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Preliminary communication

FUMARATE, MALEATE AND MALEIC ANHYDRIDE COMPLEXES OF PLATINUM(0).

M. TERESA CHICOTE, MICHAEL GREEN, JOHN L. SPENCER, F. GORDON A.STONE and JOSE VICENTE.
Department of Inorganic Chemistry, The University, Bristol BS8 1TS (U.K.).
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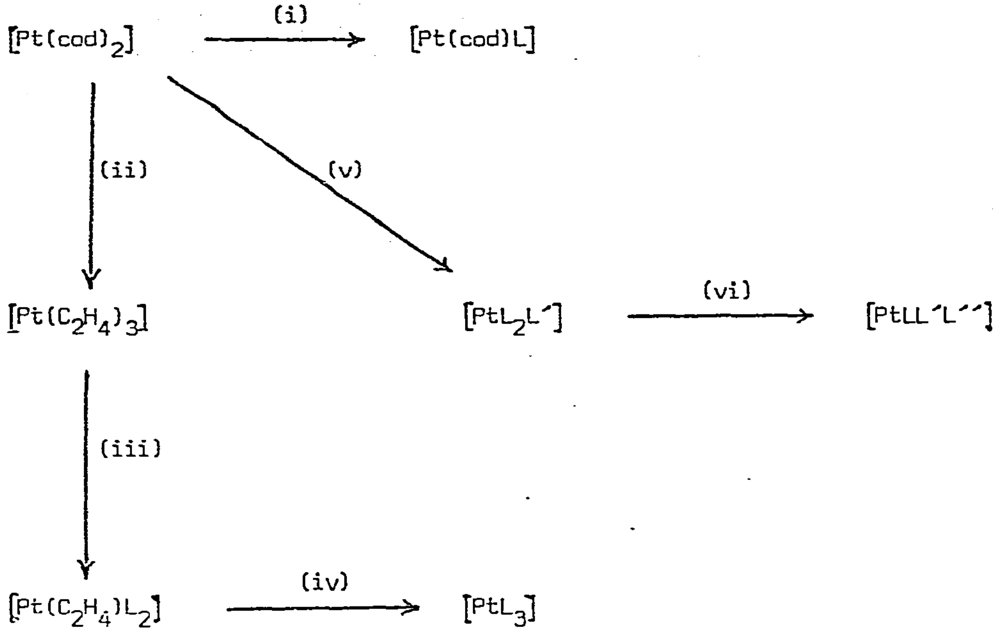
SUMMARY

Dimethyl fumarate (dmf), diethyl fumarate (def), dimethyl maleate (dmm), and maleic anhydride (ma) react with [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) and with [Pt(C$_2$H$_4$)$_3$] to give 'mixed' olefin platinum(0) complexes, e.g., [Pt(cod)(def)], [Pt(cod)(ma)], [Pt(C$_2$H$_4$)(dmf)$_2$] or [Pt(C$_2$H$_4$)(dmm)$_2$]. Tris-(olefin)platinum complexes [Pt(def)$_3$] and [Pt(dmf)$_3$] have also been obtained.

The ready displacement of the cyclo-octa-1,5-diene (cod) or ethylene ligands in [Pt(cod)$_2$] or [Pt(C$_2$H$_4$)$_3$] enable these compounds [1] to be used in the synthesis of a variety of organo-platinum complexes [2]. In such platinum(0) 'pure' olefin complexes the chemical reactivity and types of product formed will depend on the nature of the olefinic ligands, and it is, therefore, advantageous for synthetic purposes to extend the range of such compounds. Moreover, the replacement of one of the cod ligands in [Pt(cod)$_2$] or one or two of the C$_2$H$_4$ groups in [Pt(C$_2$H$_4$)$_3$] by other alkene ligands would yield 'mixed' olefin-platinum complexes likely to have reactivities towards other reagents different from those of the parent compounds. This has been accomplished by displacing cod or C$_2$H$_4$ groups from [Pt(cod)$_2$] or [Pt(C$_2$H$_4$)$_3$], respectively, with trans-CH(CO$_2$R):CH(CO$_2$R) [R = Me{dmf} or Et{def}], cis-CH(CO$_2$Me):CH(CO$_2$Me){dmm}, and $\overline{\mathrm{CH{:}CH\cdot C(O)\cdot O\cdot C}}\mathrm{(O)}${ma}. The reactions delineated in Scheme 1 were carried out at room temperature using diethyl ether as solvent and can be extended to other olefins and presumably to [Pd(cod)$_2$] [1].

Treatment of [Pt(cod)$_2$] with a mixture of def, dmf, dmm or ma and t-butyl isocyanide in a 2:1 molar ratio affords [Pt(olefin)$_2$Bu^{t}NC], analogues of the synthetically useful tertiary phosphine complexes [Pt(olefin)$_2$R$_3$P] [2d]. Three co-ordinate platinum complexes, e.g. [Pt(dmf)Bu^{t}NC(cyclo-C$_6$H$_{11}$)$_3$P] involving three different ligands can be obtained by these versatile displacement reactions. The new compounds have been fully characterised by microanalyses, infra-red and ^{1}H and ^{13}C n.m.r. spectroscopy. They are all white crystalline solids stable in air in the solid state but the complexes



Scheme 1.

(i) L = def, dmf or ma; C_2H_4 gas, ref. [1];
(iii) L = dmf or dmm; (iv) L = def or dmf;
(v) L = def, dmf, dmm or ma and L′ = Bu^tNC; L = def and L′ = Ph_3P;
(vi) L = dmf, L′ = Bu^tNC and L′′ = $(cyclo\text{-}C_6H_{11})_3P$.

$[Pt(C_2H_4)L_2]$ (L = dmf or dmm) are the least stable in solution.

In the ^{1}H n.m.r. spectra of the fumarate complexes [Pt(cod)(def)] and [Pt(cod)(dmf)] the C<u>H</u> protons of the <u>trans</u>-$CH(CO_2R)$:$CH(CO_2R)$ group appear as a single peak both at +30°C and at -78°C, but only at low temperature is ^{1}H-^{195}Pt coupling observed (80 Hz), indicating ligand dissociation at ambient temperatures. In the complexes of the type $[PtL_2L']$ (Scheme 1), which presumably have a trigonal planar configuration in the ground state [1], isomers are possible depending on the relative orientation with respect to each other of the two <u>cis</u>-CH:CH or <u>trans</u>-CH:CH groups in the maleate or fumarate complexes. Only in the case of the complex $[Pt(dmf)_2Bu^tNC]$ were two isomers detected by n.m.r. studies.

During the course of the work isomerisation of dimethyl maleate to dimethyl fumarate was observed. Thus treatment of $[Pt(C_2H_4)_3]$ with dimethyl maleate affords the complex $[Pt(dmf)_3]$, also obtained from dimethyl fumarate.

Moreover, reaction of $[Pt(cod)_2]$ with dimethyl maleate followed by t-butyl isocyanide affords $[Pt(dmm)_2(Bu^tNC)]$ but if the mixture is allowed to stand for several days the compound $[Pt(dmf)_2Bu^tNC]$ is also formed. Cis-trans isomerizations of this type have been previously observed in palladium(II) catalysed reactions [3], e.g. trans-$CHMe{:}CHCO_2Et \rightleftharpoons$ cis-$CHMe{:}CHCO_2Et$. The mechanisms of these reactions are not known but a π-σ rearrangement to give a Pd(II)-bonded carbonium ion $Pd{\cdot}CHMe{\cdot}\overset{+}{C}HX$ with sufficient lifetime for rotation is an attractive suggestion [3].

In the context of the conversion of dimethyl maleate into the fumarate it is likely that the reversible formation of a dipolar intermediate [2c, 4] is involved leading to cis to trans conversion, followed by preferential co-ordination of the trans (dmf) olefin.

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