New Cobalt Arene and Carbide Carbonyl Complexes

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FEW arene and carbide carbonyl clusters are known.[1,2] We have prepared the new arene carbonyl clusters, $MeCCo_3(CO)_6$(arene), and a series of novel carbide carbonyl clusters in which there are more than three cobalt atoms per cluster, *e.g.* $Co_5(CO)_{15}C_3H$. It appears that zerovalent cobalt has a strong affinity for carbon and this family of closely related complexes may give further insight into the nature of the carbon atom in carbide complexes.

Typical of the arene complexes is the mesitylene derivative, $MeCCo_3(CO)_6(C_6H_3Me_3)$, prepared by direct reaction of the arene with $MeCCo_3(CO)_9$ at 160°. Purification by fractional sublimation gave the complex as air-stable, volatile, black prisms, soluble in organic solvents without decomposition. The parent molecular ion was observed in the mass spectrum at *m/e* 492 and the principal secondary fragmentation process was loss of cobalt as in the parent carbonyl.[3] The presence of co-ordinated arene was confirmed by the n.m.r. spectrum which showed signals at τ_H 4·54 and τ 7·64, in addition to the C–CH_3 signal at τ 6·36 [*cf.* $MeCCo_3(CO)_9$, τ 6·83]. Six bands were observed in the CO stretching region, 2060s, 2016vs, 2002s, 1992w, 1983s, and 1969w, consistent with a structure in which the mesitylene is symmetrically co-ordinated to one cobalt atom (C_s symmetry).

In contrast, the comparable reaction of $ClCCo_3(CO)_9$ and mesitylene yielded a number of cobalt carbide carbonyl complexes which could be separated on silica-gel plates.

The first product (black needles) is formulated as $Co_5(CO)_{15}C_3H$ on the basis of complete analytical data, molecular weight, and mass spectrum. In the mass spectrum the molecular ion $Co_5(CO)_{15}C_3H^+$ successively lost carbonyl groups to give the ions $Co_5C_3H^+$ and $Co_5C_3^+$ in high abundance (these latter ions have been mass measured). Ions of lower *m/e* values are in low abundance while doubly-charged ions $Co_5(CO)_{15-n}C_3H^{2+}$ (n = 1—15) are in moderate abundance which suggests that the Co_5C_3 cluster is particularly stable to electron impact. Significantly, non-carbon-containing ions of the type, Co_5^+, Co_4^+, *etc.*, were not observed. The i.r. spectrum is complicated in the CO stretching region but there are no bands due to bridging CO groups.

We have been unable to obtain mass spectra of the other major products but on the basis of analytical data, molecular weights, and n.m.r. spectra we can formulate them as $Co_6(CO)_{18}C_4$ and $Co_6(CO)_{17}C_5$. It is noteworthy that Dahl and his co-workers[4] have found that sulphur forms a related series of cluster carbonyls with 3—6 cobalt atoms.

In conclusion we must stress the different behaviour of $XCCo_3(CO)_9$ compounds (X = Me, Cl, or Br) towards arenes. There is no evidence that $ClCCo_3(CO)_9$ forms an arene complex. Ercoli, Allegra, and Peronaci[5] have reported that $BrCCo_3(CO)_9$ in boiling toluene gives the dimer, $[Co_3(CO)_9C]_2$, and an insertion product, $[Co_3(CO)_9C]_2CO$. We find these products in only small amounts in reactions with $ClCCo_3(CO)_9$. However, it is possible that the structures of the carbide clusters are based on that of the dimer.†

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† Single-crystal *X*-ray structure determinations of these complexes are being carried out by Dr. B. Penfold, University of Canterbury, New Zealand.

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