

Bis-azoarene Complexes of Rhodium: X-Ray Crystal Structure of Bis(azoarene)rhodium Acetate

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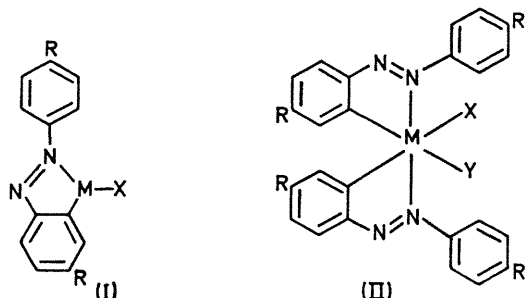
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Summary Rhodium complexes in which two azoarene groups act as chelating ligands have been obtained both from rhodium trichloride and from rhodium carbonyl chloride and shown to yield bis(arylazo)biphenyls on carbonylation; the structure of the mononuclear bis(azoarene)rhodium acetate has been established by X-ray crystallography.

THAT azoarenes can function as chelating ligands (I), linked both through C-2 and the non-adjacent nitrogen atom was first shown in the case of the cyclopentadienyl-nickel¹ (I; M = Ni, X = C₅H₅) and the dimeric chloro-palladium and -platinum² complexes. Heck³ converted the palladium derivative into analogous complexes of manganese, rhenium, and cobalt carbonyls, while more recent studies have been concerned with mercuration and oxidation of the nickel complex,⁴ with halogenation,⁵ carbonylation,⁶ and spectroscopic study⁷ of the palladium complex, and with ruthenium complexes.⁸



Analogues (II) with two chelating azoarene groups on the same metal atom were obtained by us⁹ from both iron (II; M = Fe, X = Y = CO) and palladium (II; M = Pd, no X, Y), but the minute quantities available by our methods made detailed study impractical. We therefore turned to the related rhodium complexes described by Jo, Hagihara, and Murahashi.¹⁰ Their simplest product was believed to have structure (II; M = Rh, X = Cl, Y = OC₂H₅, R = H) with a co-ordinated molecule of tetrahydrofuran. Repetition of their procedure led to somewhat divergent results, in that we were unable to obtain discrete adducts with tetrahydrofuran or other donor solvents or ligands. Benzene extraction afforded a red crystalline product, difficult to purify, but probably having a chloride-bridged dimeric structure (C₁₂H₉N₂)₂RhCl₂Rh-(C₁₂H₉N₂)Cl, whereas treatment with sodium acetate or chromatography on alumina, which had been neutralised with ethyl acetate, gave the well-crystallised dark-red acetato-complex (II; M = Rh, X, Y = O₂CMe, R = H).

The structure of the latter has been determined by X-ray diffraction from single crystals. *Crystal data:*

C₂₆H₂₁N₄O₂Rh, *M* = 524.4, monoclinic, *a* = 8.847, *b* = 16.760, *c* = 15.710 Å, β 96.14°, *U* = 2316 Å³, *Z* = 4, *D*_m = 1.50 ± 0.02, *D*_c = 1.50, space group *Cc*, 1846 'non-zero' diffractometer observations, *R* = 8.8%, solved by Patterson and Fourier methods.

The analysis establishes that the rhodium bonds to two azobenzene ligands each of which acts as a bidentate ligand with the metal bonded to an *ortho* carbon of one phenyl group and the further nitrogen, thus forming a five-membered ring. The two Rh-C bonds are *cis* and the two Rh-N bonds *trans* to one another. The chelating acetato-group completes the octahedral co-ordination polygon of the rhodium and lies on an idealised molecular two-fold axis. The (unrelated by symmetry) azobenzene ligands do not exhibit significantly different bond-lengths and average values are shown in the Figure. The phenyl-

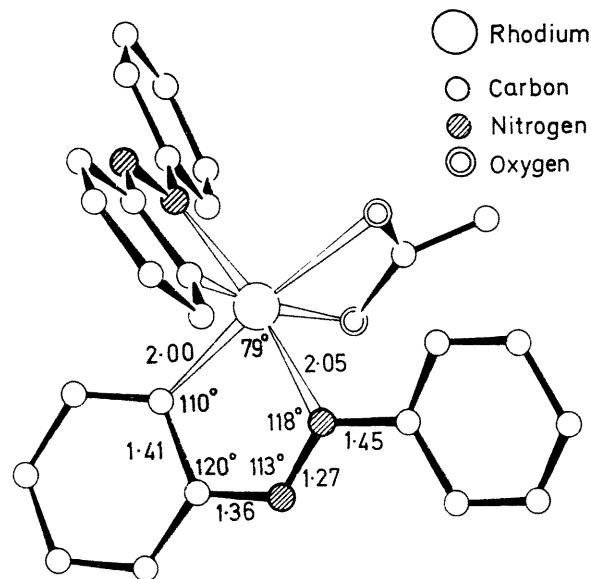


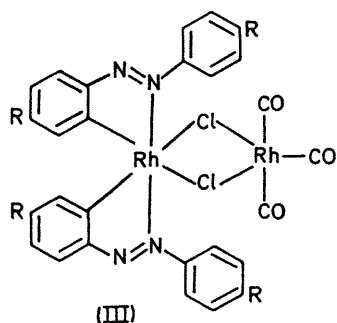
FIGURE. A view of bis(azobenzene)rhodium acetate showing mean bonding parameters.

nitrogen distances differ by almost 0.1 Å, that which involves the ring bonded to the metal being the shorter.

This structure determination provides the first direct confirmation that the chelating azoarenes bond through the nitrogen lone pair, rather than the N-N π-electrons as originally suggested by Kleiman and Dubeck.¹

We have also prepared a second series of complexes, from azoarenes and [Rh(CO)₂Cl]₂. They are converted with sodium acetate into the above acetato-complexes (II; M = Rh, X, Y = O₂CMe) and we formulate them

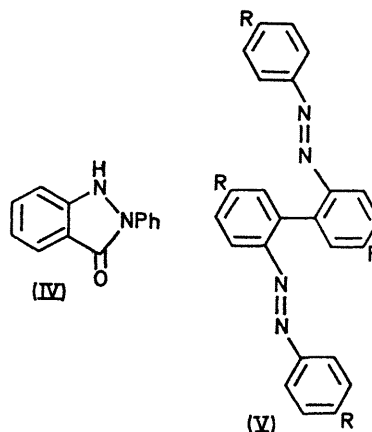
tentatively as chlorine-bridged dimers (III; R = H, OMe etc.) containing both Rh^I and Rh^{III}.



The most striking feature of these structures is the fact that they provide a ready explanation for the unusual behaviour of these Rh complexes on carbonylation. Whereas the palladium complex [dimer of (I); M = Pd, X = Cl, R = H] reacts with CO⁶ forming the phenylindazolone (IV) and a related cobalt complex is believed to be intermediate in the formation of this heterocycle by the cobalt carbonyl catalysed carbonylation of azobenzene,¹¹ all our Rh complexes yield the bis-azo-compounds (V).

In all probability formation of the new carbon-carbon

bond requires the observed *cis*-arrangement and results during the displacement of the chelating azoarene groups



from the metal by CO. It is not clear whether this is the first step, or is preceded by displacement of nitrogen from the metal as in the reactions of the ruthenium⁸ and palladium¹² complexes with triphenylphosphine.

(Received, December 4th, 1970; Com. 2094.)

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