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Nonacarbonyl(dinitrosyl)triosmium: a New Nitrosyl Cluster†

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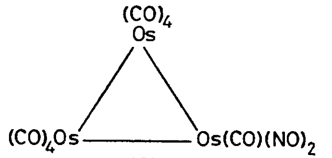
Summary Nitric oxide reacts with [$Os_3(CO)_{12}$] in n-octane at 126 °C to produce [$Os_3(CO)_9(NO)_2$] which reacts with CO at 81 °C to form the known cluster [$Os_3(CO)_{10}(NO)_2$].

In 1972 Collman and his co-workers[1] reported that dodecacarbonyltriosmium reacts with nitric oxide under moderate conditions (60 lb in^2, 100 °C, 24 h) to produce low yields (*ca.* 13%) of the compound [$Os_3(CO)_{10}(NO)_2$] (**1**). The structure of this compound was shown to possess C_{2v} symmetry and resembles [$Fe_3(CO)_{12}$] with a double-nitrosyl bridge in place of the double carbonyl bridge. We report the synthesis of a new, but closely related, dinitrosyl cluster of osmium [$Os_3(CO)_9(NO)_2$], which contains two terminally bound NO groups and which may be regarded as pseudo-[$Os_3(CO)_{12}$] with two NO groups replacing three CO groups about one osmium atom.



(2)

Figure. Probable structure of [$Os_3(CO)_9(NO)_2$].

On passing nitric oxide through a solution of [$Os_3(CO)_{12}$] in n-octane at 126 °C, the complex [$Os_3(CO)_9(NO)_2$] (**2**) is produced together with small amounts of the previously reported[1] dinitrosyl cluster [$Os_3(CO)_{10}(NO)_2$] (**1**). After separation on silica, complex (**2**) may be obtained as dark red crystals from pentane and has been characterised on the basis of analytical and spectroscopic data. On electron impact (80 eV) the molecular-ion [$Os_3(CO)_9(NO)_2$]$^+$ is observed together with ions produced by the stepwise loss of nine CO and two NO groups. The i.r. spectrum of (**2**) is clearly different from that of (**1**) and shows a complicated series of nine CO bands, none in the bridging region, and two nitrosyl bands at 1731 and 1705 cm^{-1} (see Table). Although it is difficult to characterise the NO bonding type solely on the basis of the N–O stretching vibration, these bands are in the region usually associated with a terminal and linear M–N–O (formally NO$^+$) arrangement. The ^{13}C n.m.r. spectrum (CFT, XL-100) of an isotopically enriched sample (*ca.* 60% ^{13}CO) in [$^2H_8$]toluene at 40 °C exhibits four signals of relative intensity 4 : 2 : 2 : 1. These data may be taken to indicate that the complex is of low symmetry and are best interpreted in terms of (**2**) involving one

Table. I. r. spectroscopic data for complexes (**1**)—(**4**).[a]

Complex	ν_{CO}/cm^{-1}	ν_{NO}/cm^{-1}
(**1**)[b,c]	2108w, 2068s, 2063s, 2054s, 2025s, 2017w, 2008s, 1996m	1503m, 1484s
(**1′**)	2069w, 2033m, 2020vs, 1996vs	
(**2**)	2117m, 2073vs, 2067s 2033vs, 2023s, 2019s, 2013m, 2083m, 1991w	1731s, 1705s
(**3**)	2104m, 2056vs, 2021vs, 2006s, 1993s, 1985m, 1979s	1705s, 1672s
(**4**)[b]	2100m, 2063vs, 2033m, 2019vs, 2011s, 2001s, 1995s, 1979s	1470m, 1455m

[a] m, medium; vs, very strong; s, strong; w, weak; all spectra were taken in cyclohexane unless indicated otherwise. [b] ν_{NO} refers to spectra of KBr disc. [c] ν_{CO} of (**1**) refers to spectrum taken in tetrachloroethylene.

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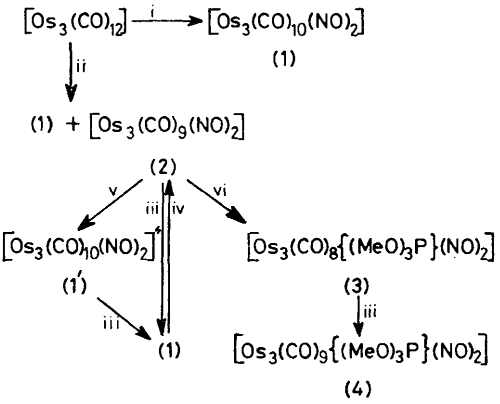
† No reprints available.

$Os(CO)(NO)_2$ and two $Os(CO)_4$ units, which is, in effect, pseudo-$[Os_3(CO)_{12}]$ with three CO groups replaced by two NO groups (Figure).

Carbon monoxide reacts with (**2**) in cyclohexane at 81 °C to give $[Os_3(CO)_{10}(NO)_2]$ in quantitative amounts. This reaction is not simple and we have evidence to suggest the formation of an unstable intermediate complex. Thus at 25 °C, (**2**) in cyclohexane slowly reacts with CO to produce a solution which exhibits an i.r. spectrum (Table) unlike that of either (**1**) or (**2**). In particular no bands which can be easily assigned to co-ordinated NO groups are apparent. However, on removal of solvent (**2**) is reformed quantitatively and if the temperature of the solution is raised to 81 °C and the reaction with CO continued, high yields (*ca.* 90%) of (**1**) are obtained. Clearly these observations confirm that NO is present in the intermediate which we tentatively formulate as the adduct $[Os_3(CO)_{10}(NO)_2]$ (**1′**), a complex with the same molecular formula but different structure to Collman's compound (**1**). We have also examined the reaction of (**2**) with $(MeO)_3P$ at 25 °C to produce $[Os_3(CO)_8(NO)_2\{(MeO)_3P\}]$ (**3**) which, according to its i.r. spectrum (Table), contains two terminally bound NO groups. In this case no evidence for the formation of an intermediate complex was found. However, at 100 °C in n-heptane this complex reacts with CO to produce $[Os_3(CO)_9(NO)_2\{(MeO)_3P\}]$ which, on the basis of the i.r. spectrum, contains a double-nitrosyl bridge.



Scheme. i, NO, C_6H_6, 60 lb in², 100 °C; ii, NO, n-octane, 126 °C; iii, CO, cyclohexane, 81 °C; iv, n-octane, 126 °C; v, CO, cyclohexane, 25 °C; vi, $(MeO)_3P$, cyclohexane, 25 °C.

We believe that these reactions are best interpreted as shown in the Scheme. Complex (**2**) undergoes addition of a donor ligand L [L = CO or $(MeO)_3P$] to form an unstable adduct $[Os_3(CO)_9(NO)_2]\cdot L$ of unknown geometry which may either undergo CO loss to form $[Os_3(CO)_8(NO)_2L]$ or rearrangement to produce the double-nitrosyl bridged compound $[Os_3(CO)_9(NO)_2L]$. Finally we note that $[Os_3(CO)_{10}(NO)_2]$ (**1**) undergoes CO-elimination at 126 °C in n-octane to produce small amounts of (**2**).

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[1] J. R. Norton, J. P. Collman, E. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 1972, **11**, 382.