A Transition-metal Complex of Benzyne

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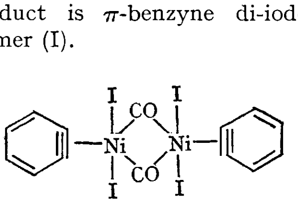
IT IS well known that bonds between carbon and the heavier halogens are readily broken in reactions with transition-metal carbonyls. So, for example, the first transition metal–π-cyclobutadiene complex was prepared by the action of tetracarbonylnickel on 1,2-dichlorotetramethylcyclobut-3-ene.[1] We now report the results of some reactions between *o*-dihalogenobenzenes and tetracarbonylnickel, carried out in the hope that these would give π-complexes of benzyne.

A concentrated solution of *o*-di-iodobenzene in either pentane or cyclohexane was heated to 70° in a sealed tube with an approximately equimolar quantity of tetracarbonylnickel. After 1 hr. the tube was allowed to cool and then opened. The black, slimy residue was washed with a little benzene, fine, black, needle-like crystals being left. The product is π-benzyne di-iodo-μ-carbonylnickel dimer (I).



(I)

Prepared as described above, the compound, $[NiC_7H_4I_2O]_2$, is analytically pure. The solid complex may be exposed to the air for short periods without apparent decomposition.

The presence of bridging carbonyl groups is indicated by a strong peak at 1790 cm.$^{-1}$ in the infrared spectrum. The compound is moderately soluble in most organic solvents to give brown air-sensitive solutions which decolourise instantly when shaken with water. Nickel(II) and iodide ions are then found to be present in the aqueous layer. The compound is diamagnetic, as evidenced by its n.m.r. spectrum. This is of A_2B_2 type ($|J| = 3{\cdot}5$ c./sec., δ 14 c./sec., centred about τ 2·33) measurements being made on a Varian A60 in deuteriomethanol. Evidently, the C_6 group retains its aromatic character in the complex.

The mass spectrum supports the proposed structure. A parent peak is not observed, the heaviest ion being $NiI_2C_6H_4^+$ ($m/e = 388$). Other ions produced include $C_6H_5I_2^+$ ($m/e = 331$) and species derived from this by removal of H or I atoms. Peaks corresponding to $C_{12}H_8^+$ (biphenylene$^+$?) ($m/e = 152$) and related ions with one, two, and four added CO groups also occur. Other ions observed include $PhCO^+$, I_2^+, CO^+, and Ph^+ and related species. We have little direct evidence to support the dimeric nature of structure (I), although intuitively higher polymers seem less probable. The presence of only one bridging carbonyl peak in the infrared spectrum suggests, but does not prove, that the molecule is centrosymmetric and that all carbonyl groups are symmetry related.

The reaction between *o*-di-iodoperfluorobenzene and tetracarbonylnickel leads to crystalline products of variable composition which may be black, green, or orange. Some of the orange crystals have the interesting, and possibly important, property of turning black under nitrogen, becoming orange again when exposed to the air. This colour change, which may be repeated indefinitely, is not accompanied by any significant change in weight of the crystal and may be a surface effect.

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[1] R. Criegee and G. Schröder, *Annalen*, 1959, **623**, 1.