Some Remarkable Reactions of the Alkylidyne Cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ ($NC_5H_4C_5H_4N$ = 4,4'-bipyridine) with Electrophiles. Crystal and Molecular Structures of the Novel Water-soluble Dicationic Cluster Complex $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)][BF_4]_2\cdot H_2O$†

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Protonation of the μ_3-alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ **1** ($NC_5H_4C_5H_4N$ = 4,4'-bipyridine) took place in two consecutive steps upon treatment with strong protonic acids such as HBF_4 or CF_3CO_2H in dichloromethane. Initial protonation occurs at the organic ligand to give quantitatively the monocationic dihydrido species $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)]^+$ **2**. In the presence of an excess of acid a second protonation takes place at the metal core and **2** is rapidly converted into a water-soluble dicationic trihydrido cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)]^{2+}$ **3**. The crystal structure of the bis(tetrafluoroborate) salt as its monohydrate has been determined, and reveals the presence of extensive hydrogen bonding. The formation of complexes **1**–**3** is found to be reversible by successive protonation and deprotonation processes, and is reminiscent of typical acid–base equilibria. On the other hand, the reaction of **1** with $[Me_3O]^+BF_4^-$ in dichloromethane afforded the *N*-methylated derivative, $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NMe)]^+$ **4**, which gave another dicationic complex $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NMe)]^{2+}$ **5** on protonation with HBF_4 or CF_3CO_2H. Similar to **3**, complex **5** is very soluble in water.

In a previous communication we have reported the preparation, crystal structure and some chemistry of a dihydridotriosmium alkylidyne carbonyl cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ **1**.[1] In order to test the presumed nucleophilicity of the pendant nitrogen atom of complex **1** it is of primary importance to investigate the reactivity of **1** towards protonic acids. The objective is to establish the site(s) of protonation and the structure(s) of the protonated cluster(s). The possibility of observing intermediates in multistep protonation processes and the ease with which hydrogen can be gained or lost is fundamental to the understanding of the chemistry of this class of compounds.

Herein the reactions of complex **1** with Brönsted acids are described. To pinpoint the site of electrophilic attack on **1** by other electrophiles its reactions with some alkyl carbocations have also been investigated. In particular, methylating reagents are good candidates to compare the electrophilic properties towards **1**.

Results and Discussion

Reaction with Brönsted Acids.—Experimental results show that the triosmium alkylidyne complex $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ **1** undergoes successive protonation steps in the presence of strong acids such as $HBF_4\cdot Et_2O$ or CF_3CO_2H (Scheme 1). In a typical experiment, initial protonation of **1** by 1 equivalent of $HBF_4\cdot Et_2O$ in dichloromethane occurs at the pendant nitrogen atom of the 4,4'-bipyridine ligand to give quantitatively the monocationic dihydrido species $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)]^+$ **2** on the basis of IR and ^1H NMR spectroscopic data (Table 1) and the solution changes from purple to blue. The ν(CO) IR spectrum of **2** in acetone has a very similar spectral pattern to that of the parent complex **1**, exhibiting only a small shift of approximately 2 cm^{-1} to high energy in the same solvent. This suggests that the overall molecular symmetry remains more or less unchanged upon protonation and is consistent with the proposed pyridinium formulation. The positive FAB mass spectrum of **2** shows a molecular ion peak at *m/z* 995. The ^1H NMR spectrum in $(CD_3)_2CO$ shows resonances due to the 4,4'-bipyridyl groups in the range δ 8.35–9.94. A singlet at δ −18.98 is also observed and integration against the aromatic resonances shows that it corresponds to two protons. However, the proton signal arising from the pyridinium NH moiety is not observed, presumably due to broadening *via* coupling to the quadrupolar nitrogen atom.[2]

In the presence of an excess of acid, a second protonation of complex **1** takes place at room temperature along the unbridged Os–Os edge of the alkylidyne metal core and a yellow suspension of the dicationic trihydrido cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)]^{2+}$ **3** results (Scheme 1). The orange-yellow solid was fully characterised by spectroscopic methods (Table 1) and isolated as its BF_4^- salt. The second protonation at the metal centre is indicated by the simplicity of the IR spectrum in the carbonyl region which exhibits four bands in acetone. This spectrum also shows a shift of the main carbonyl bands of *ca.* 32 cm^{-1} to lower energy as compared to the values for **1**. This is consistent with the formation of a dicationic species of much higher symmetry. A KBr disc of the salt also shows similar IR spectral features in the ν(CO) region and an intense ν(BF) absorption in the region 1084–1035 cm^{-1}. The ^1H NMR spectrum of the yellow solution of **3** in $(CD_3)_2CO$ shows little change in the aromatic region aside from a small shift of the resonances. In the hydride region, however, a new, sharp resonance appears at δ −18.38, which integrates as three protons. Similar to **2**, the NH proton is not observed in the ^1H NMR spectrum. It is also worth noting that complex **3** shows an intense molecular ion signal due to $[\mathbf{3} - H]^+$ at *m/z* 995 in the positive FAB mass spectrum, together with signals characteristic of dicationic species. These include the stepwise

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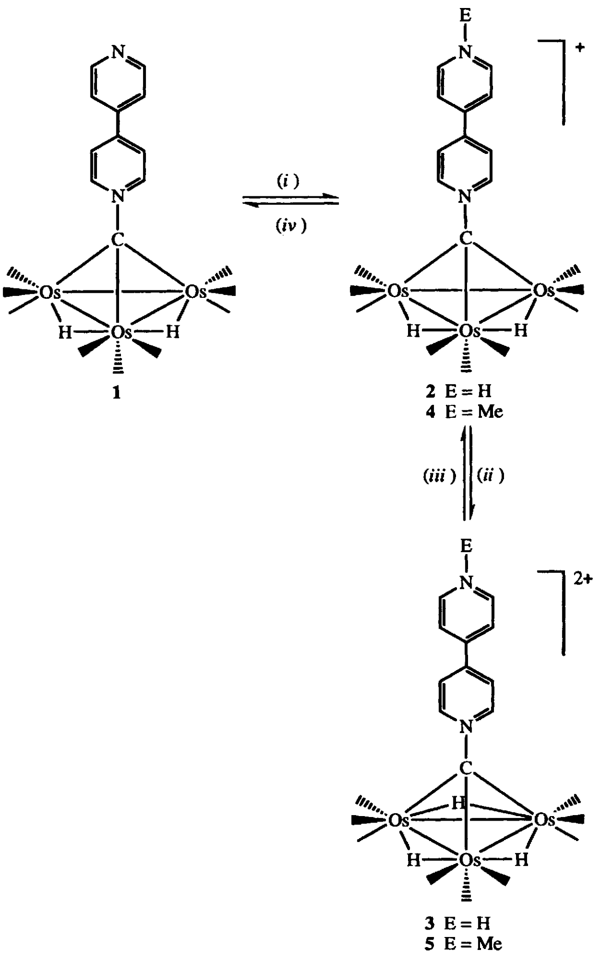
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

loss of carbonyl ligands and the presence of a signal due to [$3 + 2\ BF_4^-$]$^{2+}$ at *m*/*z* 585. The solubility of the BF_4^- salt in dichloromethane is rather limited and depends on the history of the particular sample. However, it is readily soluble in more polar solvents such as acetone, acetonitrile and water without cluster decomposition. Of great importance is the potential application of such a water-soluble complex to the study of aqueous cluster chemistry.

It was also found that the dication **3** readily reverts back to **2** upon deprotonation with KOH–MeOH (1 equivalent) or dbu. Further deprotonation of **2** to give the starting complex **1** can also be achieved but is only observed in the case of an excess of KOH–MeOH. These reversible acid–base processes were monitored by IR and ^1H NMR spectroscopies and the interrelationship among the clusters **1**–**3** is illustrated in Scheme 1. All these protonation and deprotonation reactions are essentially quantitative and instantaneous. However, no evidence of agostic interaction was obtained during the successive protonations of **1**.[3]

In order to establish the molecular geometry of the cationic species and to confirm the nature of the anions, a crystal structure analysis was undertaken. Single crystals of [$Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)$][$BF_4$]$_2$·$H_2O$ were obtained in CD_3CN by slow evaporation at room temperature. The crystal lattice is reinforced by a water molecule providing three hydrogen bonds [N(2) ··· O(10) 2.64, O(10) ··· F(5) 2.710 and O(10) ··· F(4) 2.83 Å (Table 2)], linking adjacent cations and anions together as shown in Fig. 1. However, the relatively long separation O(10) ··· F(2) 3.01 Å indicates the absence of a hydrogen bond between O(10)–H and F(2).

The molecular geometry of the dication **3** is illustrated in Fig. 2 and selected bond lengths and interbond angles are presented in Table 2. The structure contains an Os_3C alkylidyne metal core with almost equivalent Os–C(alkylidyne) bond distances and the average length [2.10(2) Å] is comparable to that observed in **1** [2.07(2) Å].[1] The three osmium atoms form a triangle of sides 2.8805(9), 2.888(1) and 2.887(1) Å consistent with the presence of three Os–H–Os bridges. The three hydride ligands, located by the semiquantitative potential-energy method of Orpen,[4] lie beneath the Os_3 triangular plane. Each



Scheme 1 (*i*) E = H, 1 equivalent of H^+; E = Me, excess of [Me_3O]$^+$-BF_4^-; (*ii*) E = H or Me, excess of H^+; (*iii*) E = H or Me, 1 equivalent of KOH–MeOH or 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu); (*iv*) E = H, excess of KOH–MeOH

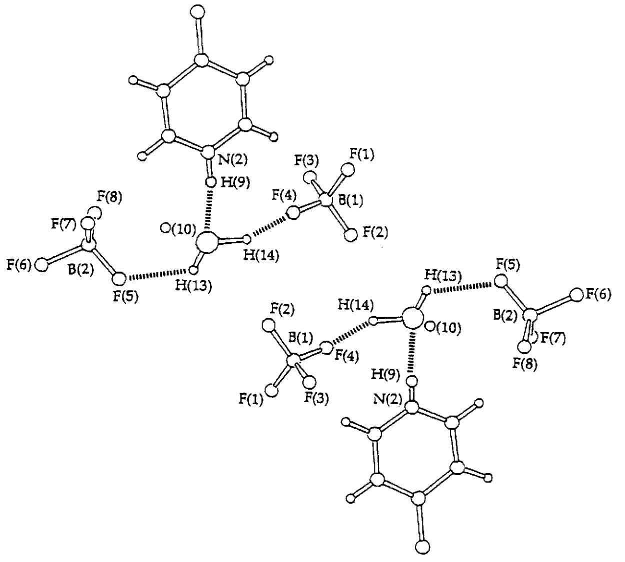


Fig. 1 The three hydrogen bonds (indicated by broken lines) linking one cation and two anions together in the crystal structure of complex **3**

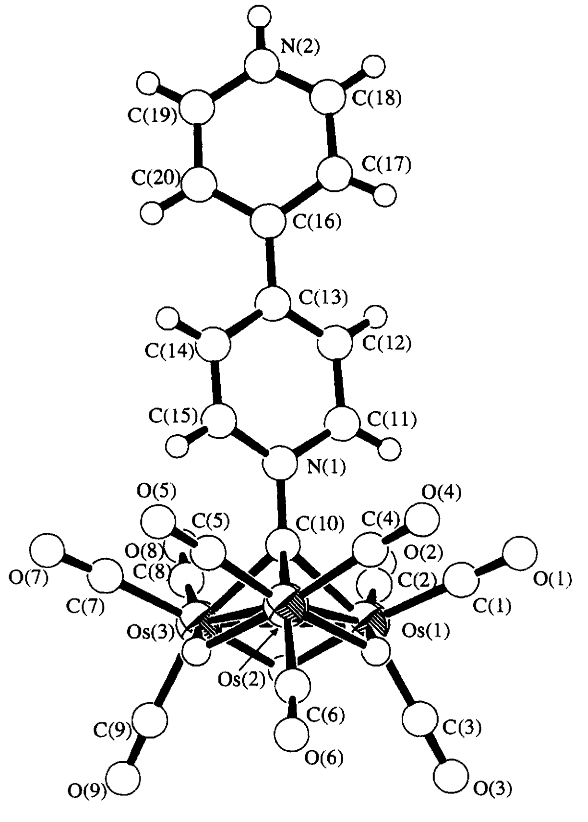


Fig. 2 Molecular structure of the dication [$Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)$]$^{2+}$ **3**

Table 1 Spectroscopic data for complexes **1–5**

Compound	IR,[a] $\tilde{\nu}$(CO)/cm^{-1}	^{1}H NMR, δ[b]	Mass spectrum, *m*/*z*[c]
1	2092m, 2054s,	9.87 (d, 2 H, *J* 7.1, pyridyl H)	994
	2023vs, 1981s,	8.83 (m, 2 H, pyridyl H)	(994)
	1953m, 1937m	8.27 (d, 2 H, *J* 7.1, pyridyl H)	
		8.00 (m, 2 H, pyridyl H)	
		−19.03 (s, 2 H, OsH)	
2	2094m, 2055s,	9.94 (m, 2 H, pyridyl H)	995
	2025vs, 1982s,	9.03 (m, 2 H, pyridyl H)	(995)
	1955m, 1939m	8.35 (m, 4 H, pyridyl H)	
		−18.98 (s, 2 H, OsH)	
3	2124m, 2099vs,	10.16 (m, 2 H, pyridyl H)	995[d]
	2043s, 2029 (sh)	9.01 (m, 2 H, pyridyl H)	(996)
		8.83 (m, 2 H, pyridyl H)	
		8.64 (m, 2 H, pyridyl H)	
		−18.38 (s, 3 H, OsH)	
4	2094m, 2055s,	10.02 (d, 2 H, *J* 6.6, pyridyl H)	1009
	2025vs, 1983s,	9.35 (d, 2 H, *J* 6.6, pyridyl H)	(1009)
	1955m, 1939m	8.88 (d, 2 H, *J* 6.6, pyridyl H)	
		8.42 (d, 2 H, *J* 6.6, pyridyl H)	
		4.69 (s, 3 H, Me)	
		−18.91 (s, 2 H, OsH)	
5	2124m, 2099vs,	10.11 (m, 2 H, pyridyl H)	1009[e]
	2043s, 2029 (sh)	9.27 (d, 2 H, *J* 6.8, pyridyl H)	(1010)
		8.80 (d, 2 H, *J* 6.8, pyridyl H)	
		8.61 (m, 2 H, pyridyl H)	
		4.66 (s, 3 H, Me)	
		−18.42 (s, 3 H, OsH)	

[a] Recorded in Me_2CO. [b] Recorded in $(CD_3)_2CO$, *J* values in Hz. [c] Simulated values given in parentheses. [d] Based on [**3** − H]$^+$. [e] Based on [**5** − H]$^+$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **3** and the geometry of the hydrogen bonds

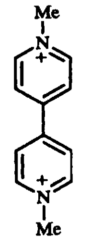
Os(1)–Os(2)	2.8805(9)	Os(1)–Os(3)	2.888(1)
Os(2)–Os(3)	2.887(1)	Os(1)–C(10)	2.10(2)
Os(2)–C(10)	2.10(1)	Os(3)–C(10)	2.09(2)
N(1)–C(10)	1.44(2)	N(2)–H(9)	0.88
Os(2)–Os(1)–Os(3)	60.07(3)	Os(1)–Os(2)–Os(3)	60.09(3)
Os(1)–Os(3)–Os(2)	59.84(2)	Os(1)–C(10)–N(1)	129(1)
Os(2)–C(10)–N(1)	126(1)	Os(3)–C(10)–N(1)	126(1)

D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
N(2)–H(9)···O(10)	0.88	1.77	2.64	168
O(10)–H(13)···F(5)	0.91	2.11	2.71	143
O(10)–H(14)···F(4)	1.08	1.71	2.83	158

osmium atom is bonded to one axial and two equatorial terminal carbonyl ligands and hence the molecular symmetry of the dication is approximately C_{3v}.[5] This is in accord with the solution IR spectral patterns in the ν(CO) region. No unusual structural or bonding feature is present in the organic moiety of complex **3**. Besides, the bonding parameters of the 4,4′-bipyridine ligands in both **1** and **3** are, as expected, very similar. The dihedral angle between the two pyridine rings in **3** is 31.3°, reduced by 14.1° as compared to its precursor complex **1**.[1]

To date, very few cationic cluster species have been structurally characterised,[6–9] and no examples of cationic osmium carbonyl clusters with charges greater than one have been investigated by X-ray diffraction although some dicationic cluster species have previously been prepared.[9–11] Hence, the isolation of the triosmium alkylidyne cluster **3** in this study represents the first structurally characterised example of a dicationic osmium carbonyl cluster.

Methylation.—Initial attempts to methylate the pendant pyridyl ring in complex **1** with iodomethane failed to give any observable reaction. The use of $[Me_3O]^+BF_4^-$ as the methylating agent in dichloromethane, however, led to a blue solution and some deep blue solid gradually precipitated. The solid is only sparingly soluble in dichloromethane but readily dissolves in acetone. Based on the spectroscopic data obtained (Table 1), it was characterised as the *N*-methylated derivative of **1**, $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NMe)]^+$ **4** (Scheme 1). The IR spectrum in the ν(CO) region in acetone is almost identical to that of **2**, suggesting monocationic character and very similar molecular symmetry. The positive FAB mass spectrum shows an intense molecular ion peak at *m*/*z* 1009 (15 units greater than for **1**) and this corresponds to the addition of one methyl group to the starting cluster **1**. Stepwise loss of carbonyl ligands is also observed. The ^{1}H NMR spectrum in $(CD_3)_2CO$ gives rise to four sets of doublets, each with *J* 6.6 Hz and they are assigned to the protons of the 4,4′-bipyridine ligand. A singlet hydride signal is also observed at δ −18.91 which integrates as two protons. A prominent methyl resonance appears at δ 4.69, which integrates in a ratio of 3:2 with the hydride resonance. Chemical shifts in the range δ 4.5–5.0 for methyl protons are typical of a *N*-methyl group and is consistent with the methyl signal observed for **I** (δ 4.50 in D_2O). Indeed, compounds **5** and **I** bear a close relationship in the sense that the cluster core $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}C)$ also functions as an electron sink and hence another positive charge resides on the nitrogen atom directly attached to the cluster framework.[12,13]



I

On addition of more $[Me_3O]^+BF_4^-$, further methylation of complex **4** is not observed. However, protonation along the non-bridged Os–Os edge occurs when a sample of **4** in solution is treated with a drop of $HBF_4{\cdot}Et_2O$ and the solution changes from blue to yellow. Quantitative conversion into $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NMe)]^{2+}$ **5** is observed within a minute by IR and ^1H NMR spectroscopies (Scheme 1). Complex **5**, similar to **3**, is soluble in acetone and water. The solution IR spectrum in acetone displays four ν(CO) absorption bands and is analogous to that of complex **3**. High molecular symmetry is indicated. The ^1H NMR spectrum, as expected, shows aromatic resonances in the range δ 8.61–10.11 in $(CD_3)_2CO$ and a strong methyl signal at δ 4.66. A sharp hydride signal also appears at δ −18.42 which integrates as three protons against the methyl resonance. In addition, the positive FAB mass spectrum exhibits an intense molecular ion peak at *m*/*z* 1009, together with sequential loss of carbonyls. A less-intense peak is also observed at *m*/*z* 1097 which arises from the ionic fragment $[\mathbf{5} + BF_4^-]^+$. Deprotonation of **5** to give back **4** can be achieved with dbu or KOH–MeOH but regeneration of the starting complex **1** is presently not accessible as it involves cleavage of the strong N–Me bond.

The difference in chemical reactivities between the isolobal fragments CH_3^+ and H^+ towards the cationic cluster species **4** can be attributed to the steric requirement along the non-bridged Os–Os bond. This edge is a less-hindered site for protonation but steric congestion is much more pronounced for the methyl carbocation. In spite of this a bridging methyl group along an Os–Os edge in $[Os_3H(CO)_{10}Me]$ has previously been reported by Calvert and Shapley[14] and shown to involve a C···H···Os interaction. Another counterexample for the different reactivity patterns exhibited by these two fragments towards triosmium carbonyl clusters is clearly provided by the protonation and methylation of $[Os_3H(\mu\text{-}CO)(CO)_{10}]^-$.[15,16] The *O*-protonated triosmium carbonyl cluster '$[Os_3H(\mu\text{-}COH)(CO)_{10}]$' is not observed during protonation and the proton adds at the metal framework. This appears to contrast with the situation in **1** where the more basic site is the free pyridyl nitrogen atom, followed by the cluster core.

Experimental

Materials and Methods.—All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques and were monitored by solution IR spectroscopy (CO stretching region). Solvents were purified and distilled from appropriate drying agents[17] and stored under nitrogen prior to use. The starting alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ was prepared as described previously.[1] Trimethyloxonium tetrafluoroborate was obtained from Aldrich and used as received. Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer using 0.5 mm solution cells, ^1H NMR spectra on a JEOL GSX 270FT-NMR spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ (δ 0). Mass spectra were recorded on a Finnigan MAT 95 instrument with the fast atom bombardment (FAB) technique and the matrices *m*-nitrobenzyl alcohol (for **1**–**3**) and α-thioglycerol (for **4** and **5**).

Table 3 Crystal and data collection parameters for complex **3**

Formula	$C_{20}H_{14}B_2F_8N_2O_{10}Os_3$
M	1186.55
Colour, habit	Orange-yellow, block
Crystal size/mm	0.18 × 0.24 × 0.30
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	9.016(1)
b/Å	30.435(9)
c/Å	11.186(3)
β/°	102.72(2)
U/Å^3	2993(2)
Z	4
D_c/g cm^{-3}	2.633
μ(Mo-Kα)/cm^{-1}	128.24
F(000)	2152
T/K	298
2θ range/°	2.0–45.0
Scan type	ω–2θ
Scan speed in ω/° min^{-1}	1.08 to 16.48
Scan range/°	0.75 + 0.35 tan θ
Background measurement	25% at both ends
Reflections collected	4289
Independent reflections	4096
Observed reflections	2627 $[F_o > 3\sigma(F_o)]$
Weighting scheme	$w = 4F_o^2/[\sigma^2(F_o^2) + 0.016\,(F_o^2)^2]$
R, *R*′	0.040, 0.048
Goodness of fit	1.50
Largest Δ/σ	0.04
Number of parameters	233
Residual extrema in final difference map (close to Os)/e Å^{-3}	1.71 to −1.19

Protonation of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ **1**.—To a CH_2Cl_2 solution (5 cm^3) of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ **1** (10 mg, 0.01 mmol) was added 1 equivalent of $HBF_4{\cdot}Et_2O$ (0.01 mmol). A change from purple to blue was observed at once. Solution IR spectroscopy indicated the formation of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)]^+$ **2** in quantitative yield. Addition of one drop of $HBF_4{\cdot}Et_2O$ to the resulting solution of **2** led to the rapid formation of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NH)]^{2+}$ **3** (8 mg, 80%) which slowly precipitated in the form of a yellow solid. Compound **3** was obtained as a pure BF_4^- salt by filtration and removal of all volatile components *in vacuo*. Recrystallisation from MeCN gave orange-yellow crystals.

Treatment of complex **3** in acetone with 1 equivalent of KOH–MeOH or dbu resulted in a change back to the monocationic species **2** as evident from solution IR spectroscopy. Further deprotonation of **2** to give the starting complex **1** was achieved upon the addition of an excess of KOH–MeOH.

Methylation of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4N)]$ **1**.—A suspension of $[Me_3O]^+BF_4^-$ (7 mg, 0.05 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of complex **1** (10 mg, 0.01 mmol) in the same solvent (5 cm^3). Reaction was instantaneous, accompanied by a rapid change from purple to deep blue. Slow evaporation of part of the solvent gave some blue powder which was characterised as consisting of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4C_5H_4NMe)]^+$ **4** (6 mg, 60%) on the basis of spectroscopic data. Addition of more $[Me_3O]^+BF_4^-$ (7 mg) to a solution of **4** (6 mg) in acetone (5 cm^3) revealed no colour change, and no further methylation was observed. However, protonation of **4** ensued upon addition of $HBF_4{\cdot}Et_2O$ (1 equivalent) to an acetone solution (5 cm^3) of **4** (6 mg). A change from blue to yellow was observed immediately. The solution was stirred for 5 min and the solvent removed under reduced pressure. The yellow residue was identified as the BF_4^- salt of the dicationic complex [Os$_3$-

Table 4 Atomic coordinates for the salt **3** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.166 24(8)	0.174 77(3)	0.183 77(7)	C(1)	0.120(2)	0.120 8(7)	0.247(2)
Os(2)	0.446 78(8)	0.147 09(2)	0.124 25(7)	C(2)	−0.038(2)	0.189 1(7)	0.116(2)
Os(3)	0.287 67(8)	0.222 81(2)	0.004 17(7)	C(3)	0.177(2)	0.201 2(7)	0.342(2)
F(1)	0.797(3)	0.068 9(8)	1.111(2)	C(4)	0.419(2)	0.087 2(8)	0.167(2)
F(2)	0.709(3)	0.025 8(7)	0.963(2)	C(5)	0.548(2)	0.133 0(6)	0.000(2)
F(3)	0.889(4)	0.013(1)	1.117(3)	C(6)	0.634(2)	0.152 3(7)	0.247(2)
F(4)	0.691(4)	0.012(2)	1.134(3)	C(7)	0.370(2)	0.221 5(8)	−0.138(2)
F(5)	0.556(3)	0.118 2(7)	0.646(1)	C(8)	0.098(2)	0.240 1(7)	−0.090(2)
F(6)	0.515(2)	0.166 4(5)	0.494(1)	C(9)	0.361(2)	0.281 2(7)	0.053(2)
F(7)	0.507(2)	0.095 2(6)	0.462(2)	C(10)	0.226(2)	0.157 0(5)	0.019(1)
F(8)	0.324(2)	0.122 5(8)	0.522(3)	C(11)	0.018(2)	0.105 8(7)	−0.068(2)
O(1)	0.089(2)	0.087 5(6)	0.286(1)	C(12)	−0.065(2)	0.081 5(7)	−0.171(2)
O(2)	−0.163(2)	0.198 7(5)	0.075(1)	C(13)	−0.014(2)	0.077 2(6)	−0.273(2)
O(3)	0.181(2)	0.218 1(5)	0.435(1)	C(14)	0.120(2)	0.099 5(6)	−0.280(2)
O(4)	0.401(2)	0.052 6(7)	0.197(2)	C(15)	0.194(2)	0.123 7(6)	−0.185(2)
O(5)	0.611(2)	0.125 8(5)	−0.079(1)	C(16)	−0.103(2)	0.052 1(6)	−0.376(2)
O(6)	0.752(2)	0.156 7(5)	0.315(1)	C(17)	−0.191(2)	0.015 2(7)	−0.359(2)
O(7)	0.423(2)	0.222 5(6)	−0.222(2)	C(18)	−0.275(2)	−0.006 9(7)	−0.456(2)
O(8)	−0.020(2)	0.246 2(6)	−0.152(1)	C(19)	−0.195(3)	0.039 1(8)	−0.589(2)
O(9)	0.408(2)	0.314 8(7)	0.085(2)	C(20)	−0.109(2)	0.062 7(8)	−0.496(2)
O(10)	0.473(2)	0.040 6(5)	0.730(1)	B(1)	0.770	0.029	1.078
N(1)	0.146(1)	0.129 5(5)	−0.080(1)	B(2)	0.460	0.126	0.541
N(2)	−0.277(2)	0.004 7(6)	−0.567(2)				

$(\mu\text{-H})_3(CO)_9(\mu_3\text{-CNC}_5H_4C_5H_4NMe)]^{2+}$ **5** (5 mg, 83% based on **4**).

Compound **5** readily reverted back to the monocationic complex **4** upon deprotonation by dbu or KOH–MeOH, as shown by solution IR spectroscopy.

X-Ray Data Collection, Solution and Refinement.—An orange-yellow crystal of complex **3** suitable for a diffraction study was mounted in a Lindemann glass capillary. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Three check reflections were monitored periodically throughout data collection and showed no significant variations. All intensity data were corrected for Lorentz polarisation effects and an absorption correction by the ψ-scan method was also applied.[18] Crystal data and a summary of data collection and structure solution parameters are shown in Table 3. The structure was solved by direct methods (SIR 88)[19] and refined by full-matrix least-squares analysis with Os atoms anisotopic. Hydrogen atoms attached to nitrogen and oxygen atoms (H_2O) were located by a Fourier-difference synthesis, while other hydrogen atoms on the 4,4′-bipyridine carbon atoms were generated in their idealised positions (C–H 0.95 Å). Three hydride atom positions were estimated by potential-energy calculations. All calculations were carried out on a Silicon Graphics computer using the TEXSAN package.[20] Final atomic coordinates for the non-hydrogen atoms are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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