^{192}Os, ^{101}Ru. [d] Decomposes. [e] Solubility problems.

photofragmentation pathway where the intermediate $[Ru_3(\mu\text{-}CO)(CO)_{11}]$, formed by heterolytic cleavage of a Ru–Ru bond, with concomitant movement of a carbonyl from a terminal to a bridging position, is very unstable and further reaction unselective.[12]

The photostability of complex **2a** may be explained both by any increased selectivity of the possible photogenerated intermediate $[Ru_3H(CO)_9(C_5H_4N)]$ and the increased strength of the Ru–CO bonds in **2a** as compared to **1a**. These factors may be a consequence of the strong σ-donor ability of orthometallating ligands which greatly enriches the electron density at the metal centres in **2a** and hence increases the extent of 'back bonding' to carbonyl ligands.

Owing to the increased stability of trinuclear osmium complexes over their ruthenium analogues different products are often formed. Broad-band UV photolysis of a dichloromethane solution of $[Os_3(CO)_{12}]$ **1b** in the presence of a stoichiometric excess of pyridine leads to the formation of the simple photosubstituted complex $[Os_3(CO)_{11}(py)]$ **3b** as characterised by comparison of spectral data (Table 1) with those in the literature.[13] The mild conditions involved in photolytic activation allow for the controlled synthesis of **3b** rather than, in the case of thermolysis or pyrolysis, the generation of the orthometallated complex $[Os_3H(CO)_{10}(C_5H_4N)]$ **2b**.[14]

Although structurally similar, complexes **1a** and **1b** are significantly different electronically.[15] The metal–metal orbital interactions are greater in **1b** than in **1a** with the consequence that photofragmentation is much less efficient for **1b**. As a result, it is not possible to assume simply that the mechanism for photosubstitution of CO by py in **1a** is the same as that in **1b**. For **1b** the reaction times are again significantly longer with pyridine as a ligand as compared to those for olefins. This suggests some form of relatively long-lived photogenerated intermediate. On the basis of previous photophysical studies, this intermediate has been proposed to be an isomeric form of **1b**, formed by insertion of a terminal carbonyl into an Os–Os bond.[16] Furthermore, photofragmentation and photosubstitution reactions both proceed *via* this intermediate.[17] As a result, the pyridine does not act as a photofragmentation inhibitor in the case of **1b**. This is confirmed by the observation that photolysis of a dichloromethane solution of **1a** containing acrylonitrile after doping with a small volume of pyridine leads to the formation of $[Os(CO)_4(\eta^2\text{-}H_2C{=}CHCN)]$ in good yield. Had the photofragmentation pathway been inhibited, no mononuclear products would have been produced.

Photoreactions with 2-methylpyridine

Not unexpectedly, the photochemistry of complexes **1a** and **1b** with 2-methylpyridine is similar to that with pyridine. For **1a** photolysis leads initially to the formation of $[Ru_3H(CO)_{10}(2\text{-}MeC_5H_3N)]$ **5a** as characterised by comparison of spectra data (Table 1) with those in the literature.[18] In the case of **1b** photolysis results in the formation of the simple substitution product $[Os_3(CO)_{11}(mpy)]$ **6b**, as characterised by comparison of IR data (Table 1) with those of the pyridine analogue. The photoreactions with mpy are thought to occur by a mechanism akin to that for pyridine, the heterocycle acting as a simple substituting ligand and, in the case of **1a**, as a photofragmentation inhibitor.

Photoreactions with 2,6-dimethylpyridine

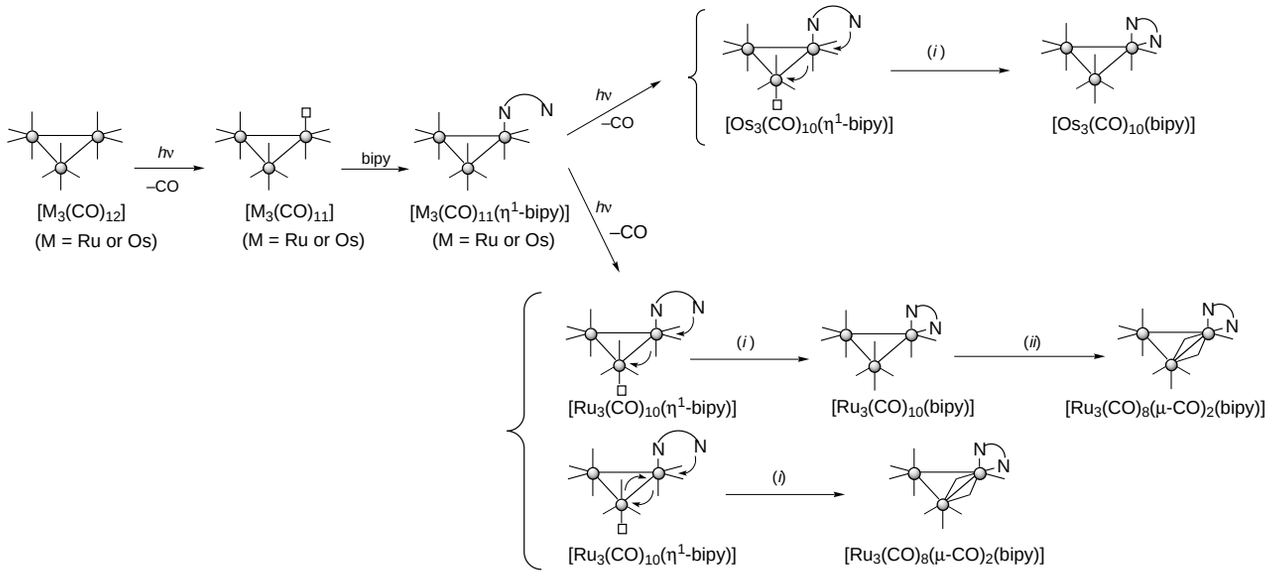
When dichloromethane solutions of complexes **1a** and **1b** containing 2,6-dimethylpyridine are irradiated no net photoreaction is observed. This may be attributed to the considerable steric shielding of the nitrogen of the pyridine ring in dmpy and the concomitant steric hindrance to formation of complexes with the clusters.

When a dichloromethane solution of complex **1a** containing acrylonitrile was irradiated after doping with a small volume of dmpy the mononuclear η^2-olefin complex $[Ru(CO)_4(\eta^2\text{-}H_2C{=}CHCN)]$ was formed in good yield. This demonstrates that, in addition to being unable to co-ordinate to **1a** to form substituted products, dmpy does not act as an inhibitor of the photofragmentation pathway. Again this may be attributed to the steric crowding concomitant with interaction of the heterocycle with **1a**.

Photoreactions with 2,2′-bipyridine

Broad-band UV photolysis of a dichloromethane solution of complex **1a** with an excess of 2,2′-bipyridine leads initially to the formation of $[Ru_3(CO)_{10}(bipy)]$ **7a** in 40% yield by comparison of spectral data (Table 1) with those in the literature.[19] The IR spectrum of **7a** shows a broad band at 1740 cm^{-1} indicative of bridging CO groups. Photolysis over a longer time results in the formation of a black precipitate, this being uncharacterised at present, however it is proposed that the black products are charged in nature. This is not wholly unexpected since the photochemistry of $[Ru(CO)_5]$ with polydentate heterocycles has been shown to result in ruthenium(III) complexes as a result of a proposed photooxidation process.[8] Again, the addition of the nitrogen heterocycle to a dichloromethane solution of **1a** inhibits photofragmentation. This is confirmed by the fact that there is no observable photoreaction when a bipy-doped dichloromethane solution of **1a** containing acrylonitrile is irradiated. If the photolysis with bipy is repeated with the dichloromethane solution of **1a** doped with a donor solvent such as acetonitrile the yield of **7a** is increased significantly. This points towards the donor solvent acting as a stabilising group for the highly reactive intermediates formed in the photolysis. The importance of this in determining the photosubstitution mechanism is discussed later.

Broad-band UV photolysis of a dichloromethane solution of complex **1b** in the presence of an excess of bipy for 4 h leads to



Scheme 1 Proposed mechanism for photochemical generation of $[M_3(CO)_{10}(bipy)]$ (M = Ru **7a** or Os **7b**). (*i*) Migration of CO and chelation of bipy; (*ii*) 2 CO move from terminal to bridging

the formation of the chelate complex $[Os_3(CO)_{10}(bipy)]$ **7b** in approximately 30% yield as characterised by comparison of spectral data (Table 1) with those in the literature.[20] As in the case of **1b**, if the photolysis with bipy is repeated with the dichloromethane solution of **1b** doped with a donor solvent such as acetonitrile the yield of **7b** is increased greatly.

To generate $[M_3(CO)_{10}(bipy)]$ (M = Ru **7a** or Os **7b**) from $[M_3(CO)_{12}]$ (M = Ru **1a** or Os **1b**) either two photosubstitutions at the same metal atom are required or a rearrangement is necessary at some stage if two substitutions were to occur at different metal centres. Since co-ordination of one N of a bipy ligand to one of the osmium centres increases the strength of the M–CO bonds on that metal atom (due to the σ-donor character of the heterocycle) it is more likely that the second photosubstitution occurs at a second metal atom in the cluster. An initial photosubstitution of CO by one end of the bipy moiety could yield $[M_3(CO)_{11}(\eta^1\text{-bipy})]$. This would be followed by photolabilisation of a CO group from a neighbouring metal centre. Migration of a CO from the metal centre containing the η^1-co-ordinated bipy to that which is co-ordinatively unsaturated could then occur, this being concomitant with chelation of the bipy unit. In the case of **7a**, the rearrangement of two carbonyl groups could be envisaged yielding the more stable di-μ-CO bridged isomer, this occurring either after the carbonyl migration or else concomitant with it. The proposed mechanism is shown in Scheme 1.

Photoreactions with pyridazine

Broad-band UV photolysis of a dichloromethane solution of complex **1a** with an excess of pyridazine leads to the formation of $[Ru_3(CO)_{10}(pydz)]$ **8a** as characterised by comparison of spectral data (Table 1) with those in the literature.[21] The IR spectrum of **8a** shows a broad band at 1815 cm^{-1} indicative of bridging CO groups. The mode of co-ordination, *via* the two nitrogen atoms, is easily verified by the absence of a hydride signal in the ^{1}H NMR spectrum of **8a**. Again, the heterocycle acts as a photofragmentation inhibitor as demonstrated by the absence of net photoreaction if a dichloromethane solution of **1a** with acrylonitrile is doped with pydz.

When a dichloromethane solution of complex **1b** is irradiated with an excess of pyridazine a very dark brown precipitate is formed. This is very insoluble but can be characterised as the simple substitution product $[Os_3(CO)_{10}(pydz)]$ **8b** by comparison of spectral data (Table 1) with those in the literature.[22]

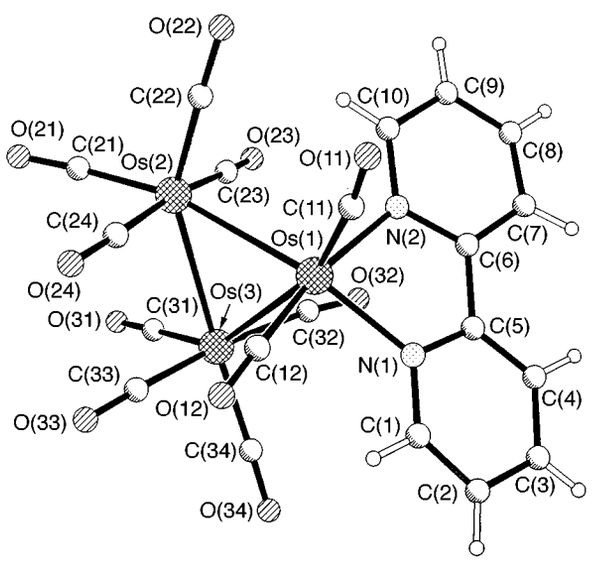


Fig. 1 Molecular structure of $[Os_3(CO)_{10}(bipy)]$ **7b**

The solid can be partially solvated in boiling xylene but dissolves as the orthometallated isomer $[Os_3H(CO)_{10}(C_4H_3N_2)]$ **9b**, characterised by IR spectroscopy and the distinctive hydride resonance in the ^{1} HMR spectrum (Table 1).[23]

Molecular structure of $[Os_3(CO)_{10}(bipy)]$ 7b

The molecular structure of $[Os_3(CO)_{10}(bipy)]$ **7b** has been determined by single-crystal X-ray diffraction studies and is shown in Fig. 1. Selected bond lengths and angles are in Table 2.

The solid-state structure is consistent with that in solution, the bipyridine unit chelating to one metal centre. The three osmium atoms in complex **7b** define an almost equilateral triangle, the Os–Os bond lengths (mean 2.875 Å) being very similar to those in $[Os_3(CO)_{12}]$ **1b** (mean 2.877 Å).[24] The bipyridine unit co-ordinates with one nitrogen axially bonded to Os(1) and one nitrogen equatorially bonded [Os(1)–N(1) 2.09(2), Os(1)–N(2) 2.18(2) Å]. This is in contrast to the ruthenium analogue **7a** where the bipy unit lies perpendicular to the metal triangle.[19,25] The M–CO bond *trans* to the co-ordinated nitrogen of the bipy moiety in **7b** is significantly shorter than the other axial M–CO bonds in the molecule

Table 2 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_{10}(bipy)]$ **7b**

Os(1)–C(12)	1.86(3)	Os(1)–C(11)	1.89(3)	N(2)–C(10)	1.36(4)	N(2)–C(6)	1.39(3)
Os(1)–N(1)	2.09(2)	Os(1)–N(2)	2.18(2)	C(2)–C(3)	1.39(4)	Os(3)–C(31)	1.86(4)
Os(1)–Os(2)	2.841(2)	Os(1)–Os(3)	2.901(2)	Os(3)–C(33)	1.90(4)	Os(3)–C(34)	1.90(3)
N(1)–C(1)	1.32(3)	N(1)–C(5)	1.38(3)	Os(3)–C(32)	1.96(3)	C(3)–C(4)	1.37(5)
C(1)–C(2)	1.36(4)	Os(2)–C(22)	1.86(3)	C(4)–C(5)	1.37(4)	C(5)–C(6)	1.44(4)
Os(2)–C(21)	1.88(4)	Os(2)–C(24)	1.90(3)	C(6)–C(7)	1.37(3)	C(7)–C(8)	1.35(4)
Os(2)–C(23)	1.96(4)	Os(2)–Os(3)	2.884(2)	C(8)–C(9)	1.35(4)	C(9)–C(10)	1.44(4)
C(12)–Os(1)–C(11)	89.1(11)	C(12)–Os(1)–N(1)	95.2(10)	C(21)–Os(2)–Os(3)	106.5(10)	C(24)–Os(2)–Os(3)	95.6(8)
C(11)–Os(1)–N(1)	103.0(10)	C(12)–Os(1)–N(2)	168.8(11)	C(23)–Os(2)–Os(3)	77.0(9)	Os(1)–Os(2)–Os(3)	60.87(4)
C(11)–Os(1)–N(2)	86.8(10	N(1)–Os(1)–N(2)	75.6(9)	C(10)–N(2)–C(6)	120(3)	C(10)–N(2)–Os(1)	124(2)
C(12)–Os(1)–Os(2)	94.5(9)	C(11)–Os(1)–Os(2)	102.7(7)	C(6)–N(2)–Os(1)	115(2)	C(1)–C(2)–C(3)	115(3)
N(1)–Os(1)–Os(2)	152.6(6)	N(2)–Os(1)–Os(2)	96.6(6)	C(31)–Os(3)–C(33)	95.6(14)	C(31)–Os(3)–C(34)	104.7(14)
C(12)–Os(1)–Os(3)	84.6(9)	C(11)–Os(1)–Os(3)	161.1(7)	C(33)–Os(3)–C(34)	86.9(12)	C(31)–Os(3)–C(32)	96.4(12)
N(1)–Os(1)–Os(3)	95.2(7)	N(2)–Os(1)–Os(3)	102.4(7)	C(33)–Os(3)–C(32)	168.0(13)	C(34)–Os(3)–C(32)	89.1(11)
Os(2)–Os(1)–Os(3)	60.29(4)	C(1)–N(1)–C(5)	114(2)	C(31)–Os(3)–Os(2)	91.6(9)	C(33)–Os(3)–Os(2)	84.1(9)
C(1)–N(1)–Os(1)	126(2)	C(5)–N(1)–Os(1)	119(2)	C(34)–Os(3)–Os(2)	162.1(11)	C(32)–Os(3)–Os(2)	96.5(6)
N(1)–C(1)–C(2)	130(3)	C(22)–Os(2)–C(21)	102.5(14)	C(31)–Os(3)–Os(1)	147.3(9)	C(33)–Os(3)–Os(1)	94.9(10)
C(22)–Os(2)–C(24)	90.2(13)	C(21)–Os(2)–C(24)	92(2)	C(34)–Os(3)–Os(1)	106.8(11)	C(32)–Os(3)–Os(1)	75.5(8)
C(22)–Os(2)–C(23)	97(2)	C(21)–Os(2)–C(23)	89(2)	Os(2)–Os(3)–Os(1)	58.83(4)	C(4)–C(3)–C(2)	118(3)
C(24)–Os(2)–C(23)	172.5(13)	C(22)–Os(2)–Os(1)	90.6(11)	N(1)–C(5)–C(6)	114(2)	C(7)–C(6)–N(2)	120(3)
C(21)–Os(2)–Os(1)	166.6(9)	C(24)–Os(2)–Os(1)	85.3(8)	C(7)–C(6)–C(5)	124(3)	N(2)–C(6)–C(5)	116(2)
C(23)–Os(2)–Os(1)	92.4(9)	C(22)–Os(2)–Os(3)	150.2(11)				

[Os(1)–C(12) 1.86(3) *cf.* mean axial Os(2)–C and Os(3)–C bond lengths of 1.93 Å]. The $M(CO)_4$ units of Os(1) and Os(2) show a tendency to twist from the idealised D_{3h} symmetry observed in **1b** to D_3. This may be attributed in part to the steric hindrance of the bipy ligand and also to the potential-energy surface for distortion being soft. In the related cluster **7a** two asymmetrically bridging carbonyl groups are found. However, as observed for the majority of third-row elements, for osmium terminal CO bonding is favoured over bridging.

Compared to free bipy, the N(1)–C(5) and N(2)–C(6) bonds are slightly elongated and the C(5)–C(6) bond slightly shortened in complex **7b**.[26] The bite angle of the chelating bipy is 75.6(9)°, this being comparable to that in $[Os_3(CO)_{10}(Pr^iN{=}CHCH{=}NPr^i)]$ (N–Os–N 76.6°).[27]

Conclusion

The photolysis of dichloromethane solutions of $[M_3(CO)_{12}]$ (M = Ru **1a** or Os **1b**) with these nitrogen heterocycles leads to photosubstitution products. The heterocycles inhibit the photofragmentation pathway as has been observed previously in the case of donor solvents such as diethyl ether or ethyl acetate. With pyridine, **1a** forms the orthometallated complex $[Ru_3H(CO)_{10}(C_5H_4N)]$ **2a** but, in the case of osmium, the simple substitution product $[Os_3(CO)_{11}(py)]$ **3b** can be isolated because of its greater kinetic stability. The photochemistry of **1a** and **1b** with 2-methylpyridine mirrors that with pyridine, $[Ru_3H(CO)_{10}(2\text{-}MeC_5H_3N)]$ **5a** and $[Os_3(CO)_{11}(mpy)]$ **6b** being formed. With 2,6-dimethylpyridine no net photoreaction is observed. This may be attributed to the steric shielding of the nitrogen in dmpy and the steric crowding implicit in the formation of any metal complexes with this ligand. On irradiation of the dichloromethane solutions of **1a** and **1b** with 2,2′-bipyridine the simple substitution adducts $[M_3(CO)_{10}(bipy)]$ (M = Ru **7a** or Os **7b**) are generated. Addition of acetonitrile to the photolysis mixture increases the yield of product. This is interpreted in terms of the MeCN acting as a stabiliser for any photogenerated intermediates. The molecular structure of **7b** has been obtained by single-crystal X-ray diffraction study. This has shown that **7b** is similar to other α-diimine-substituted triosmium clusters but shows significant differences compared to **7a**. Irradiation of dichloromethane solutions of **1a** and **1b** with pyridazine leads to the formation of $[M_3(CO)_{10}(pydz)]$ (M = Ru **8a** or Os **8b**). The osmium analogue **8b** is significantly less soluble than **8a**, solvation in boiling xylene leading to the formation of the orthometallated species $[Os_3H(CO)_{10}(C_4H_3N_2)]$ **9b**.

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 $[Ru_3(CO)_{12}]$ **1a**[28] and $[Os_3(CO)_{12}]$ **1b**.[29]

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 ^{1}H NMR spectra were recorded using a Bruker AM400, WM250 or WP80SY Fourier-transform spectrometer and data reported using the chemical shift scale in 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 thioglycerol as a matrix and CsI as calibrant.

Photolyses

Dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with pyridine. A dichloromethane solution of $[Ru_3(CO)_{12}]$ **1a** (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 (5 h). From comparison with literature data it was proposed that the yellow-green orthometallated cluster $[Ru_3H(CO)_{10}(C_5H_4N)]$ **2a** was formed in 85% yield together with small amounts of $[Ru(CO)_4(py)]$. Prolonged photolysis (8 h) led to no further photoproducts.

Pyridine-doped dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with acrylonitrile. A pyridine-doped (0.5 cm^3) dichloromethane solution of $[Ru_3(CO)_{12}]$ **1a** (30 mg in 150 cm^3) containing an excess of acrylonitrile (2 cm^3) was irradiated as above. After 6 h the only product observed was $[Ru_3H(CO)_{10}(C_5H_4N)]$ **2a** in 5%

yield. It was concluded that pyridine acts as an inhibitor to the photofragmentation pathway.

Dichloromethane solution of $[Os_3(CO)_{12}]$ 1b with pyridine. A dichloromethane solution of $[Os_3(CO)_{12}]$ **1b** (40 mg in 150 cm^3) containing an excess of pyridine (1 cm^3) was irradiated as above. The reaction was deemed complete when there was no further change in the IR spectrum (6 h). From comparison with literature data it was proposed that the orange-yellow cluster $[Os_3(CO)_{11}(py)]$ **3b** was formed in 60% yield.

Dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with 2-methylpyridine. The photolysis was performed as with pyridine but using 2-methylpyridine (1 cm^3) as the heterocycle. The yellow-green orthometallated cluster $[Ru_3H(CO)_{10}(2\text{-}MeC_5H_3N)]$ **5a** was formed in 70% yield after 6 h, as characterised by comparison with literature data.

2-Methylpyridine-doped dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with acrylonitrile. The photolysis was performed as with pyridine but using 2-methylpyridine (0.5 cm^3) as the dopant. After 6 h the only product observed was $[Ru_3H(CO)_{10}(2\text{-}MeC_5H_4N)]$ **5a** in 3% yield. It was concluded that 2-methylpyridine acts as an inhibitor to the photofragmentation pathway.

Dichloromethane solution of $[Os_3(CO)_{12}]$ 1b with 2-methylpyridine. The photolysis was performed as with pyridine but using 2-methylpyridine (1 cm^3) as the heterocycle. The yellow-green orthometallated cluster $[Os_3(CO)_{10}(mpy)]$ **6b** was formed in 60% yield after 6 h, as characterised by comparison with literature data for **2b**.

Dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a and $[Os_3(CO)_{12}]$ 1b with 2,6-dimethylpyridine. The photolysis was performed as with pyridine but using 2,6-dimethylpyridine (1 cm^3) as the heterocycle. No net photoreaction was observed.

2,6-Dimethylpyridine-doped dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with acrylonitrile. The photolysis was performed as with pyridine but using 2,6-dimethylpyridine (0.5 cm^3) as the dopant. The mononuclear η^2-olefin complex $[Ru(CO)_4(\eta^2\text{-}H_2C{=}CHCN)]$ was formed in 90% yield after 2 h.

Dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with 2,2′-bipyridine. The photolysis was performed as with pyridine but using 2,2′-bipyridine (22 mg) as the heterocycle. The purple cluster $[Ru_3(CO)_{10}(bipy)]$ **7a** was formed in 40% yield after 6 h, as characterised by comparison with literature data.

Acetonitrile-doped dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with 2,2′-bipyridine. An acetonitrile-doped (5 cm^3) dichloromethane solution of $[Ru_3(CO)_{12}]$ **1a** (30 mg in 150 cm^3) containing an excess of 2,2′-bipyridine (2 cm^3) was irradiated as above. The purple cluster $[Ru_3(CO)_{10}(bipy)]$ **7a** was formed in 60% yield after 6 h, implying that the acetonitrile acts as a stabiliser for any photogenerated intermediates.

Dichloromethane solution of $[Os_3(CO)_{12}]$ 1b with 2,2′-bipyridine. The photolysis was performed as with pyridine but using 2,2′-bipyridine (22 mg) as the heterocycle. The deep red cluster $[Os_3(CO)_{10}(bipy)]$ **7b** was formed in 30% yield after 6 h, as characterised by comparison with literature data.

Acetonitrile-doped dichloromethane solution of $[Os_3(CO)_{12}]$ 1b with 2,2′-bipyridine. The photolysis was as in the case of complex **1a** but using $[Os_3(CO)_{12}]$ **1b** (40 mg) and bipy (20 mg) as the heterocycle. The deep red cluster $[Os_3(CO)_{10}(bipy)]$ **7b** was formed in 60% yield after 6 h, implying again that the acetonitrile acts as a stabiliser for any photogenerated intermediates.

Dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with pyridazine. The photolysis was performed as with pyridine but using pyridazine (1 cm^3) as the heterocycle. The yellow-green cluster $[Ru_3(CO)_{10}(pydz)]$ **8a** was formed in 70% yield after 6 h, as characterised by comparison with literature data.

Pyridazine-doped dichloromethane solution of $[Ru_3(CO)_{12}]$ 1a with acrylonitrile. The photolysis was performed as with pyridine but using pyridazine (0.5 cm^3) as the dopant. After 6 h the only product observed was $[Ru_3(CO)_{10}(pydz)]$ **8a** in 3% yield. It was concluded that pyridazine acts as an inhibitor to the photofragmentation pathway.

Dichloromethane solution of $[Os_3(CO)_{12}]$ 1b with pyridazine. The photolysis was performed as with pyridine but using pyridazine (1 cm^3) as the heterocycle. The yellow-green cluster $[Os_3(CO)_{10}(pydz)]$ **8b** was formed in 60% yield after 6 h, as characterised by comparison with literature data for **3b**. Complex **8b** is highly insoluble in common organic solvents and, attempts to dissolve it in boiling xylene led to the formation of the yellow orthometallated isomer $[Os_3H(CO)_{10}(C_4H_3N_2)]$ **9b**.

Crystallography

Crystal data. $C_{20}H_8N_2O_{10}Os_3$ **7b**, $M = 1006.88$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.849(2)$, $b = 9.151(2)$, $c = 15.151(4)$ Å, $\alpha = 102.39(2)$, $\beta = 96.52(2)$, $\gamma = 103.02(2)°$, $U = 1150.5(5)$ $Å^3$ (from refinement of 2θ values of 25 independent reflections), $Z = 2$, $D_c = 2.907$ g cm^{-3}, $T = 293 \pm 0.2$ K, dark red rectangular plate 0.05 × 0.05 × 0.20 mm, μ(Mo-Kα) = 16.584 mm^{-1}, $F(000) = 900$.

Data collection and processing. All X-ray measurements were made with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) on a Rigaku AFC7R diffractometer using the ω–2θ scan mode, 4676 reflections collected, 3959 independent ($R_{int} = 0.13$) ($-10 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 10$, $-17 \leqslant l \leqslant 17$; $5.12 \leqslant 2\theta \leqslant 50°$). Semiempirical absorption correction based on ψ-scan data was applied (minimum and maximum transmission factors 0.8188 and 1.0000 respectively).[30]

Structure solution and refinement. The osmium atom positions were determined by direct methods (SHELXTL PLUS)[31] and all non-hydrogen atoms located by subsequent Fourier-difference syntheses. Full-matrix least-squares refinement on F^2 (SHELXL 93)[32] was performed with anisotropic parameters for all non-hydrogen atoms. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme of the form $w^{-1} = [\sigma(F_o^2) + (0.284P)]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced which produced a flat analysis of variance. At final convergence (maximum $\Delta/\sigma = 0.004$) $wR(F^2) = 0.1412$ for all data, $R(F) = 0.0676$ for 2138 observed reflections [$I > 2\sigma(I)$] and 316 parameters. The final difference synthesis showed no Δρ above 1.539 or below −1.482 e $Å^{-3}$, the major features lying near the osmium 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 186/547.

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