Platinacyclopentene Formation *via* δ-Hydrogen Abstraction

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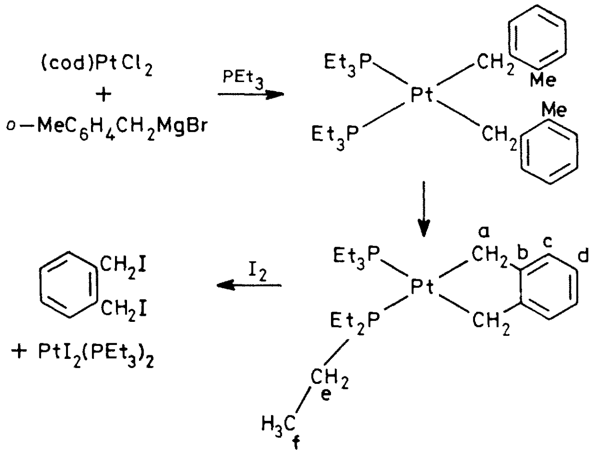
Summary Refluxing $\text{Pt(PEt}_3)_2(o\text{-CH}_2\text{C}_6\text{H}_4\text{Me})_2$ in xylene affords a five-membered ring compound $\overline{\text{Pt(CH}_2\text{C}_6\text{H}_4\text{CH}_2)}(\text{PEt}_3)_2$ *via* δ-hydrogen abstraction.

The decomposition of di- and poly-alkyl complexes of transition metals occurs *via* reductive elimination[1] or *via* loss of alkane, the extra hydrogen atom being abstracted from an α,[2] β,[1] or γ[3,4] carbon atom of another alkyl ligand. We now report a rare example of loss of hydrocarbon from a dialkyl metal complex in which the abstracted hydrogen atom comes from the δ-carbon atom of another alkyl group. δ-Hydrogen abstraction from phosphines, phosphites, amines, *etc.* is well known,[5] but to our knowledge the only other example of δ-hydrogen abstraction from an alkyl ligand occurs in loss of methane from methyl(naphthylmethyl)bis(triphenylphosphine)platinum(II).[6]

Reaction of $o\text{-MeC}_6\text{H}_4\text{CH}_2\text{MgBr}$ with $\text{PtCl}_2\text{(cod)}$ (cod = cyclo-octa-1,5-diene) and PEt_3 affords white crystals of *cis*-$\text{Pt(PEt}_3)_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_2$,† analogous to $\text{Ni(PBu}_3)_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_2$.[7] The *cis*-sterochemistry is confirmed by the ^{13}C signal from the methylene protons of the *o*-methylbenzyl group (δ 27·45 dd; $J_{\text{PH}cis}$ 9 Hz, $J_{\text{PH}trans}$ 94 Hz).

When this complex is refluxed in xylene for several hours, a new compound, $\overline{\text{Pt(CH}_2\text{C}_6\text{H}_4\text{CH}_2)}(\text{PEt}_3)_2$,† may be isolated as white crystals (see Scheme). The compound is monomeric in benzene and the mass spectrum shows a parent ion peak at 535 a.m.u. (^{195}Pt) and fragmentation pattern as expected for $\overline{\text{Pt(CH}_2\text{C}_6\text{H}_4\text{CH}_2)}(\text{PEt}_3)_2$. In the ^1H n.m.r. spectrum, apart from multiplets arising from co-ordinated PEt_3, the only high-field resonance is an apparent quartet (δ 3·55), flanked by satellites ($J_{\text{Pt-H}}$ 66 Hz), typical[8] of a *cis*-dialkyl bisphosphine complex of platinum. The phenyl resonances show a typical AA′BB′-type pattern with broadening of the low-field half of the spectrum arising from coupling to phosphorus and platinum. The alkyl region of the ^{13}C n.m.r. spectrum (δ 10·96 p.p.m., 1:4:1t $J_{\text{Pt-C}}$ 9·5 Hz, C_f; δ 19·99, d of 1:4:1t, J_{PC} 26·3 Hz, $J_{\text{Pt-C}}$ 13 Hz, C_e; δ 36·05, dd of 1:4:1t $J_{\text{PC}cis}$ 9·0 Hz, $J_{\text{PC}trans}$ 92·4 Hz, $J_{\text{Pt-C}}$ 620 Hz, C_a‡ is qualitatively similar to that of the dialkyl complex but lacks the resonance from the *o*-Me carbon atoms. Furthermore, the symmetrical nature of the phenyl ring is confirmed by there being only three resonances in the phenyl region (δ



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† Satisfactory analyses have been obtained on both complexes.

‡ For assignments see Scheme.

126·65 p p m , 1:4:1t, $J_{\text{Pt-C}}$ 4 Hz, C_d, δ 132·69, t of 1·4·1t, J_{PC} 3 Hz, $J_{\text{Pt-C}}$ 86 Hz, C_c, δ 157·46, t of 1:4:1t, J_{PC} 4 Hz, $J_{\text{Pt-C}}$ 37 Hz, C_b,‡ as opposed to six for the dialkyl complex

Final confirmation of the presence of a benzoplatinacyclopentene ring arises from the reaction of the compound with an excess of iodine to give 1,2-bis(iodomethyl)benzene

The synthesis of a benzotitanacyclopentene from $(Me_3SiC_5H_4)_2TiCl_2$ and o-$C_6H_4(CH_2MgCl)_2$ has recently been reported [9]

We are currently investigating other complexes of the 2-methylbenzyl ligand and preliminary results for $PtL_2(CH_2C_6H_4Me)_2$ suggest that a similar metallation occurs for L = PPh_3, but that for L = P(o-tolyl)$_3$, refluxing in xylene causes metallation of the phosphine

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