Tetranuclear Carbonyliridates

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THE known carbonylmetallates are derived from the transition metals, belonging to sub-Groups V, VI, and VIIA and to the first triad of Group VIII.[1] We have now found that tricarbonyliridium reacts very smoothly with alkali, giving two tetranuclear carbonyliridates, which have been isolated in a pure state as salts of bulky anions.

By treating a methanol suspension of $Ir_4(CO)_{12}$ with potassium carbonate at room temperature, in carbon monoxide atmosphere, a clear solution was obtained which, on addition of trimethylbenzylammonium (tba) chloride, gave a yellow crystalline salt-like diamagnetic substance corresponding analytically to $[tba][HIr_4(CO)_{11}]$ (Analysis: Found: C, 20·3; H, 1·3; N, 1·2; O, 14·8. Calc. for $C_{21}H_{17}NO_{11}Ir_4$: C, 20·5; H, 1·4; N, 1·14; O, 14·4%.) The presence of the hydride hydrogen was proved by the n.m.r. spectrum at τ 5·5 (internal reference Me_4Si).

By a similar reaction performed in nitrogen atmosphere or, more rapidly, by heating $Ir_4(CO)_{12}$ with dilute methanolic potassium hydroxide in carbon monoxide atmosphere, a dark solution resulted from which brown crystals were recovered. The analysis of this substance, only slightly different from that of the yellow salt, gave an Ir : CO ratio of 4 : 10 and, since no hydride hydrogen could be detected in the n.m.r. spectrum (up to τ 30), in order to account for its diamagnetism, we formulated it as the dimeric $[tba]_2[Ir_4(CO)_{10}]_2$.

The i.r. spectra of the salts of the two carbonyliridate anions, in the CO stretching region, are very similar (tetrahydrofuran as solvent):

$[tba][HIr_4(CO)_{11}]$:	2065sh, 2015s, 1965sh, 1800s cm.$^{-1}$;
$[tba]_2[Ir_4(CO)_{10}]_2$:	2050sh, 2020s, 1975sh, 1825sh, 1770s, 1710sh cm.$^{-1}$,

and indicate the presence of both terminal and bridging carbon monoxide. We suggest for the structure of the yellow anion, a tetrahedral cluster of iridium atoms, bound both by intermetallic bonds and CO bridges; in the brown salt two such clusters would be held together by another intermetallic bond.

These structures would then be strictly related to that of the parent $Ir_4(CO)_{12}$ which has no bridges.[2] That polynuclear carbonyls may or may not have CO bridges, with only minor changes in the disposition of the metal atoms, is well known, *cf.*, cobalt chemistry.[3]

The terminal and the bridging CO contribute the same number of electrons to the metal, but it appears that the bridging CO helps to dissipate more negative charge from it than the terminal ones. This can be deduced, among other things, from the fact that most polynuclear carbonylmetallate anions, in which the metals have a formally negative charge, seem to have CO bridges.

The two tetranuclear carbonyliridates react readily with tertiary phosphines giving substitution derivatives of $Ir_4(CO)_{12}$. With triphenylphosphine (L), $Ir_4(CO)_{10}L_2$ was obtained from the yellow salt and $Ir_4(CO)_9L_3$ from the brown one. The i.r spectra of these neutral compounds:

$Ir_4L_2(CO)_{10}$: 2060s, 2030s, 2000s, 1830s, 1790s cm.$^{-1}$;

$Ir_4L_3(CO)_9$: 2042s, 1985s, 1964sh, 1780s cm.$^{-1}$,

are similar to those of the parent carbonyliridate, and we consider that the tetrahedral structure with CO bridges has been preserved. With other tertiary phosphines (PPh_2Me, PPh_2Et) more CO substitution can be achieved; the compounds deriving from the yellow salt seem to have always a phosphine less than those deriving from the brown one.

Attempts to obtain the free hydridocarbonylmetals have been initiated. The brown anion on the action of acids, both in nitrogen and carbon monoxide atmosphere, decomposed. The yellow anion, on the contrary, when acidified in carbon monoxide atmosphere, gave pure tricarbonyliridium, while, in nitrogen atmosphere, it yielded an unstable brown-yellow compound, which showed in the i.r. spectrum absorptions at 2130m, 742, and 728 cm.$^{-1}$, which might be assigned to the stretching and bending bands of a hydride which, from the elemental analysis and way of formation, might well be $H_2Ir_4(CO)_{11}$. The n.m.r. signal of this hydride was found at τ 5·53.

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[3] K. Noak, *Spectrochim. Acta*, 1963, **19**, 1925; G. Bor, *ibid.*, p. 2065.