# An Improved Method for the Preparation of $Os_3(CO)_{12}$, and Some Derivatives Thereof

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THE study of the reactions of certain polynuclear Group VIII metal carbonyls is hindered by the difficulty of preparing them in good yields. Thus the usual high-pressure synthesis[1] of $Os_3(CO)_{12}$ affords yields of 5% or less. The recent report by Bruce and Stone[2] of an improved low-pressure synthesis of $Ru_3(CO)_{12}$ prompts us to report a new method for preparing $Os_3(CO)_{12}$ and to describe several new types of compounds which it forms.

We have prepared[3] $Os_3(CO)_{12}$ in yields of 70% readily by heating $OsO_4$ (10·8 g.) in xylene (200 ml.) at 175° for 16 hr. in a glass-lined 1 l. autoclave containing carbon monoxide at 128 atmospheres (at 25°). The large yellow crystals of $Os_3(CO)_{12}$ (9 g.) are readily separated by hand from the white oxycarbonyl,[4] presumably $Os_4O_4(CO)_{12}$; it is then recrystallised from benzene. The infrared spectrum of solid $Os_3(CO)_{12}$ in the C–O stretching region gives bands at 2070 s, 2019 s, 1998 m, and 1986 m; shoulders are observed at 2041 and 2028 cm.$^{-1}$. There is a marked change to a simpler spectrum (2066 s, 2033 s, 2012 m, and 2000 m) on dissolution in chloroform.

Substitution products of $Os_3(CO)_{12}$ with triphenylphosphine and *o*-phenylenebisdimethylarsine (Diars) have been prepared by heating $Os_3(CO)_{12}$

TABLE

*Some derivatives of* $Os_3(CO)_{12}$

| | | Mol. wt. | | |
|---|---|---|---|---|
| Compound[a] | Colour | Found | Calc. | C–O stretching[b] |
| $Os_3(CO)_{12}$ | Yellow | — | 907 | See Text |
| $[Os(CO)_3PPh_3]_3$[c] | Orange red | 1654 | 1610[d] | 2053 w, 1988 s, 1969 s, 1927 s, 1957 sh |
| $[Os(CO)_2Diars]_3$ | Brownish Yellow | 1474 | 1597[d] | 1998 m, 1917 s |
| $[Os(CO)_3(PPh_3)Cl_2]$ | White | 712 | 607 | 2123 w, 2048 s, 2017 w, 1978 s |
| $[Os(CO)_3(PPh_3)Br_2]$ | Light yellow | 798 | 698 | 2154 w, 2067 s 2023 s, 1982 sh |
| $[Os(CO)_3(PPh_3)I_2]$[e] | Yellow | — | 790 | Impure |
| $(CO)_3(PPh_3)ClOsHgCl$ | White | — | 808 | 2076 w, 2032 m, 1998 s |

[a] Good elemental analyses for these compounds have been obtained; [b] Nujol mull; [c] The corresponding Ru compound has also been reported recently (ref. 6); [d] For trimer; [e] Not obtained pure as yet.

with the ligand in xylene. Their properties are described in the Table. The reactions of these substitution products with halogens and mercuric halides have also been studied. The former yield products of the type $Os(CO)_3(PPh_3)X_2$ and the latter give new metal–metal bonded Os–Hg compounds of the type $(CO)_3(Ph_3P)ClOs–HgCl$. Good analytical data and CO infrared spectra consistent with the structures assigned have been obtained.

Collman and Roper[5] have reported a series of derivatives which appear to be of the type $[Os(CO)_3(PPh_3)_2HgCl]HgCl_3$ obtained from $Os(CO)_3(PPh_3)_2$ by reduction of $OsCl_2(CO)_2(Ph_3P)_2$ but $Os_3(CO)_{12}$ was not used as the starting material.

The relative rates of reaction of $Os_3(CO)_{12}$ and its substitution products towards chlorine are very interesting. The substitution products react rapidly in the cold in benzene solution, whereas $Os_3(CO)_{12}$ has to be heated in benzene solution to achieve a reasonable rate of reaction.

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