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Preliminary communication

ISOLATION OF INTERMEDIATES IN METAL CARBONYL SUBSTITUTION: ADDUCTS OF $H_2Os_3(CO)_{10}$

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Summary

Ligand molecules L readily add to the compound $H_2Os_3(CO)_{10}$ at room temperature to give species of type $H_2Os_3(CO)_{10}L$ (L = CO, PMe_2Ph, PPh_3, PhCN); at higher temperatures CO is lost to give substitution products $H_2Os_3(CO)_9L$ when L is tertiary phosphine, whereas the addition of CO or PhCN is reversible.

The dihydride $H_2Os_3(CO)_{10}$ (I) is more reactive than most cluster carbonyls of osmium and readily gives bridging ethenyl complexes with alkynes at room temperature [1]. We suggested that the double metal—metal bond contributes to this reactivity and we now report that donor ligands other than acetylene readily add to I*. It seems probably that as nucleophilic attack occurs at the cluster there is a reduction of the double osmium—osmium bond.

Addition of equimolar amounts of PMe_2Ph or PPh_3 to I in hexane gives an instantaneous colour change from purple to yellow followed by precipitation of $H_2Os_3(CO)_{10}L$ as excellent yellow crystals. Elemental analyses** support the formulations. The mass spectra of $H_2Os_3(CO)_{10}L$ (L = PPh_3 or PMe_2Ph) do not show the parent molecule but only the decomposition species $H_2Os_3(CO)_9L$ and $Os_3(CO)_{11}L$ (source temp. 160°). On heating solutions of the adducts in refluxing hexane (2 h) loss of CO gives $H_2Os_3(CO)_9L$ (L = PMe_2Ph or PPh_3), which are substitution products of the starting material I. An associative mechanism is one pathway for carbonyl substitution of $Ru_3(CO)_{12}$ with intermediates possibly having only two Ru—Ru bonds [2], but the case now reported appears to be the first where such intermediates are readily isolated.

If CO is bubbled through a hexane solution of I a yellow solution of the undecacarbonyl $H_2Os_3(CO)_{11}$ is formed (30 min), but on raising the temperature to the boiling point or by treatment with nitrogen at room temperature the purple

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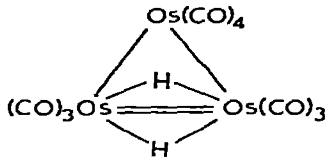
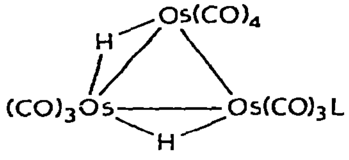
*Since submitting this paper, brief note has been made of the 1/1 adducts between I and PPh_3 or CO [5].

**Satisfactory elemental analyses (all elements except Os) were obtained for new complexes described in this paper.


(I)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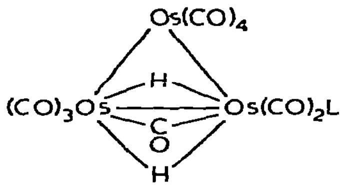
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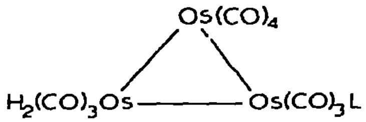
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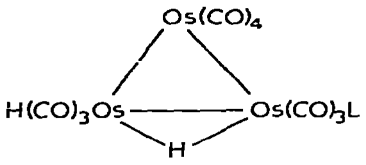
(V)

colour of the decacarbonyl is again observed. Continued treatment with CO at the higher temperature eventually gives $Os_3(CO)_{12}$ (3 h). The IR spectra of these solutions show no carbonyl species other than $H_2Os_3(CO)_{10}$, $H_2Os_3(CO)_{11}$, and

TABLE 1

^{1}H NMR (HYDRIDE)^a AND IR DATA^b

	Temp. (°C)	τ hydride	ν(CO)(cm^{-1})
$H_2Os_3(CO)_{10}$	27	21.36s	2076s 2064s 2025vs 2010s 1989m
$H_2Os_3(CO)_{11}$	−82^c	20.24d J(HH) 3.6 29.97d	2137vw 2088s 2066vs 2058vs 2054vs 2030m 2026m 2018m 2004(sh) 2002m 1988m
$H_2Os_3(CO)_{10}(PMe_2Ph)$	−62	20.53s J(PH) 12.0^d 30.45d	2106m 2065s 2050s 2024vs 2016vs 2007s 2001m 1985m 1977m
$H_2Os_3(CO)_{10}(PPh_3)$	−54	20.11d J(HH) 4.1 29.72dd J(PH) 10.7	2105m 2066s 2051s 2025vs 2017vs 2004m 1983m 1971m
$H_2Os_3(CO)_9(PMe_2Ph)$	27	20.74d J(PH) 6.5	2092m 2053s 2014vs 2005m(sh) 1991m 1984m 1975m 1958m
$H_2Os_3(CO)_9(PPh_3)$	35	20.06d J(PH) 7.0	2093m 2053s 2015s(sh) 2012vs 2004m 1991m 1976m 1962w
$H_2Os_3(CO)_{10}(PhCN)$	−58	19.91d J(HH) 4.0 27.05d	2103w 2067vs 2049s 2024vs 2008(sh,br) 1985m 1966w

[a] At 100 MHz at temperature given in $CDCl_3$. J in Hz. [b] In cyclohexane. [c] In CH_2Cl_2. [d] J(HH) not resolved (signals broad).

$Os_3(CO)_{12}$. $H_2Os_3(CO)_{12}$ [3] is not formed. $H_2Os_3(CO)_{11}$ was isolated as yellow crystals and shows the parent molecular ion in its mass spectrum.

The phenyl cyanide adduct is similar in that it is isolated as yellow crystals from solutions containing excess of the ligand. $H_2Os_3(CO)_{10}(PhCN)$ even more readily reverts to I on redissolving in hexane or on drying the crystals under vacuum.

All adducts $H_2Os_3(CO)_{10}L$ show non-equivalent hydrides at low temperatures in their ^1H NMR spectra and all show intramolecular hydride exchange leading to signal broadening and coalescence on raising the temperature. The structures of the adducts are unknown, but the non-equivalence of the hydride ligands in $H_2Os_3(CO)_{11}$ (unlike the decacarbonyl) and the lack of bridging CO (unlike the related $[HFe_3(CO)_{11}]^-$) [4] rule out structures such as II or III. Structure IV is most easily accommodated by the effective atomic number rule, but the large difference in chemical shift between the two hydride signals (see Table 1) might suggest that only one is terminal. In the tertiary phosphine compounds only one hydride is coupled to ^{31}P which might also support structure V.

References

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