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Preliminary communication

DOUBLE OXIDATIVE ADDITION REACTIONS OF ALDEHYDES AND KETONES AT TRIOSMIUM CLUSTERS*

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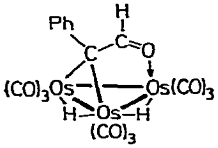
Summary

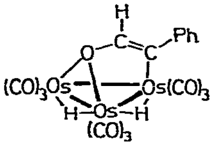
Cyclohexanone ($C_6H_{10}O$) reacts with $Os_3(CO)_{12}$ in refluxing decane to give $H_2Os_3(\mu^3\text{-}C_6H_8O)(CO)_9$, formed by double metallation (oxidative addition) at an α-CH_2 group of the ketone. Structurally similar products from phenol, phenylacetaldehyde or other aldehydes (described earlier) and from cyclohexenone are derived by reaction with $Os_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$.

Both aldehydes and ketones can give triosmium clusters derived from $Os_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$ in which both hydrogen atoms of an α-CH_2 group are transferred to the metal atoms, however, the initial hydrogen transfer is from the CHO group for aldehydes and from the alkene group in the case of cyclohexenone. Triply-bridging ligands X in $H_2Os_3(X)(CO)_9$ with a carbon atom bridging two Os atoms with an organic carbonyl coordinated through O to the third Os atom of the cluster appear to be particularly favourable as they may be formed in various ways.

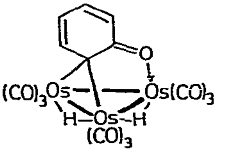
As an example, $PhCH_2CHO$ reacts slowly with $Os_3(CO)_{12}$ (refluxing xylene, 17 h) to give $HOs_3(\mu^2\text{-}PhCH_2CO)(CO)_{10}$ (1) (12%), the AB quartet for the CH_2 in the ^{1}H NMR spectrum indicating that the μ^2-acyl ligand is locked as such and does not interchange between the two osmium atoms it bridges. Thermolysis of 1 (nonane, 150°C, 5 h) gave complex 2 $H_2Os_3(\mu^3\text{-}PhCCHO)(CO)_9$ (17%) which was believed incorrectly [1,2] to have structure **2b** while present evidence favours structure **2a**. The ν(CO) spectrum is very similar to that of **3** derived



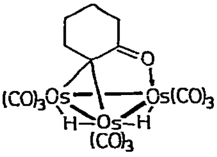
(2a)



(2b)



(3)



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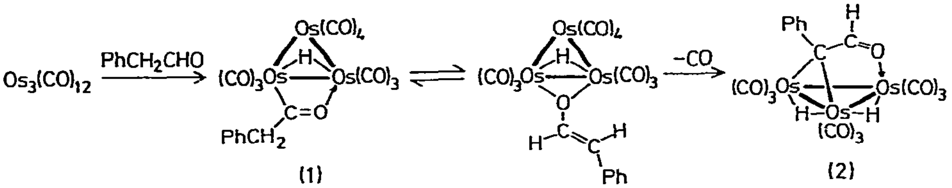
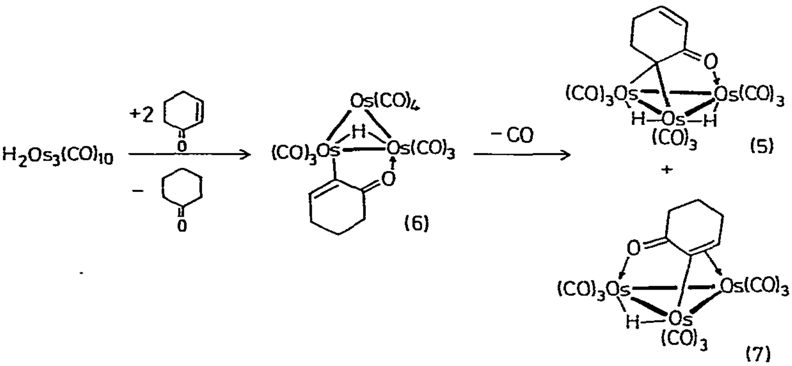
*No reprints available.

from phenol [3] (the X-ray structure of the 2-benzyl-substituted compound has been determined [2]) and the absorptions at 1497 cm^{-1} and δ 11.27 (singlet) for the CHO group in the infrared and ^1H NMR spectra all support 2a. Thus 2 is formed by removal of both hydrogen atoms from the α-CH_2 group even though the aldehydic H is first transferred (Scheme 1). Vinyloxo complexes have been isolated [1], but the proposed intermediate in this case was not isolated or even detected.



SCHEME 1

Ketones give analogues of 2 and 3 but these must be formed by a different route to that for complexes of type 2. Thus cyclohexanone reacts with $Os_3(CO)_{12}$ (refluxing decane, 15 h) to give a poor yield of 4 (17%), the saturated form of complex 3. Attempting to form a cluster intermediate between 3 and 4 by reaction of $Os_3(CO)_{12}$ with cyclohexenone (refluxing decane, 6 h) did not give 5 (Scheme 2) but only a low yield of 4 (20%). The difficulty with these high-temperature reactions is the formation of many products of which perhaps only one can be purified and characterised and it is difficult to say anything about reaction paths leading to them. The more reactive $H_2Os_3(CO)_{10}$ allows the use of lower temperatures and reacts with cyclohexenone (refluxing hexane, 4 h) to give complex 6 as the major product (32%) and we presume by analogy with other reactions of alkenes that cyclohexanone is a byproduct. Thus surprisingly oxidative addition occurs at the alkene rather than the more acidic α-CH_2 group. The lack of ν(CO) due to free ketone is consistent with the structure shown. An unexpected feature of the cluster chemistry of organic carbonyl compounds is the pronounced tendency towards coordination through oxygen so that 6 does not adopt a structure like that of $HOs_3(\mu^2\text{-}CH{=}CH_2)(CO)_{10}$, that is the carbonyl group effectively competes with the alkene function for coordination at osmium. Decarbonylation of 6 (refluxing octane, 2 h) quite remarkably gave complex 5



SCHEME 2

TABLE 1

SELECTED INFRARED AND ^{1}H NMR DATA[a]

Compound	ν(CO) (metal-coordinated) (cm^{-1})	δ(OsH) (in $CDCl_3$) (ppm)	Temperature (°C)
1	2111m, 2073s, 2061s, 2030s, 2015s, 2013w, 2000m, 1992(sh), 1985m	−14.04s	+27
2	2113m, 2087s, 2059s, 2027s, 2017s, 2003s, 1990m, 1985m	−11.79d, −13.88d	−50
3	2112m, 2086s, 2057s, 2034s, 2027s, 2013s, 2002s, 1987(sh), 1980m	−11.66d, −14.06d	−60
4	2105m, 2080s, 2051vs, 2023s, 2020(sh), 2010m, 1998s, 1979m	−12.36d, −14.03d	+27
5	2107m, 2082s, 2053vs, 2024vs, 2012m, 2000s, 1982m	−12.27d, −14.02d	+27
6	2106m, 2067s, 2053s,, 2024s, 2010m, 2003s, 1995m, 1984w, 1977m	−12.84s	+27
7	2090m, 2056s, 2038s, 2015m, 1999s, 1982m, 1969m	−17.21s	+27

[a] Compounds 1 to 7 gave satisfactory elemental analyses and the complete ^{1}H NMR data are consistent with the formulations as given and will be reported in full later.

which is formed formally from cyclohexenone by a double oxidative addition of the α-CH_2 group. In reality considerable rearrangement is necessary to obtain 5 so we hesitate to suggest mechanisms for any of these oxidative additions. The co-product, complex 7, containing the same ligand as in 6 but presumably as a 5*e*-donor, and possibly as shown, is isomeric with 5. Table 1 contains some of our evidence for these complexes as formulated but full details of these ketonic products and of those obtained from a range of acylic ketones will be given elsewhere.

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