Interaction of β-Diketones with Platinum and Palladium Dienyl Halide Complexes

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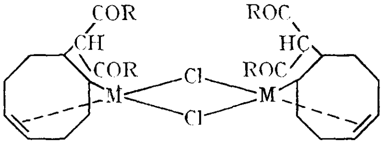
WE have been studying a series of β-diketone–metal complexes in which the diketone is bonded to the metal *via* the γ-carbon atom rather than oxygen. Recently,[1] we reported that a useful criterion in establishing the bond type is that a C–O stretching frequency in the region 1670—1710 cm.$^{-1}$ together with a C–H stretching frequency below 3000 cm.$^{-1}$ is indicative of γ-C-bonding, while a C–O frequency of *ca.* 1600 cm.$^{-1}$ together with a C–H above 3000 cm.$^{-1}$ indicates O-bonding.

This criterion specifically referred to complexes in which the diketone molecule was directly attached to the metal. We now extend it to include complexes in which the diketone is bonded through its γ-C atom to co-ordinated ligands. We must emphasise, therefore, that the above criterion does not differentiate between diketones C-bonded to metal or organic moieties. During the course of an investigation of transition-metal–diketone complexes we have prepared a large number of complexes of general formula (diene–diketone)M(diketone) (M = Pd or Pt, diene = cyclo-octa-1,5-diene, norbornadiene, and dicyclopentadiene). All are colourless or pale yellow crystalline solids and are monomeric non-electrolytes in chloroform and acetone solutions respectively. Reactions of these complexes with acids, HX, yield the halogen-bridged dimers [(cyclo-oct-1-ene–diketone)MX]$_2$ (X = Cl, Br, I, or SCN). On decomposition with aqueous KCN the free olefins are produced, and have been fully characterised by analytical, infrared, n.m.r., and mass spectral data. The complexes themselves have proton n.m.r. and infrared spectra entirely consistent with the above formulations (see Figure).

The infrared spectra of the (cyclo-oct-1-ene–diketone)M(diketone) complexes show bands associated with both O- and C-bonded diketone molecules, whereas in the spectra of the dimeric complexes only bands associated with C-bonded diketones are observed.

The halogen-bridged dimers readily react with triphenylphosphine to form the monomeric complexes (cyclo-oct-1-ene–diketone)M(Ph$_3$P)X; the phosphine group bonding *cis*- to the metal carbon σ-bonded group. The isolation of a phosphine complex, is indicative that the normal diene bonding pattern has been modified, and we suggest this as a chemical means of identifying such a bonding system.

In the complexes (diene)MX$_2$ there are two possible sites for nucleophilic attack; the metal and the ethylenic carbon atoms. Nucleophiles which do not form strong bonds with Pd and Pt, for example OMe$^-$, preferentially attack the diene,[2] this reaction being the first used to establish this class of compound. Very recently,[3] the preparation of the compounds (COD–L)PdCl$_2$ [L = -CH(CO$_2$Et)$_2$ or -CH(COMe)(CO$_2$Et), COD = cyclo-octa-1,5-diene] from the reaction of the appropriate carbanion with CODPdCl$_2$ was reported. In this case the nucleophiles clearly prefer to attack the diene. We believe that in the reactions reported here the diketones are behaving in an analogous way.



(*Received, December 3rd,* 1965; *Com.* 754.)

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[3] J. Tsuji and M. Tatahashi, *J. Amer. Chem. Soc.*, 1965, **87**, 3275.