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Oxidative Addition to Binuclear Rhodium(I) and Iridium(I) Pyrazole Bridged Complexes. The Formation of An Unusual Carbonyl Bridged Derivative

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Two center oxidative addition reactions to give binuclear metal–metal bonded rhodium(II) and iridium(II) complexes have been reported for only a few bimetallic Rh(I) and Ir(I) compounds containing bridging bisdiphenylphosphinomethane (3 atom bridge) [1], diisocyanide ligands (7–10 atom bridges) [2] or thiolates (1 atom bridges) [3]. We now report that binuclear rhodium(I) and iridium(I) pyrazole bridged complexes (2 atom bridges) will undergo two center oxidative addition reactions though the nature and the stability of the product formed is sensitive to steric factors.

The complexes $[M(CO)_2(\mu\text{-}3,5\text{-}dRp)]_2$, *1*, (M = Rh, Ir; dRp = dimethylpyrazolyl (dmp), diphenylpyrazolyl (dpp)) react with tertiary phosphines, arsines or phosphites, L, to give *trans*-$[M(CO)L(\mu\text{-}3,5\text{-}dRp)]_2$, *2*, ($\nu_{CO}$ 1950–2000 cm^{-1}) as orange crystalline compounds readily characterized by spectroscopy and elemental analyses**. Reaction of *2* (M = Rh, Ir; dRp = dmp; L = $PhMe_2P$, Ph_2MeP, $(PhO)_3P$, $PhMe_2As$) with a stoichiometric amount of I_2, or alternately, with 1,2-diiodoethane (better yields) gives the binuclear M(II) compounds $[M(CO)LI(\mu\text{-}3,5\text{-}dmp)]_2$, *3*, ($\nu_{CO}$ 2000–2070 cm^{-1}) as well defined crystalline compounds. The structure of *3* (M = Ir, L = $(PhO)_3P$) has been obtained by X-ray crystallography (see Fig. 1). The molecule contains an almost linear I–Ir–Ir–I arrangement with an Ir–Ir bond length of 2.688 Å.

In contrast, reaction of *2* (M = Rh, R = CH_3, L = Ph_3P; or R = C_6H_5, L = Ph_2MeP, $PhMe_2As$) with 1,2-diiodoethane yields deep red-brown crystalline compounds which show a strong band in their IR spectra at *ca.* 1790 cm^{-1} and no bands corresponding to terminally bonded carbonyl groups. The band at 1790 cm^{-1} is suggestive of a bridging carbonyl ligand.

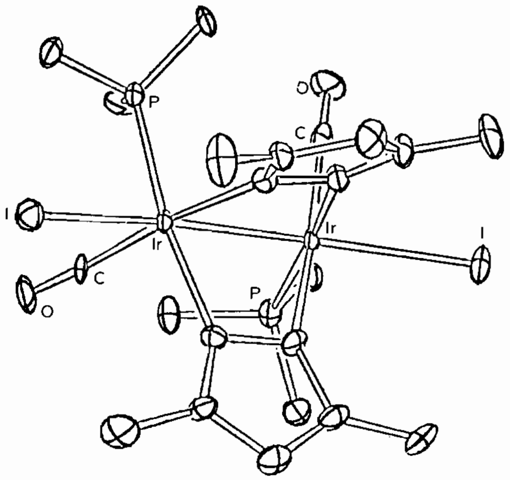

Fig. 1. Perspective view of $[Ir(CO)(PhO)_3PI(\mu\text{-}3,5\text{-}dmp)]_2$. The I–Ir–Ir–I arrangement is approximately linear, the Ir–Ir bond length is 2.688 Å. (Phenyl rings omitted.)

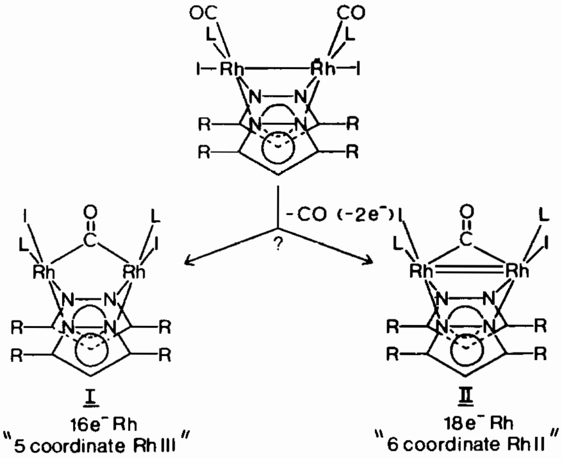

Fig. 2. Possible structural representations for compounds 4.

Elemental analysis is consistent with the formulation $[\{RhLI(\mu\text{-}3,5\text{-}dRp)\}_2\mu\text{-}CO]$ *4*. Furthermore, when *3* (M = Rh, R = CH_3, L = $PhMe_2P$) is left to sit in solution for several days it slowly transforms into a compound which shows a strong band in its IR spectrum at 1750 cm^{-1} and no bands corresponding to terminally bonded CO ligands (*i.e.* structurally the same as *4*). Two possible structural representations for compounds *4* are I and II (Fig. 2). The X-ray crystallographic study of *4* (M = Rh, R = CH_3, L = Ph_3P) confirms that the transformation of *3* to *4* involves loss of coordinated CO and I is the more appropriate representation of the structure (Fig. 3). The conversion of *3* to *4* results in an increase in the metal–

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**Only the rhodium compounds were isolated. The iridium complexes are very air sensitive and were characterized by ^1H NMR and solution IR spectra.

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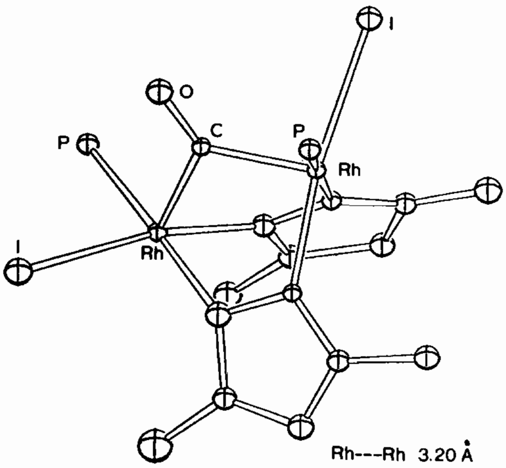

Fig. 3. Perspective view of $[\{Rh(Ph_3P)I(\mu\text{-}3,5\text{-dmp})\}_2\mu\text{-}CO]$. The Rh- - -Rh separation is 3.20 Å. (Phenyl rings omitted.)

metal separation consistent with the loss of a metal–metal bond. Formation of *4* from *3* is promoted by bulky L and bulky substituents in the 3,5 positions of the pyrazole ring. Thus *4* is most readily formed for L = $Ph_3P > Ph_2MeP \sim PhMe_2As > PhMe_2P$ and R = Ph > Me. The structure of *4* may be regarded as containing 16 electron, five coordinate, formally Rh(III) (assuming a ketonic bridging CO). The approximately square pyramidal coordination about each rhodium is very similar to that observed for the five coordinate Rh(III) acyl complexes $[Rh(COR)Cl_2(PPh_3)_2]$ (R = CH_3, CH_2CH_2Ph) [4].

The isolation of the carbonyl bridged derivative *4* can be considered to be a consequence of the geometry of the *cis*-μ-pyrazolyl ligands, their remarkable stability to bridge cleavage reactions and the steric consequences of the 3,5-substituents. The stability of the bridging pyrazolyl unit should enable one to obtain more details concerning oxidative addition across two metal centers. In contrast to rhodium, the complexes *3* (M = Ir) do not lose CO. Investigations of other oxidative additions to *2* and the reactivity of the bridging CO in *4* are currently in progress.

Acknowledgement

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