Chelate Compounds of Platinum(II) containing only Sigma and Pi Carbon-to-Metal Bonds

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Summary Compounds of platinum(II), containing two σ- and two π-type bonds have been prepared using the ligand *o*-allylphenyl, and their properties and reactions are summarised.

EARLIER[1] we reported the synthesis of chelate complexes of transition metals with ligands of the type o-XC_6H_4Y where X is a σ-donor, *e.g.* PPh_2, $AsMe_2$, or $AsPh_2$ and Y is $CH:CH_2$, $CH_2{\cdot}CH:CH_2$, or $CH:CH{\cdot}Me$. The work has now been extended[2] to the use of charged ligands in which $X = -O^-$ and S^-. When $X = O^-$ and $Y = CH_2{\cdot}CH{=}CH_2$, monomeric bis-chelate platinum(II) complexes containing co-ordinated double bonds are formed whilst the thioallyl phenols form hexameric derivatives {*i.e.* $[Pt\text{-}(S\text{-}C_6H_4{\cdot}CH_2\text{-}{\cdot}CH{=}CH_2\text{-}o)_2]_6$} in which the double bond is not co-ordinated. The structure of these may involve an octahedral Pt_6 cluster[3] as in $[PtCl_2]_6$ or a 12-membered ring as in certain $[Ni(SR)_2]_6$ complexes.[4]

The platinum(II) complex (I) (scheme) of the charged ligand o-$CH_2{=}CH{\cdot}CH_2{\cdot}C_6H_4^-$ is formed by treating the Grignard reagent of *o*-chloroallylbenzene in THF with anhydrous platinum(II) bromide or chloride in benzene suspension. The *cis*-planar structure (I) is assigned on the basis of analyses (C, H, Pt, and absence of halogen), i.r. and n.m.r. spectra, mol. wt. and conductivity studies, and the electric dipole moment ($\mu = 3{\cdot}3$ D). Unfortunately, twinning of the crystal has, so far, precluded a single crystal *X*-ray study but ring-substituted derivatives are being prepared for this purpose. The i.r. data for this and related compounds are shown in the Table. This complex is one of the few examples known of a Pt^{II} atom co-ordinated to six carbon atoms, although Pt^{II} complexes of the type $(diene)_2PtR_2$ (R = Me and Ph) have been reported.[5]

Compound (I) reacts with Ph_3P to yield (II) in which there are two un-coordinated C=C double bonds. By treating compound (I) with anhydrous HCl, however, compound (III) is isolated; when excess Ph_3P in benzene solution is added to (III) *cis*-$PtCl_2(Ph_3P)_2$ is precipitated and the presence of allylbenzene in the filtrate was established by gas chromatography. The planar, monomeric structures assigned to (II) and (III) are based on analysis, mol. wt., and the i.r. spectrum of the C=C bond. Compound (II) appears to be *cis* from the low solubility but (III) is probably *trans* by analogy with $PtCl_2(PPh_3)_2$.

Compound (II) reacts with Br_2 and Cl_2 to yield a yellow

TABLE

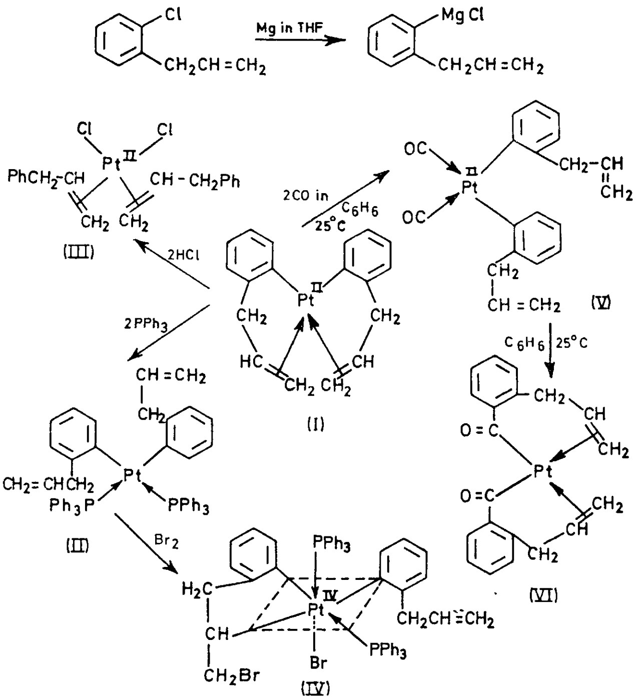
	Compound[a]	Colour	M.p.	Absorption bands of $CH:CH_2$ group[b]
(I)	$Pt(C_9H_9)_2$[c]	Pale yellow	186°	1532 (HCH scissor) and 1262 (C:C stretch)
(II)	$(Ph_3P)_2Pt(C_9H_9)_2$	White	179°	1639 (C:C stretch) 1256 (HCH scissor)
(III)	$Cl_2Pt(C_9H_{10})_2$	White	168°	1492 (C:C stretch)

[a] All compounds are diamagnetic in benzene or chloroform and are non-electrolytes in nitromethane [b] In *o*-chloroallylbenzene bands at 1639 (s) and 1256 cm^{-1} (w), presumably due to C:C stretching and $-CH_2$ scissoring respectively, are observed [using the Hiraishi assignment (J. Hiraishi, *Spectrochim. Acta*, 1969, **25** *A*, 749)]. [c] N.m.r. spectra of this compound have been obtained and they confirm the co-ordination of double bonds, the usual up-field proton shift being observed.

compound the properties of which by analogy[6] with those of the oxidation product of $PtBr_2[PMe_2(o\text{-}C_6H_4C_3H_5)]_2$ indicate that it has structure (IV) in which there are four Pt–C bonds (see Figure). The bromo-derivative (IV) reacts with lithium iodide with the replacement of only one Br atom, probably the one attached to the Pt^{IV} atom.

The reaction of compound (I) in benzene with carbon monoxide at room temperature first yields compound (V) in which there is a broad band at 2080 cm^{-1} resolvable into peaks at 2075 and 2115 cm^{-1} presumably indicating two *cis*-CO groups bound to the Pt^{II} atom, both C=C bonds having been displaced from the co-ordination sphere.

This dicarbonyl, when set aside under a pressure of CO in benzene at 25° yields a compound with a strong band at 1700 cm^{-1}, characteristic of a ketonic CO and a band at 1535 cm^{-1} indicative of a co-ordinated C=C bond. We believe that intra-molecular *cis*-insertion of the two co-ordinated CO groups has occurred yielding compound (VI).[7] Further studies of the reactions of $o\text{-}MgCl{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{=}CH_2$ with other metal halides and of related chelate groups such as $o\text{-}BrCH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{=}CH_2$ are in progress.



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