Transition-metal Nitrosyl Compounds. Part XI.[1] The Preparation and the Study of Fluxional Behaviour of Some Cationic Acetylene Complexes of Osmium

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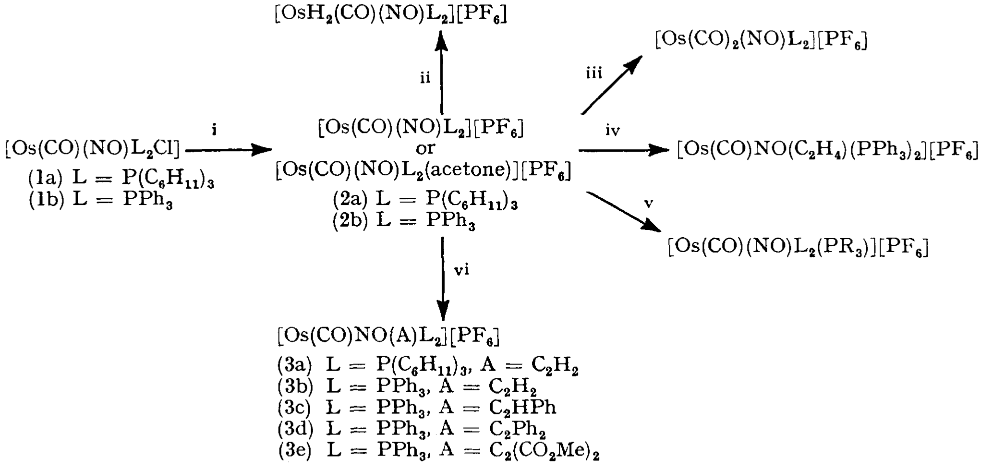
Cationic nitrosyl acetylene complexes of the type $[Os(CO)NO(A)L_2][PF_6]$ [L = PPh_3, A = C_2H_2, C_2HPh, C_2Ph_2, or $C_2(CO_2Me)_2$; L = $P(C_6H_{11})_3$, A = C_2H_2] have been prepared. Their ^1H n.m.r. spectra measured and, for the species where A = C_2H_2, variable-temperature studies are consistent with acetylene rotation about the metal–acetylene bond with $\Delta G_{T_c}^{\ddagger} = 11.5 \pm 0.2$ kcal mol^{-1} (L = PPh_3) and 14.4 ± 0.5 kcal mol^{-1} [L = $P(C_6H_{11})_3$].

We have previously reported[2] that compounds of the type $[Os(CO)(NO)L_2Cl]$, L = $P(C_6H_{11})_3$ (1a) or PPh_3 (1b), in dichloromethane–acetone react with $Ag[PF_6]$ to give the highly reactive and as yet uncharacterised species (2a) and (2b) (see Scheme). These intermediates were found to combine readily with ligands (L′), such as CO, C_2H_4, or tertiary phosphines, to give cationic derivatives of the type $[Os(CO)(NO)L_2L'][PF_6]$[2,3] and with hydrogen at atmospheric pressure to give the six-co-ordinate dihydride complexes $[OsH_2(CO)(NO)L_2][PF_6]$.[4] Here we report the reactions of (2a) and (2b) with acetylenes to produce new species of the type $[Os(CO)(NO)(acetylene)L_2][PF_6]$ (3).

In Part X[1] of this series we reported the formation of the complex $[Os(CO)(NO)(C_2H_4)(PPh_3)_2][PF_6]$ (4) which is of special interest since it allowed direct experimental confirmation that ethylene rotation occurs about the metal–ethylene co-ordination axis. Recently molecular orbital calculations have led Jonassen and his co-workers[5] to propose a new model for metal–acetylene and -olefin bonding in zero- and bi-valent platinum complexes; furthermore, these authors have considered in their scheme that *acetylene rotation* about the metal–acetylene bond could occur. It seemed reasonable, by analogy with the ethylene complex (4), that acetylene complexes of type (3) would possess the appropriate symmetry properties to allow the above hypothesis to be tested by ^1H n.m.r. spectroscopy. A preliminary report of this work has been given.[6] Other experimental evidence indicating that acetylene rotation can occur has been obtained by Herberhold *et al.*[7] from studies on $[(\pi\text{-cp})Cr(CO)NO(C_2H_2)]$.



Scheme i, $AgPF_6$/acetone; ii, H_2; iii, CO; iv, C_2H_4 (L = PPh_3 only); v, tertiary phosphine or phosphite; vi, acetylene (A)

Preparation.—As illustrated in the Scheme the reactions of (2a) and (2b) † with various acetylenes produced species of the type $[Os(CO)(NO)(A)L_2][PF_6]$, where A = C_2H_2; L = PPh_3 or $P(C_6H_{11})_3$ and A = C_2HPh, C_2Ph_2, or $C_2(CO_2Me)_2$; L = PPh_3. All these derivatives are air-sensitive and very reactive in solution. They are unstable in most donor solvents and are very soluble in dichloromethane where chlorination slowly takes place to yield, amongst other products, $[OsCl(CO)(NO)L_2]$ and, in the presence of O_2, $[OsCl(CO_3)(NO)(PPh_3)_2]$. The compounds (3a) and (3e) are moderately

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† These intermediate species are thought to have either of the formulae shown in the Scheme. I.r. absorption at 1 657 cm^{-1} [L = $P(C_6H_{11})_3$] is consistent with co-ordinated acetone and $[PF_6]^-$ is also present. However the ν(CO) and ν(NO) absorptions at 1 927 and 1 561 cm^{-1} are low for a co-ordinatively saturated cationic species.

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[3] B. F. G. Johnson and J. A. Segal, *J.C.S. Chem. Comm.*, 1972, 1312.

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[6] J. Ashley-Smith, B. F. G. Johnson, and J. A. Segal, *J. Organometallic Chem.*, 1973, **49**, C38.

[7] M. Herberhold, H. Alt, and C. G. Kreiter, *J. Organometallic Chem.*, 1972, **42**, 413; H. Alt, M. Herberhold, C. G. Kreiter, and H. Strack, *ibid*, 1974, **77**, 353.

stable in acetone but other polar solvents such as acetonitrile or tetrahydrofuran give rapid decomposition in all cases. The products of these reactions have not been characterised.

As expected from a consideration of the relative electron-withdrawing properties of the acetylenes, $C_2(CO_2Me)_2$ forms the most stable derivative. In agreement the complex (3e) shows the highest CO and NO stretching frequencies (see Table). It is, therefore, surprising that no isolable product could be obtained from the reaction with hexafluorobut-2-yne. Conductivity measurements on (3e) in nitrobenzene showed it to be a 1 : 1 electrolyte ($\Lambda_M = 27.1\ \Omega^{-1}\ cm^2$) but reliable data could not be obtained for the other less-stable derivatives.

Colour, i.r. data[a] (2 160—1 700 cm^{-1}), and microanalytical results for the acetylene complexes

				Found (%)				Required (%)			
Complex[b]	Colour	ν (CO)	ν(NO)	C	H	N	P	C	H	N	P
$[Os(CO)NO(C_2H_2)\{P(C_6H_{11})_3\}_2][PF_6]$[c] *	Yellow	2 020vs	1 731vs	47.6	7.2	1.3	9.5	47.8	7.0	1.4	9.5
$[Os(CO)NO(C_2H_2)(PPh_3)_2][PF_6]\cdot CH_2Cl_2$ †	Yellow	2 035vs	1 747vs	45.9	3.6	1.1	8.7	46.7	3.3	1.4	9.0
$[Os(CO)NO(C_2HPh)(PPh_3)_2][PF_6]$ ‡	Orange	2 039vs	1 747vs	52.8	3.5	1.3	9.0	53.0	3.6	1.4	9.1
$[Os(CO)NO(C_2Ph_2)(PPh_3)_2][PF_6]$	Red	2 032vs	1 743vs	56.0	3.9	1.3	8.2	55.9	3.7	1.3	8.5
$[Os(CO)NO\{C_2(CO_2Me)_2\}(PPh_3)_2][PF_6]$[d]	Yellow	2 077s 1 717m[e]	1 778vs	48.8	3.6	1.2	9.0	48.7	3.4	1.3	8.8

[a] CH_2Cl_2 solutions. [b] All species showed i.r. absorptions at *ca.* 850 cm^{-1} characteristic of $[PF_6]^-$. [c] The poor analytical data are either a result of association with CH_2Cl_2 or oxidative halogenation by CH_2Cl_2 during crystallisation. [d] Band at 1 825w, sh cm^{-1} assigned to $\nu(C{\equiv}C)$. [e] $\nu(C{=}O)$ in $C_2(CO_2Me)_2$. Chlorine analysis (%) Found (required) * 0.0 (0.0), † 6.4 (6.9), ‡ 0.0 (0.0).

Stereochemistry.—The complex $[Os(CO)_2NO(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$ has been previously shown by *X*-ray analysis [8] to possess an essentially trigonal bipyramidal configuration with a linear Os–N–O unit and the triphenylphosphine ligands occupying axial positions (Figure 1). We suggest that this stereochemistry is maintained in all the species reported here. Thus, in the complex (3e) the acetylenic molecule may be considered as occupying a co-ordination site in the trigonal plane; alternatively, the geometry may be viewed as pseudo-octahedral with the carbon atoms of the co-ordinated acetylene occupying two adjacent sites (Figure 2). Consistent with this structure is the appearance of the NO stretching vibration at 1 778 cm^{-1} which leads to the formulation of the compound as a NO$^+$ derivative of d^8 Os^0.[9] The ^{1}H n.m.r. spectra of (3a), (3b), and (3e) also support the proposed arrangement.

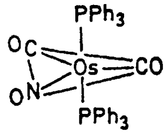

FIGURE 1 Structure of $[Os(CO)_2(NO)(PPh_3)_2]^+$

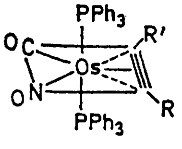

FIGURE 2 Probable structure of $[Os(CO)(RC{\equiv}CR')(NO)(PPh_3)_2]^+$

Stereochemical Non-rigidity.—The ^{1}H n.m.r. spectra of the acetylene complexes (3a) and (3b) exhibit a temperature dependence which is very similar to that previously reported [1] for the ethylene compound (4). At −30 °C the spectrum of $[Os(CO)NO(C_2H_2)\{P(C_6H_{11})_3\}_2][PF_6]$ in CD_2Cl_2 shows two resonances of equal intensity (1H) at τ 1.62 and 4.25. The higher field signal is observed as a triplet (J_{PH} 2.5 Hz) whereas the lower field signal is a broadened singlet. This difference in coupling may suggest that the acetylene molecule is tilted as illustrated in Figure 3. Since the NO$^+$ ligand is generally recognised as being a strongly *trans*-directing ligand we suspect that the Os–C$^\alpha$ distance will be greater than Os–C$^\beta$ in the pseudo-octahedral structure (Figure 2). In deuterioacetone a considerable shift in the resonances is seen, each one appearing as a broad singlet at τ 0.94 and 3.15 respectively, and the separation of the lines is also shortened. This effect could be caused by a different interaction of the uncomplexed acetylenic π-bond with the two solvents {considerable solvent effects were also observed [7] in the variable-temperature studies on $[(\pi\text{-cp})Cr(CO)NO(C_2H_2)]$}. As the temperature is raised the two peaks broaden and collapse until at +70 °C a broad resonance is observed at τ 2.15. Higher temperatures could not be attained owing to decomposition of the complex. The analogous triphenylphosphine derivative (3b) exhibits similar behaviour. Thus at +30 °C the ^{1}H n.m.r. spectrum in CD_2Cl_2 shows a singlet at τ 3.62 (2H) which may be assigned to the acetylenic protons. As the complex is cooled to −75 °C the spectrum passes through the coalescence point and a new singlet, corresponding to one proton, is observed at τ 5.11. The expected second resonance (estimated to be at τ 2.13) is obscured by the signal of the PPh$_3$ ligands. For this complex no

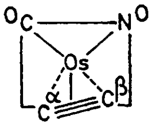

FIGURE 3 Alignment of RC≡CR' group in $[Os(CO)(RC{\equiv}CR')(NO)(PPh_3)_2]^+$

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[8] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.

[9] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

^{1}P–H coupling was observed either in the high or low temperature spectra.

It is attractive to interpret these data in terms of acetylene rotation about the co-ordination bond in the manner previously described for ethylene rotation in the analogous cation $[Os(CO)NO(C_2H_4)(PPh_3)_2]^+$.[1] A similar interpretation has been presented for the system [(π-cp)Cr(CO)NO(acetylene)].[7] Although this is the most reasonable way of rationalising the experimental results it has not been possible to exclude other plausible mechanisms.* Thus, for example, we have not totally excluded a dissociative mechanism since ^{31}P–H coupling is not observed in the high-temperature region. However there is some support for an intramolecular process from preliminary evidence which suggests that the acetylenes are not readily displaced by CO to give $[Os(CO)_2NO(PPh_3)_2]^+$. The occurrence of proton migration should also be treated seriously in these cationic species. Other mechanisms, similar to those discussed by Cramer [10] for ethylene systems, are also not entirely eliminated. We note, however, that rotation about the C–C axis is not a problem here as in metal–olefin complexes [1] since such a mode is degenerate and can have no physical significance. Nevertheless if a rotational process does indeed occur it could be coupled to a Berry rearrangement of the five-co-ordinate skeleton [11] as was discussed previously for compound (4).[1]

The rate of the exchange process is apparently susceptible to changes in the substituents of the acetylene. Thus no site exchange was observed for the complex (3e), presumably as a result of the bulky electronegative ester groups of the $C_2(CO_2Me)_2$ ligand; the complex showed methyl resonances at τ 6.50 and 6.69 (35 °C). Values of $\Delta G_{T_c}^{\ddagger}$ for the C_2H_2 complexes [11.5 ± 0.2 kcal mol^{-1} for L = PPh$_3$ and 14.4 ± 0.5 kcal mol^{-1} for $L = P(C_6H_{11})_3$], calculated using an approximate formula,[1,12] also show a dependence on the nature of the other ligands. These figures are higher than found for the ethylene complex (4) and may reflect stronger co-ordination of the acetylene molecule.

The ^{1}H n.m.r. spectrum of (3c) in CD_2Cl_2 is somewhat complex owing to the instability of this compound in solution. However, at 0 °C two resonances are observed at τ 1.70 (singlet) and τ 4.44 (triplet J_{PH} 2 Hz). The appearance of two signals is in accord with the presence of the two possible ground-state isomers (H *trans* to CO and H *trans* to NO) and thus provides further evidence to support the assigned stereochemistries.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating instrument and ^{1}H n.m.r. spectra on a Varian Associates HA 100 spectrometer at 100 MHz. Microanalyses were determined by Mr. D. Flory of this laboratory. The neutral chlorides [OsCl(CO)(NO)L$_2$] [L = PPh$_3$ or $P(C_6H_{11})_3$] were prepared by previously reported methods.[2,13] All reactions were carried out under an atmosphere of dry oxygen-free nitrogen.

Carbonyl(dimethyl acetylenedicarboxylate)nitrosylbis(triphenylphosphine)osmium(0) *Hexafluorophosphate*.—A red solution of [OsCl(CO)NO(PPh$_3$)$_2$] {from [OsHCl(CO)PPh$_3$)$_2$] (0.300 g) and diazald (0.105 g)} in dichloromethane (25 ml) was treated with silver hexafluorophosphate (0.069 g) in acetone (1 ml). An immediate colour change to yellow took place and after the mixture had been shaken for a few seconds it was quickly filtered through Kieselguhr into a flask containing a vigorously stirred solution of dimethyl acetylenedicarboxylate (0.090 g) in dichloromethane (6 ml). After evaporation to reduce the volume, ether was slowly added to the solution to give yellow needles (0.192 g) which were recrystallized from acetone–ethanol and dried *in vacuo*. Conductivity measurement on a 10^{-3}M-nitrobenzene solution of this complex gave $\Lambda_M = 27.1\ \Omega^{-1}$ cm^2 mol^{-1}.

Carbonyl(diphenylacetylene)nitrosylbis(triphenylphosphine) osmium(0) *Hexafluorophosphate*.—The yellow intermediate solution, obtained as above, was filtered onto a stirred solution of diphenylacetylene (0.150 g) in dichloromethane (6 ml) causing a colour change to red. The volume of the resulting solution was reduced and then pentane was added to give fine red microcrystals (0.180 g) which were recrystallized from dichloromethane. This was effected in the presence of free diphenylacetylene by addition of ether–pentane; solutions of the complex seem to be more stable if the free acetylene ligand is present. The product was collected, washed with pentane, and dried *in vacuo*.

Carbonylnitrosyl(phenylacetylene)bis(triphenylphosphine)-osmium(0) *hexafluorophosphate* was obtained similarly as orange crystals (0.220 g).

Acetylenecarbonylnitrosylbis(tricyclohexylphosphine)-osmium(0) *Hexafluorophosphate*.—Silver hexafluorophosphate (0.044 g) in acetone (1 ml) was added to a solution of [OsCl(CO)NO{$P(C_6H_{11})_3$}$_2$] (0.150 g) in dichloromethane (20 ml). Silver chloride was precipitated rapidly and, after the mixture had been shaken for a few seconds, it was filtered off. The filtrate was collected in a flask cooled to −78 °C. This cold solution was then saturated with acetylene gas and allowed to warm to room temperature. The addition of pentane led to precipitation of the product (0.140 g). Recrystallization was effected from dichloromethane–pentane and after being washed with pentane the product was dried *in vacuo*.

Acetylenecarbonylnitrosylbis(triphenylphosphine)osmium(0) *hexafluorophosphate* was obtained similarly; yield 0.210 g from [OsHCl(CO)(PPh$_3$)$_3$] (0.300 g).

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* Data have not been reported that exclude such mechanisms in the chromium system.

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