An Arenecarbonyl Cation: Chlorotricarbonylhexamethylbenzenetungsten(II)

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OXIDATION of arenetricarbonyl derivatives of Group VI metals has not previously been reported to lead to characterisable products. We have found that tricarbonylhexamethylbenzenetungsten, $(HMB)W(CO)_3$, reacts in chloroform with antimony pentachloride precipitating the light orange product $[(HMB)W(CO)_3Cl]SbCl_6$. The tetraphenylborate, $[(HMB)W(CO)_3Cl]BPh_4$, is obtained from an acetone solution of the hexachloroantimonate by addition of the sodium salt and precipitation with ether. Recrystallisation from acetone–ether yields the pure compound as orange plates. This derivative is diamagnetic, a 1:1 electrolyte in nitrobenzene, and has well-defined bands in the C–O stretching region at 2080, 2020, and 2005 cm.$^{-1}$ in Nujol. It decomposes readily in warm acetone, but the solid is stable for several days at room temperature.

The cation may be considered to be a seven-co-ordinate derivative of tungsten(II) (accepting the formalism that hexamethylbenzene is equivalent to a terdentate ligand), similar to products obtained by halogen oxidation of tri(tertiary-arsine)-substituted Group VI carbonyls.[1,2] Oxidation of these substituted carbonyls with chlorine results in complete loss of carbon monoxide. The use of antimony pentachloride, however, results in immediate precipitation of the seven-co-ordinate cation from solution. The chloro-complexes $[W(CO)_3(v\text{-Triars})Cl]SbCl_6$, $[W(CO)_3(v\text{-Triars})Cl]BPh_4$, and $[W(CO)_3(v\text{-Triars})Cl_2]$ [v-Triars = tris-1,1,1-(dimethylarsinomethyl)ethane] have been prepared by use of this oxidising agent; the analogous bromo- and iodo-compounds have been prepared by simple halogen oxidation.

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[1] C. D. Cook, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1965, 419.

[2] R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, in the press.