(Aminoethyne)triosmium Clusters

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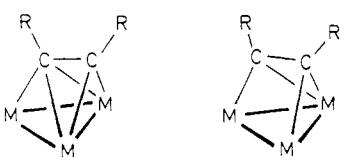
The cluster $[Os_3H(C{\equiv}CH)(CO)_9]$ (1) forms adducts with pyridine, ammonia, and diethylamine by nucleophilic attack at the α-carbon atom of the triply bridging ethynyl ligand. The zwitterionic pyridine adduct $[Os_3H(C_5H_5NC_2H)(CO)_9]$ (2) readily loses pyridine in the absence of free pyridine to regenerate 1, but the amino derivatives $[Os_3H_2(\mu_3\text{-}R_2NC_2H)(CO)_9]$ (**3a**, R = H; **3b**, R = Et) do not lose R_2NH even under acidic conditions. Compounds 3 do not adopt the normal μ_3,η^2 parallel structure normally found for clusters of the type $[Os_3H_2(\text{alkyne})(CO)_9]$, including compound 4, analogous to compound 3 but with the NR_2 group replaced by OEt. The structure of the diethylamino compound **3b** had been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 13.722 (3) Å, b = 12.576 (4) Å, c = 12.605 (3) Å, β = 106.59 (2)°, V = 2084 (1) Å^3, and Z = 4. The structure was refined to R = 0.051. The C–C axis of the organic ligand is perpendicular to an Os–Os bond rather than parallel as in the ethoxy analogue 4. The cluster is considered to be dipolar with the 1,1,2-triyl ligand $Et_2N{=}CCH$ carrying substantial positive charge at nitrogen. The dynamic behavior of the diethylamino cluster **3b** involves hydride migration at osmium to generate a time-averaged symmetry plane which is faster than rotation about the C=N bond, but the attachment of the Et_2NC_2H ligand as a whole to the Os_3 triangle is rigid. Rotation about the C=N bond (but not rotation of the whole ligand nor hydride migration) is catalyzed by acid. With an excess of acid, however, protonation is not at nitrogen but at osmium to give the clusters $[Os_3H_3(R_2NC_2H)(CO)_9]^+$.

Introduction

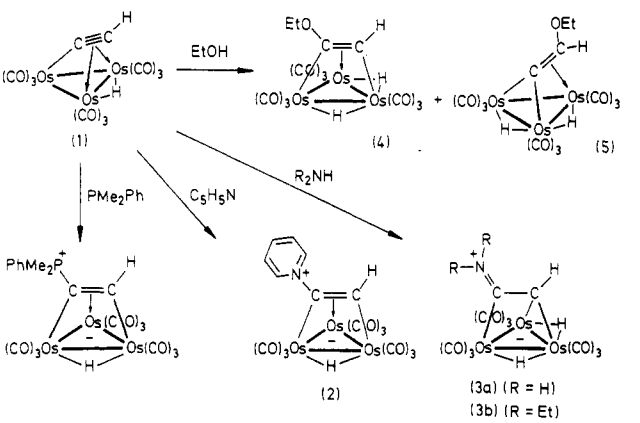
Triply bridging alkynes adopt perpendicular geometries in 46-valence electron clusters such as $[Fe_3(Ph_2C_2)(CO)_9]$,[1] $[RuFe_2(Ph_2C_2)(CO)_9]$,[2] and $[Os_3(Ph_2C_2)(CO)_7(Ph_2PCH_2PPh_2)]$,[3] which may regarded as closo clusters with trigonal-bipyramidal M_3C_2 skeletons (X). More commonly, however, trinuclear alkyne clusters have 48-valence electrons with the alkyne parallel to one metal–metal edge as in $[Os_3(Ph_2C_2)(CO)_{10}]$[4] and in many examples of the type $[Os_3H_2(R_2C_2)(CO)_9]$.[5] These clusters are nido with the carbon atoms in the basal plane of the square-pyramidal M_3C_2 skeleton (Y). Theoretical aspects



(X) (Y)

of alkyne orientations in trinuclear clusters have been discussed.[6] An example we have studied structurally and by variable-temperature NMR is $[Os_3H_2(EtOC_2H)(CO)_9]$ (and its vinylidene isomer).[7,8] Although the C–C direction is approximately parallel to one Os–Os edge, there is some distortion from this idealized geometry (Figure 1). There

Scheme I



is possibly some contribution to the parallel form (A) from form (B) with π-donation from group X (OEt in this case) (Figure 2). Substituents X with strong π-donor ability would favor a geometry with the C–C direction perpendicular to the Os–Os edge. As well as producing some geometric distortion, the ethoxy group lowers the barrier to alkyne rotation with respect to the metal triangle. Ligand rotation in 4 determined from the coalescence of the diastereotopic CH_2 protons is at the same rate as hydride exchange from which it is deduced that ligand rotation is faster than hydride migration, an unusual situation. The energy barrier to alkyne rotation in form A via the intermediate C would be lowered if C were stabilized by a contribution from B. Here we consider the situation when X is a much better π-donor (X = NH_2 or NEt_2) and show that the crystal structure of $[Os_3H_2(XC_2H)(CO)_9]$ (X = NEt_2) is of type B (Figure 2) and that this is sufficiently lower in energy than form A as to suppress the appearance of ligand rotation effects in the NMR spectra, although other dynamic effects do operate.

Results and Discussion

Synthesis and Characterization of Adducts of Cluster 1. Whereas $[Os_3H(C{\equiv}CH)(CO)_9]$ (1) reacts with ethanol to give two isomers: $[Os_3H_2(EtOC{\equiv}CH)(CO)_9]$

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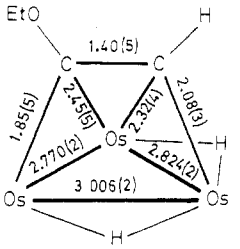

Figure 1. Structural details for the parallel attachment of the ethoxyethyne ligand in the cluster $[Os_3H_2(EtOC_2H)(CO)_9]$ (**4**).[8]

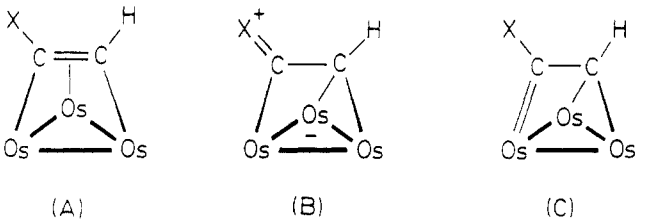

Figure 2. Three descriptions of alkyne (XC≡CH) coordination in trinuclear clusters indicating the effects of π-donation of the substituent X.

(**4**) (78%) (product of attack at the α-carbon atom) and $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**5**) (21%) (by attack at the β-carbon atom), attack of all other nucleophiles we have used is exclusively at the α-position (e.g. $EtNH_2$, NH_3, pyridine, PMe_2Ph) (Scheme I).[7-9] Other studies on nucleophilic additions at μ-alkynyl ligands in dinuclear compounds[10] or at μ_3-alkynyl ligands in other trinuclear clusters[11] have shown that the site of attack can depend upon the nucleophile used and other obvious features such as the metal or the other ligands present. Sometimes there is a fine balance of effects operating: diethylamine adds at the α-site but cyclohexylamine at the β-site of $[M_2(C_2Ph)(PPh_2)(CO)_6]$ (M = Fe, Ru, or Os).[10b] The presence of the dimethylphenylphosphonium-substituted μ_3-ethyne ligand in the PMe_2Ph adduct of **1** formed by nucleophilic attack at the α-carbon atom has been confirmed by an X-ray structure.[9]

The pyridine adduct of **1**, $[Os_3H(C_5H_5NC_2H)(CO)_9]$ (**2**), is only stable in solution in the presence of an excess of pyridine. Orange crystals are formed by addition of pentane to a neat pyridine solution of **1**, but a solution of these in cyclohexane gives the IR spectrum of **1**. The IR spectrum recorded in cyclohexane with pyridine present contains ν(CO) absorptions at wavenumbers lower by 30–40 cm^{-1} than for the parent cluster **1** (even lower than for the PMe_2Ph adduct), and we formulate the solution species as a zwitterion with a pyridinium center and a negative charge at the osmium atoms. The ^1H NMR spectrum of **1** in neat C_5D_5N solution is consistent with the formation of $[Os_3H(C_5D_5NC_2H)(CO)_9]$.

In contrast compounds **3a** and **3b** may be isolated as colorless crystals and show no tendency in solution to lose amine to revert to the ethynyl compound **1** even in acidic solutions (see below). These are dihydrido clusters resulting from amine attack at the α-carbon atom followed by proton transfer to the metal atoms. ^1H NMR spectra of **3b** at −90 °C in CD_2Cl_2 show that the ethyl groups and

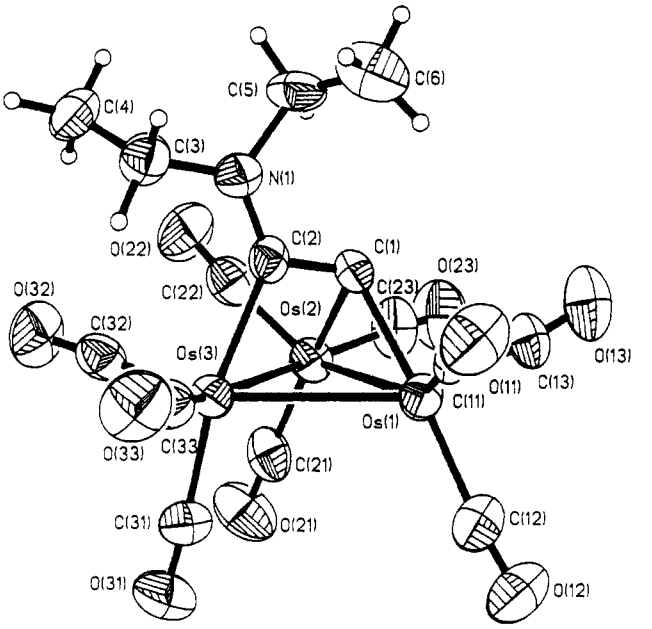

Figure 3. Molecular structure of the (diethylamino)ethyne cluster $[Os_3H_2(Et_2NC_2H)(CO)_9]$ (**3b**).

the hydride ligands are nonequivalent and that the CH_2 protons of the ethyl groups are diastereotropic although this is only clearly resolved for one of these groups. The IR spectra of **3a** and **3b** around 2000 cm^{-1} are extremely similar, showing that these compounds are isostructural. ν(CO) frequencies for each are lower than those for the ethoxy analogue $[Os_3H_2(EtOC_2H)(CO)_9]$ (**4**) but not as low as those for the pyridine adduct **2**. Cluster **4** has structure A (Figure 2), and the data for clusters **3** indicate a greater accumulation of negative charge at the metal atoms in **3** as expected for structure B. The ^1H NMR signals for triply bridging RC_2H groups are commonly at quite low field, often in the range δ 9–10. However, there is considerable variation of the ^1H NMR chemical shifts of the terminal alkyne proton in the complexes $[Os_3H_2(XC_2H)(CO)_9]$. For X = alkyl or aryl the signals are rather low field (for example, δ 8.45 when X = Ph and δ 7.30 when X = Me)[12] but are to significantly higher field when X = OEt (δ 6.24),[8] NH_2 (δ 5.45), or NEt_2 (δ 5.70). These chemical shift differences seem to be too large to result only from the differential electronegativities of X but point to major differences in the bonding of XC_2H to the cluster, which we believed would result from variation in the π-donation of group X.

The single-crystal *X*-ray structure of **3b** was determined to establish whether a parallel geometry like that of the $EtOC_2H$ cluster is adopted or, alternatively, whether the π-donation from Et_2N is sufficient to rotate the ligand into a perpendicular orientation.

Structure of 3b. The molecular structure of (3b) is shown in Figure 3. The atomic coordinates and selected bond lengths and angles are in Tables I and II, respectively. Overall the cluster is as expected with a triply bridging Et_2NC_2H ligand capping a triangle of $Os(CO)_3$ units. No hydrogen atoms were located: those on the ethyl groups were placed in idealized positions in the final stages of refinement and allowed to refine as groups. Carbon atom C(1) carries the ethyne hydrogen atom. It can be seen that there is a coordination site for it there but not at C(2). By commonly used criteria we know that the hydride ligands

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Table I. Atomic Coordinates (×10⁴) for 3b

	x	y	z
Os(1)	3940 (1)	662 (1)	1793 (1)
Os(2)	2295 (1)	−794 (1)	1189 (1)
Os(3)	3010 (1)	−317 (1)	3452 (1)
C(11)	4371 (11)	1975 (12)	2507 (14)
O(11)	4685 (10)	2729 (10)	2965 (13)
C(12)	5335 (13)	202 (12)	1955 (15)
O(12)	6142 (10)	−12 (11)	1990 (13)
C(13)	3753 (13)	1305 (12)	375 (13)
O(13)	3577 (12)	1702 (12)	−471 (11)
C(21)	2597 (14)	−2276 (13)	1324 (13)
O(21)	2822 (13)	−3165 (10)	1442 (13)
C(22)	924 (13)	−951 (13)	1209 (13)
O(22)	88 (10)	−1005 (14)	1184 (14)
C(23)	1947 (15)	−742 (15)	−398 (16)
O(23)	1769 (14)	−791 (14)	−1334 (12)
C(31)	3787 (12)	−1612 (14)	3828 (15)
O(31)	4202 (11)	−2438 (11)	4065 (13)
C(32)	1893 (12)	−967 (13)	3799 (13)
O(32)	1231 (10)	−1350 (11)	4025 (12)
C(33)	3547 (12)	414 (14)	4829 (13)
O(33)	3841 (10)	866 (12)	5622 (12)
N(1)	1462 (9)	1596 (10)	2762 (10)
C(1)	2309 (11)	895 (11)	1461 (13)
C(2)	2111 (10)	931 (10)	2538 (12)
C(3)	1221 (11)	1613 (14)	3816 (13)
C(4)	156 (14)	1181 (18)	3748 (16)
C(5)	952 (12)	2416 (14)	1940 (13)
C(6)	1583 (18)	3387 (17)	1954 (18)

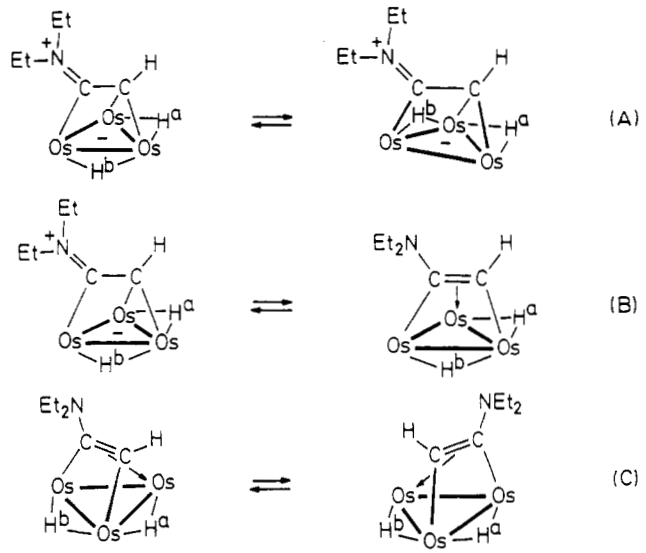
Table II. Selected Bond Lengths (Å) and Angles (deg) for 3b

Os(1)–Os(2)	2.832 (1)	Os(3)–C(31)	1.926 (16)
Os(1)–Os(3)	3.001 (1)	C(31)–O(31)	1.178 (20)
Os(2)–Os(3)	2.807 (1)	Os(3)–C(32)	1.891 (17)
Os(1)–C(11)	1.889 (16)	C(32)–O(32)	1.132 (19)
C(11)–O(11)	1.128 (19)	Os(3)–C(33)	1.917 (16)
Os(1)–C(12)	1.952 (17)	C(33)–O(33)	1.120 (20)
C(12)–O(12)	1.127 (20)	Os(1)–C(1)	2.173 (14)
Os(1)–C(13)	1.912 (15)	Os(2)–C(1)	2.144 (15)
C(13)–O(13)	1.139 (19)	Os(3)–C(2)	2.120 (14)
Os(2)–C(21)	1.901 (17)	C(1)–C(2)	1.459 (20)
C(21)–O(21)	1.155 (20)	N(1)–C(2)	1.307 (18)
Os(2)–C(22)	1.897 (18)	N(1)–C(3)	1.458 (20)
C(22)–O(22)	1.140 (21)	N(1)–C(5)	1.487 (19)
Os(2)–C(23)	1.921 (19)	C(3)–C(4)	1.536 (25)
C(23)–O(23)	1.138 (22)	C(5)–C(6)	1.490 (28)
Os(3)–Os(1)–Os(2)	57.4 (1)	Os(2)–C(1)–Os(1)	82.0 (5)
C(1)–Os(1)–Os(2)	48.6 (4)	C(2)–C(1)–Os(1)	106.1 (9)
C(1)–Os(1)–Os(3)	64.8 (4)	C(2)–C(1)–Os(2)	100.6 (8)
Os(3)–Os(2)–Os(1)	64.3 (1)	C(1)–C(2)–Os(3)	104.5 (9)
C(1)–Os(2)–Os(1)	49.5 (4)	N(1)–C(2)–Os(3)	132.9 (11)
C(1)–Os(2)–Os(3)	69.0 (4)	N(1)–C(2)–C(1)	122.5 (13)
Os(2)–Os(3)–Os(1)	58.3 (1)	C(3)–N(1)–C(2)	123.3 (12)
C(2)–Os(3)–Os(1)	67.4 (4)	C(5)–N(1)–C(2)	120.4 (13)
C(2)–Os(3)–Os(2)	67.8 (4)	C(5)–N(1)–C(3)	116.3 (12)

Os–C–O from 174.7 to 178.9

bridge the Os(1)–Os(2) and Os(1)–Os(3) edges. In particular the smallest four Os–Os–CO angles for the bridged Os(1)–Os(3) edge are 99.3 (4), 107.8 (5) (equatorial), 113.7 (4), and 101.7 (5)° (axial) and for the bridged Os(1)–Os(2) edge are 97.7 (5), 101.7 (5) (equatorial), 118.0 (5), and 121.3 (4)° (axial), whereas the corresponding angles for the nonbridged Os(2)–Os(3) edge are 94.1 (5), 94.0 (5) (equatorial), 96.4 (5), and 94.6 (5)° (axial), which are on an average 10.8 and 14.9° less than for the other edges. The Os(1)–Os(3) length of 3.001 (1) Å is the longest because of the hydride bridge, but the length of the other hydride-bridged edge, Os(1)–Os(2) [2.832 (1) Å], is only marginally longer than the nonbridged edge, Os(2)–Os(3) [2.807 (1) Å]; bond lengthening caused by the bridging hydride is counteracted by the single C(1) atom bridge which draws Os(1) and Os(2) together.

Scheme II



The geometry of the Et_2NC_2H ligand is consistent with the representation of **3b** in Scheme I. Carbon atom C(1) bonds to Os(1) and Os(2) [C(1)–Os(1) = 2.174 (14) and C(1)–Os(2) = 2.144 (15) Å] whereas C(2) is bonded only to Os(3) [C(2)–Os(3) = 2.120 (14) Å]. The distances to the other osmium atoms are nonbonding [C(2)–Os(1) = 2.934 and C(2)–Os(2) = 2.807 Å]. The bonding Os–C distances are consistent with σ-bonds and are shorter than Os–C distances in η^2-interactions. σ-Os–C bonds are typically <2.2 Å whereas η-Os–C bonds are >2.3 Å (see Figure 1, for example). In another μ_3-triyl cluster, $[Os_3H(\mu_3\text{-}CF_3CCHCF_3)(CO)_9]$, the Os–C distances are in the same range [2.06, 2.11, and 2.19 Å] as those in 3b.[13] Atoms C(2) and N(1) both have almost planar coordination geometries with the sum of their bond angles being 359.9 and 360.0° respectively. The atoms C(1), C(2), N(1), C(3), and C(5) form a closely planar set with atom C(2) furthest from the best plane through these atoms by 0.03 Å. The dihedral angle between this plane and the Os_3 plane is 89.9°, totally consistent with the bonding mode B in Figure 2. This plane would tilt by about 60–75° for a μ_3,η^2-alkyne system such as in **4**. The C(1)–C(2) length [1.46 (2) Å] and the C(2)–N(1) length [1.31 (2) Å] are also more compatible with this bonding mode (B) than any other. The C=N bond length in imines is 1.27 Å, the C—N length in amines is 1.47 Å, and therefore C(3)—N(1) [1.46 (2) Å] and C(5)—N(1) [1.49 Å] are typical single bonds whereas the C(2)–N(1) length is close to that of a double bond.

Intramolecular Behavior of Clusters 3a and 3b. The ^1H NMR spectrum of **3b** in CD_2Cl_2 at −90 °C is consistent with the molecular structure in the crystal. One of the nonequivalent ethyl groups exhibits diastereotopic CH_2 protons (AB multiplet of quartets at δ 3.46 and 3.41), but although the other ethyl group must also have diastereotopic CH_2 protons, these appear as a simple quartet (δ 3.53). Presumably it is the distal ethyl group [C(5)C(6) in Figure 3] which is not sensitive to the asymmetry of the metal cluster. Two singlets (δ −17.3 and −20.1) are observed for the nonequivalent hydride ligands. The first change in the spectrum on raising the temperature is a transformation of the AB multiplet of quartets to a simple quartet at 20 °C, a broad unresolved signal being observed at −20 °C. This process is ascribed to the hydride mi-

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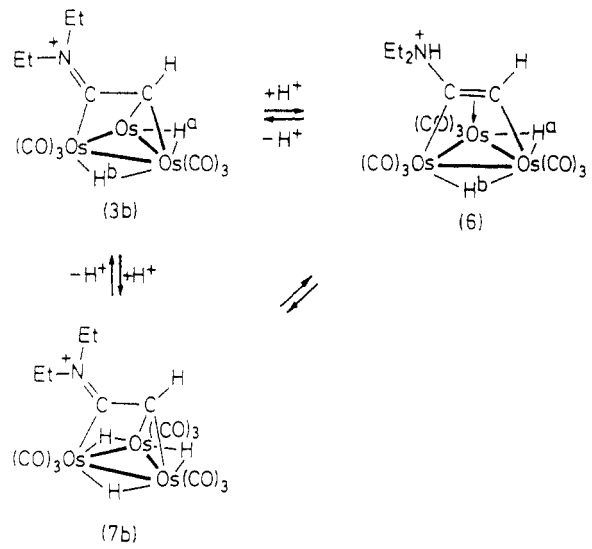
Scheme III



gration process (A) which generates a time-averaged plane of symmetry (Scheme II). Similar degenerate processes have been commonly observed for other symmetry-related molecules, for example, $[Os_3H_2(C{=}CH_2)(CO)_9]$[14] and $[Os_3H_2(Me_2XCH)(CO)_9]$ (X = N[15] or P[16]). Hydride exchange occurs more slowly and coalescence of signals at δ −16.65 and −19.72 is observed for toluene-d_8 solutions at 55 °C (200 MHz; ΔG_{328} = 14.6 ± 0.3 kcal mol^{-1}), but there is no evidence from these spectra for exchange of the ethyl groups. Separate ethyl resonances are clearly resolved even at 100 °C in toluene-d_8 solution. A mechanism for hydride exchange might have been μ_3-ligand rotation by interconversion of perpendicular and parallel isomers, process B (Scheme II). The parallel form would need to undergo rapid enantiomerization as observed for many such parallel alkyne compounds, process C (Scheme II). However, the lack of ethyl exchange indicates the rigidity of the aminoethyne ligand, and the observed hydride exchange almost certainly occurs via hydride migration. Hence, not only is the perpendicular species the lowest energy form for **3b**, but also the parallel form is sufficiently higher in energy (>6 kcal mol^{-1} higher) to be inaccessible in the dynamic behavior of **3b**.

In contrast to the above behavior we have shown for the corresponding ethoxy compound $[Os_3H_2(CHCOEt)(CO)_9]$ (**4**) that the rates of hydride exchange and exchange of the diastereotopic ethoxy CH_2 protons are the same as each other over a temperature range.[8] A single process was proposed involving mobility of the organic ligand entirely analogous to process C (Scheme II). In this case there is a fine energetic balance between the parallel and perpendicular geometries.

Ethyl exchange in **3b** is, however, catalyzed by acid. Addition of CF_3CO_2H (1.0 mol/mol of Os_3) to a $CDCl_3$ solution of **3b** at 25 °C leads to an immediate collapse of the ethyl resonances into two broad structureless resonances. Further additions of acid up to 5.0 mol/mol of Os_3 successively change these resonances into a single quartet and triplet. Reversible protonation at nitrogen to give $[Os_3H_2(Et_2NHC_2H)(CO)_9]^+$ (**6**) (Scheme III) would account for this acid-catalyzed ethyl exchange, but this must occur without hydride exchange as there is no effect at all on the hydride resonances. The parallel alkyne species **6** would need to be sufficiently rigid to account for the lack of acid-induced enhancement of hydride exchange. No detectable shift of equilibrium toward **6** is observed even with an excess of acid, but on standing for 24 h there is a total conversion to the osmium-protonated form $[Os_3H_3(Et_2NC_2H)(CO)_9]^+$ (**7b**), which is totally rigid at ambient temperatures [hydride resonances at δ −16.65 (1 H) and δ −20.70 (2 H)]. Cation **7b** could be formed by direct protonation of **3b** at the metal atoms or by an intramolecular isomerization of **6**. Protonation at the metal to give **7b** understandably prevents further protonation at nitrogen that would lead to ethyl exchange even with an excess of acid present. As well as carrying a positive charge the strength of the C=N bond in **7b** is expected to be stronger than in **3b**. Note than even with an excess of acid **3b** does not liberate Et_2NH to re-form the ethynyl cluster **1** so that reversible loss of amine is ruled out as a mechanism for ethyl exchange.

The cluster $[Os_3H_2(NH_2C_2H)(CO)_9]$ (**3a**) in CD_2Cl_2 also undergoes hydride exchange (T_c = 15 °C; ΔG_{288} = 12.6 ± 0.5 kcal mol^{-1}), but in this case the exchange of the NH_2 protons (^{1}H NMR doublets at δ 7.00 and 6.31) is only a little slower (T_c = 35 °C; 200 MHz: ΔG_{305} = 14.4 ± 0.3 kcal mol^{-1}). The exchange of the NH_2 protons occurs neither by protonation followed by deprotonation nor by these processes in the reverse order since the addition of triethylamine has no affect of the NMR spectrum of **3a**. A mechanism like that in Scheme III does not operate under these conditions, and we believe that both exchanges in **3a** are intramolecular.

Conclusions

The π-donor properties of the NR_2 substituent are strong enough to rotate the $R_2NC{\equiv}CH$ ligand from a parallel to a perpendicular orientation. Formally clusters **3** are zwitterionic, and since there is formally then a negative charge at the metal atoms, the ligand donates one less electron as a triyl rather than the endiyl system normally encountered with μ_3,η^2-alkynes. These consequences of replacing an innocent substituent by the amino function have precedents. The (diethylamino)vinyl complex $[Os_3H(CHCHNEt_2)(CO)_{10}]$[17] does not adopt a structure like that of the $CH{=}CH_2$ analogue[18] but exists as the zwitterion with an alkylidene bridge. This and several other examples of the consequences of introducing dialkylamino (NR_2) groups by replacing alkyl or hydrogen substituents (R′) are summarized in Figure 4.[19-21] In each case the number of electrons formally donated by the ligand is reduced by one, but there is a compensating location of a negative charge at the metal atoms to make these systems electron precise.

Experimental Section

Compound **1**, $[Os_3H(C_2H)(CO)_9]$, was prepared by treating $[Os_3(CO)_{10}(MeCN)_2]$[22] with acetylene to give $[Os_3(C_2H_2)(CO)_{10}]$

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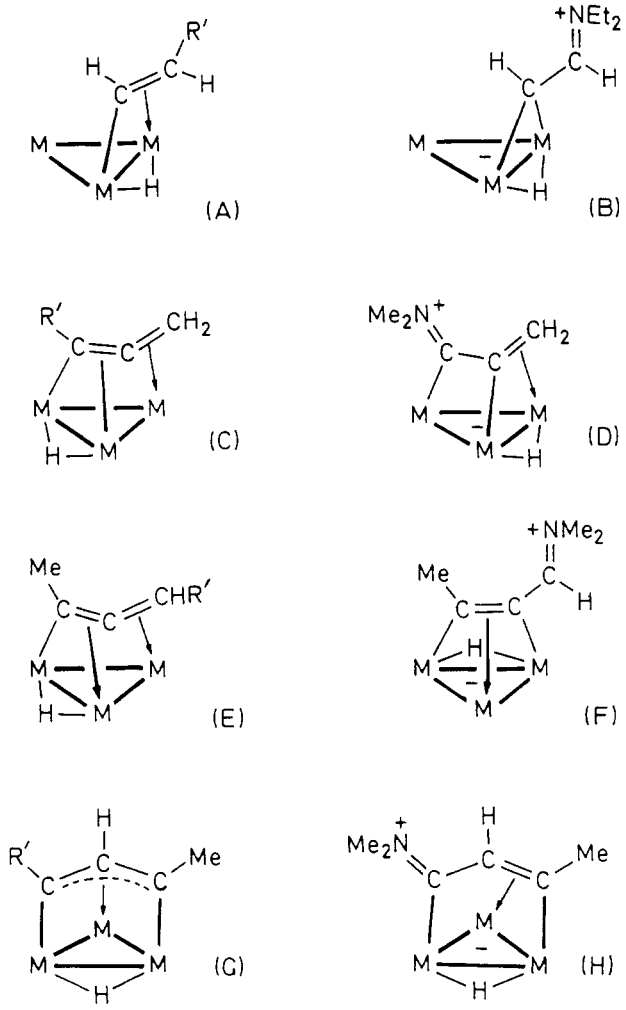

Figure 4. Modification of bridging ligand bonding by amino groups. Normal enyl bonding (A) is modified in $[Os_3H(CHCHNEt_2)(CO)_{10}]$ (B).[15] Normal allenyl bonding (C and E) is modified in $[Ru_3H(Me_2NCCCH_2)(CO)_9]$ (D)[17] and in $[Ru_3H(MeCCCHNMe_2)(CO)_9]$ (F),[18,19] and the normal allyldiyl (G) is modified in $[Ru_3H(Me_2NCCHCMe)(CO)_9]$ (H).[19]

in rather poor yield (20%) but which thermally decarbonylates in good yield to give 1.[12] ^{1}H NMR spectra were recorded at 200 MHz on a Varian XL200 or at 400 MHz on a Varian VXR400 spectrometer. IR spectra were recorded in cyclohexane solution in CaF_2 cells on a Perkin-Elmer PE983 spectrometer. Chromatographic separations were by TLC on silica (Merck, type 60, HF_{254}).

Reaction of $[Os_3H(C_2H)(CO)_9]$ (1) with Pyridine. The IR spectrum of 1 (0.020 g) in pyridine (10 mL) showed by the lowering of ν(CO) (2072 m, 2043 vs, 2011 vs, 1997 s, 1988 s, 1978 m, 1964 m, 1950 m cm^{-1}) that there had been an immediate conversion to the adduct 2 at room temperature. These wavenumbers may be compared with the ν(CO) data for 1 (*n*-hexane): 2102 w, 2076 s, 2054 s, 2022 s, 2015 s, and 1984 m cm^{-1}. The ^{1}H NMR spectrum of 1 (0.025 g) in neat C_5D_5N (0.5 mL) showed quantitative conversion to $[Os_3H(C_5D_5NC_2H)(CO)_9]$ [δ 9.04 (d, J = 1.5 Hz, C_2H) and −19.81 (d, J = 1.5 Hz, Os*H*)]. Addition of pentane gave orange crystals which, on dissolving in dichloromethane, immediately regenerated cluster 1 (IR evidence).

Synthesis of $[Os_3H_2(NH_2C_2H)(CO)_9]$ (3a). Ammonia gas evaporated from liquid ammonia was bubbled through a solution of $[Os_3H(C_2H)(CO)_9]$ (1; 0.029 g) in dichloromethane (15 mL) for 2 min. The reaction flask was stoppered and stood for 45 min at room temperature, the solvent removed under reduced pressure, and the residue chromatographed by using a petroleum ether (bp 30–40 °C)/dichloromethane mixture (10:1 by volume) to give a band yielding unreacted 1 (0.004 g, 14%) and a yellow band yielding pale yellow crystals (0.009 g, 30%) of **3a**: ν(CO) 2102 m, 2073 vs, 2047 vs, 2019 vs, 2001 s, 1987 m, 1980 m, 1972 m cm^{-1}; ^{1}H NMR (−59 °C, CD_2Cl_2) δ 7.00 (d, J = 4.9 Hz, NH), 6.31 (d, J = 4.9 Hz, NH), 5.45 (s, CH), −17.11 (s, OsH), −20.48 (s, OsH). (Anal. Calcd for $C_{11}H_5NO_9Os_3$: C, 15.25; H, 0.6, N, 1.6. Found: C, 15.3; H, 0.6; N, 1.6.)

Table III. Crystal Data and Data Collection Parameters for 3b

formula	$C_{15}H_{13}NO_9Os_3$
MW, amu	921.86
system	monoclinic
a, Å	13.722 (3)
b, Å	12.576 (4)
c, Å	12.605 (3)
β, deg	106.59 (2)
V, Å^3	2084 (1)
space group	$P2_1/c$ [No. 14]
Z	4
d(calcd), g cm^{-3}	2.94
μ, cm^{-1} (Mo Kα)	183.35
cryst size, mm^3	ca. 0.3 × 0.3 × 0.4
λ(Mo Kα), Å	0.71073
collectn range	h, 0→15; k, 0→15, l −17→+17 $5 \leq 2\theta \leq 50°$
F(000)	1623
unique data measd	3684
obsd data with $F_o > 3\sigma(F_o)$	3142
no. of variables	265
$R_F = \sum[\lvert F_o\rvert - \lvert F_c\rvert]/\sum\lvert F_o\rvert$	0.0514
weighting scheme, w	$[\sigma^2(F_o) + 0.000961\lvert F_o\rvert^2]^{-1}$
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.0512
highest residual in final diff map	2.37 e Å^{-3} (very close to Os atoms)
largest shift/esd in final difference Fourier	0.003

Protonation of $[Os_3H_2(NH_2C_2H)(CO)_9]$ (3a) with CF_3CO_2H To Give 7a. Trifluoroacetic acid (10 mol/mol of Os_3) was added to a solution of **3a** in $CDCl_3$ at 22 °C. The ^{1}H NMR spectrum indicated protonation at osmium to give $[Os_3H_3(NH_2C_2H)(CO)_9]^+$ (**7a**): δ 9.00 (s, br, NH), 8.80 (s, br, NH), 6.10 (s, CH), −16.80 (s, OsH), −20.90 (s, OsH_2).

Synthesis of $[Os_3H_2(Et_2NC_2H)(CO)_9]$ (3b). Diethylamine (0.006 g, 2 mol/mol of Os_3) was added to a cyclohexane solution (30 mL) of cluster 1 (0.034 g). After 15 min, chromatography [eluant petroleum ether (bp 30–40 °C)] gave a very pale yellow band yielding almost colorless crystals of **3b** (0.027 g, 77%) from a hexane/dichloromethane mixture: ν(CO) 2098 m, 2068 vs, 2041 vs, 2015 s, 2012 s, 1996 ms, 1979 m, 1975 m, 1965 m cm^{-1}: ^{1}H NMR (CD_2Cl_2, −90 °C) δ 5.80 (s, C_2H), 3.53 (q, J = 7.2 Hz, CH_2N), 3.46 and 3.41 (1:3:3:1, q of AB q, CH_2N), 1.11 (t, J = 7.2 Hz, CH_3), 1.18 (t, J = 7.2 Hz, CH_3), −17.3 (s, Os*H*), −20.1 (s, Os*H*). (Anal. Calcd for $C_{15}H_{13}NO_9Os_3$: C, 19.55; H, 1.4; N, 1.5. Found: C, 19.5; H, 1.3; N, 1.5.) Crystals suitable for *X*-ray structure determination were obtained by slow evaporation of hexane solutions. Most crystals were unsuitable, but a few large clear crystals were obtained. The structure was carried out on an irregular fragment of one of these.

Protonation of $[Os_3H_2(Et_2NC_2H)(CO)_9]$ (3b) with CF_3CO_2H To Give 7b. CF_3CO_2H (0.018 mL, 10 mol/mol of Os_3) was added to a $CDCl_3$ solution (0.5 mL) of **3b** (0.021 g). The ^{1}H NMR spectrum showed essentially complete conversion over 24 h to $[Os_3H_3(Et_2NC_2H)(CO)_9]^+[(CF_3CO_2)_2H]^-$. ^{1}H NMR ($CDCl_3$): δ 6.36 (s, C_2H), 3.94 (q, J = 7.2 Hz, CH_2N), 3.68 (q, J = 7.2 Hz, CH_2N), 1.40 (t, CH_3), 1.37 (t, CH_3), −16.65 (s, Os*H*), −20.70 (s, OsH_2). The solution was diluted with dichloromethane (20 cm^3), and a solution of KOH (0.020 g) in water was added. Chromatography gave cluster **3b** (0.018 g, 86%).

X-ray Structure Determination for Cluster 3b. Data Collection. A summary of the key crystal data and parameters for the data collection are given in Table III. The irregular colorless crystal used was fragment of a much bigger single crystal and was mounted on a glass fiber on a Nicolet R3m/V four-circle diffractometer operating with graphite-monochromated Mo Kα radiation. The cell constants were obtained from an automatic indexing routine and a least-squares fit of the setting angles of 35 reflections in the range $18.9 \leq 2\theta \leq 29.8°$. The crystal was monoclinic, space group $P2_1/c$. A total of 3684 unique data were

collected at room temperature. The intensities of three intensity standards showed only minor fluctuations over the period of data collection. Data were corrected for Lorentz and polarization effects and empirically for absorption (ψ-scan method), and a total of 3142 data were used in the structure refinement.

Structure Solution and Refinement. The three osmium atoms were located by direct methods (SHELXTL PLUS[23]). Alternating cycles of least-squares full-matrix refinement followed by difference Fourier synthesis located all the other non-hydrogen atoms with a convergence to $R = 0.0514$ and $R_w = 0.0512$ (see Table III for weighting scheme). All non-hydrogen atoms were refined anisotropically and, although the hydrogen atoms were not located, those of the two ethyl groups were included in idealized positions (C–H = 0.95 Å) and with a common isotropic temperature factor, $U = 0.08$ Å^2, in the final stages of refinement. The hydrogen positions were finally fixed for the last cycle of refinement. Atomic scattering factors used were those contained in the SHELXTL PLUS package.[23]

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Note Added in Proof. Since this paper was submitted, compound **3a** has been reported to be formed by photolytic decarbonylation of $[Os_3H(\mu\text{-}CHCHNEt_2)(CO)_{10}]$ (Figure 4).[24]

Registry No. **1**, 55073-02-4; **2**, 105286-42-8; **3a**, 105286-40-6; **3b**, 105286-41-7; **4**, 105286-38-2; **5**, 105286-39-3; **7a**, 118299-47-1; **7b**, 118299-48-2; $[Os_3(CO)_{10}(MeCN)_2]$, 61817-93-4; $[Os_3(C_2H_2)(CO)_{10}]$, 57373-35-0; $[Os_3H(PMe_2PhC_2H)(CO)_9]$, 82740-30-5; HC≡CH, 74-86-2.

Supplementary Material Available: More detailed crystallographic experimental and tables of all bond lengths and angles, anisotropic displacement parameters for non-hydrogen atoms, and hydrogen atom coordinates (7 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Coordinated Ligand Basicity. Synthesis and Reactivity of Terminal Phosphide Complexes of Iridium That Also Contain an Amide Donor

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The reaction of stoichiometric amounts of $LiPR_2$ (R = Ph and *m*-tol) with the square-pyramidal complex $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (**1**) generates the new terminal phosphide complexes $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$ (**2a**, R = Ph; **2b**, R = *m*-tol). On the basis of solution spectroscopic data, the structure is proposed to be intermediate between trigonal bipyramidal and square pyramidal. Although the geometry at the phosphide phosphorus is ambiguous (pyramidal versus planar), the $^{31}P\{^1H\}$ NMR chemical shift can be interpreted as a result of a dynamic equilibrium between the two forms assisted by the lone pair on the amide nitrogen of the ancillary tridentate ligand. The phosphide is nucleophilic and undergoes intermolecular methylation with methyl iodide; the stereochemistry of the octahedral methylated material is shown to be *trans*-CH_3-I-*mer*-$Ir(CH_3)I(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$.

During the last 2 decades, interest in tertiary phosphine complexes (L_nM–PR_3) of the transition metals has grown tremendously, due in part to the observation that many of these derivatives are catalyst precursors for such industrially important processes as hydrogenation, hydroformylation, and polymerization.[1] As a result, the number of phosphine-containing complexes is now legion.[2]

In addition to the well-studied phosphines, ligands having other valences of phosphorus are known but less studied. These include metalated phosphoranes (L_nM—PR_4),[3] phosphides (L_nM—PR_2),[4–20] and phosphinidenes (L_nM=PR).[21–25] Although mononuclear phosphorane and phosphinidene complexes are still extremely rare, the

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