Iridium–Maleoyl Complexes from Tricarbonyliridium Halides and Acetylenes

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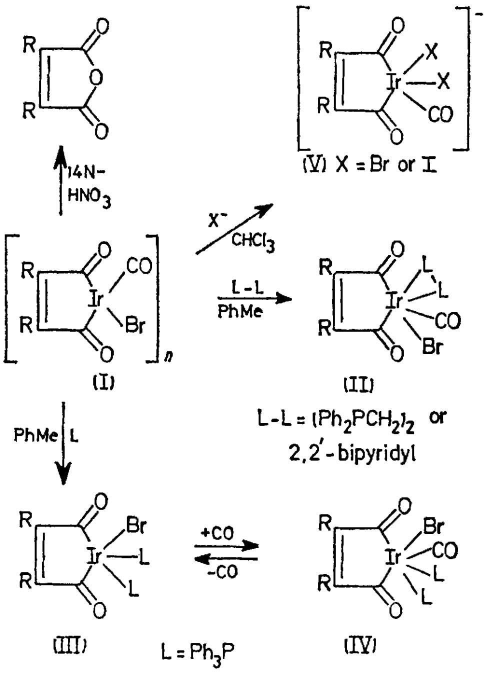
Summary Reaction of $[Ir(CO)_3X]$ (X = Br or Cl) with diphenylacetylene and with hex-3-yne gives the polymeric cyclic diacyl compounds $[Ir\{R_2C_2(CO)_2\}(CO)X]_n$ (R = Ph or Et) which depolymerize with various ligands giving monomeric cyclomaleoyl complexes of iridium(III).

Rhodia and iridia-cycles, some of which are active in the cyclotrimerization of acetylenes, have been reported.[1,2,3] The formation of cyclic diacyl complexes as well as metallacyclopentadiene compounds has also been proposed in the case of rhodium.[3]

We now report the syntheses and properties of new iridium–maleoyl compounds derived by addition of symmetrically disubstituted acetylenes to tricarbonyliridium halides. $[Ir(CO)_3X]$ (X = Br or Cl) reacts slowly with diphenylacetylene (a) and with hex-3-yne (b) in the molar ratio 1:4—1:8, in a variety of solvents (tetrahydrofuran, benzene, and toluene) under reflux under CO or an inert atmosphere, giving the cyclic diacyl derivatives $[Ir\{R_2C_2(CO)_2\}(CO)X]_n$ (Ia; R = Ph, Ib; R = Et; X = Br or Cl).



Scheme. a; R = Ph, b; R = Et.

The tricarbonyliridium halides are quantitatively transformed into compounds of type (I) and at the end of the reaction most of the excess of the acetylene has been converted into hexaphenyl- and hexaethyl-benzene respectively. The proposed formulae were inferred from elemental analyses, i.r. spectra, and chemical behaviour (see Scheme).

The pale yellow complex (Ia) was slightly soluble in polar complexing solvents and insoluble in non-complexing solvents; ν_{max} (Nujol) 2065vs (terminal CO), 1690s and 1675s (acylic CO), and 1545vs cm^{-1} (possibly due to intermolecular interaction of the acyl CO groups with the unsaturated iridium atoms[4]). The cream compound (Ib) showed a similar i.r. spectrum with the more significant bands at 2085s and 1620m cm^{-1}. Its insolubility in organic solvents and the presence of a broad and very intense band at 1560 cm^{-1} suggest that association is greater than in (Ia). Strong evidence in favour of the structures (I) comes from the reaction of (Ia) with conc. HNO_3 to give diphenylmaleic anhydride, identified both by comparison with a known sample and by hydration to diphenylmaleic acid. The Ir–C bonds in the maleoyl complexes (Ia) and (Ib) are thermally and hydrolytically stable: compound (I) was recovered mostly unchanged even when boiled for 24 h in n-butanol or toluene–ethanol in the presence of halogens.

Comparison of the i.r. spectra of the adducts in the Scheme with that of (I) shows that the $-C\equiv O$ and $>C=O$ stretching frequencies are lowered by further co-ordination as expected; moreover the disappearance of the strong bands at 1560—1545 cm^{-1} by reaction of (I) with various ligands reveals that the association of individual molecules of (I) may arise not only from bridging halogen atoms but also from the interaction between carbonyl groups and co-ordinatively unsaturated iridium atoms.[4]

Further support for the stoicheiometries and the structures proposed comes from the n.m.r. data of the monomeric adducts: *e.g.* the spectrum of the complex (IIIb) showed resonances at τ 2·4—2·6 (heterocyclic-H), 7·4 (q, CH_2), and 8·9 (t, Me). The intensity ratio of the signals (8:4:6) confirms that one molecule of bidentate ligand is bonded to an iridium atom attached to an organic residue containing two ethyl groups.

This reaction of carbonyliridium halides with acetylenes differs from those previously reported for Pt^{II} [5] and Ir^{I},[1] both in the mode of reaction and in the increased specificity.

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