Some Allyl Complexes of Platinum(II)

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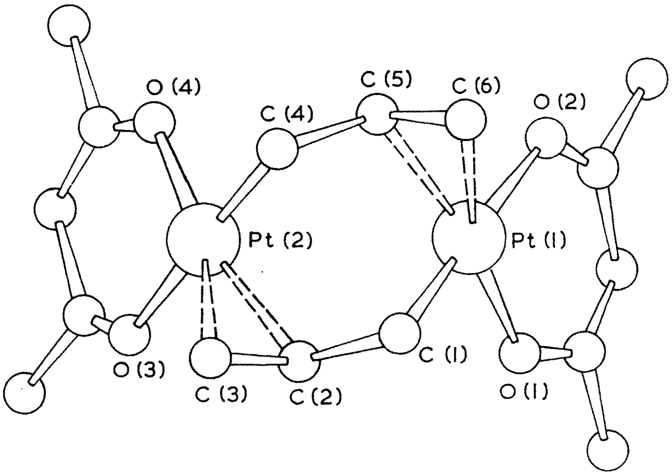
Summary The compound $[\mathrm{Pt_2(acac)_2(allyl)_2}]$ is shown by X-ray diffraction to have the platinum atoms bridged by allyl groups, and n.m.r. shows the complexes [Pt(2-methylallyl)$_2$] and $[\mathrm{Pt_2Cl_2}$(2-methylallyl)$_2]$ to exist as *syn*- and *anti*-isomers, with symmetrically bonded π-2-methylallylic groups.

TREATMENT of $[\mathrm{Pt(C_3H_5)_2}]$[1,2] with dry hydrogen chloride gives the very insoluble $[\mathrm{PtCl(C_3H_5)}]_x$[1] ($x$ unknown), which with cyclopentadienylsodium gives the known $[\mathrm{Pt(C_3H_5)(C_5H_5)}]$,[3] or with neutral ligands, L, mononuclear species $[\mathrm{PtCl(C_3H_5)L}]$ (L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, *etc.*). With thallium(I) acetylacetonate, $[\mathrm{PtCl(C_3H_5)}]_x$ gives the binuclear $[\mathrm{Pt_2(acac)_2(C_3H_5)_2}]$, the structure of which has been determined by X-ray diffraction and is shown in the Figure; principal bond lengths are given in the Table.

Bond lengths (Å) *with e.s.d.s for* $[\mathrm{Pt_2(acac)_2(C_3H_5)_2}]$

Pt(1)–Pt(2)	3·495(3)	Pt(1)–O(1)	1·98(3)
Pt(1)–C(1)	1·97(5)	Pt(1)–O(2)	2·07(3)
Pt(2)–C(4)	2·00(5)	Pt(2)–O(3)	2·07(3)
Pt(1)–C(5)	2·12(4)	Pt(2)–O(4)	1·99(3)
Pt(1)–C(6)	2·11(7)	C(1)–C(2)	1·46(7)
Pt(2)–C(2)	2·15(4)	C(2)–C(3)	1·41(7)
Pt(2)–C(3)	2·14(5)	C(4)–C(5)	1·52(6)
		C(5)–C(6)	1·37(8)

Crystals of this compound are monoclinic, space group $P2_1/c$, with a = 10·01, b = 10·00, c = 17·29 Å, β = 100·2°, Z = 4 dimeric molecules. The structure, based on 1948 independent reflections, was refined by isotropic least-squares to R = 14·6%. The molecule approximates to C_2 symmetry. Each platinum, its two attached oxygens, the



FIGURE

σ-bonded carbon and the mid-point of the olefinic C–C bond are coplanar.

The most interesting feature of the structure is the bridging allyl system. Such systems have been postulated as intermediates in allyl transfer reactions between metals.[4–6] The dehydro-hexamethyl Dewar benzene complex of platinum, $[Pt_2Cl_2(C_{12}H_{17})_2]$ also has a bridging allylic system[7] but $C_{12}H_{17}$ is a highly constrained system and cannot be considered as a typical allylic group. In the complex $[Pt_2(acac)_2(C_3H_5)_2]$ the allyl group prefers to bridge rather than be π-bonded to just one platinum atom. We find, in contrast, that the 2-methylallyl complex [Pt(acac)(2-methylallyl)] is mononuclear with a symmetrically-bonded π-2-methylallyl group, (molecular weight and n.m.r. evidence); one would expect the 2-methylallyl group to be a worse bridging group than allyl because of the methyl substituent; *e.g.*, compare the great difference in complexing power between ethylene and propylene towards rhodium(I).[8]

Treatment of platinous chloride with 2-methylallylmagnesium chloride gives $[Pt(\pi\text{-}2\text{-methylallyl})_2]$, which n.m.r. shows to exist as *syn-* and *anti-*isomers with symmetrically-bonded 2-methylallylic groups, as found for the corresponding nickel[9] and palladium[10] complexes. $[Pt(allyl)_2]$ has been given a structure with asymmetrically bonded allyl groups, from n.m.r. evidence.[2] However, the n.m.r. spectrum (which is very complex) can also be interpreted in terms of a mixture of *syn-* and *anti-*isomers of $[Pt(\pi\text{-allyl})_2]$ containing symmetrical π-allyl groups and in view of our results with $[Pt(2\text{-methylallyl})_2]$, we consider this more likely. With dry hydrogen chloride $[Pt(\pi\text{-}2\text{-methylallyl})_2]$ gives the chloro-bridged binuclear $[Pt_2Cl_2(\pi\text{-}2\text{-methylallyl})_2]$ which n.m.r. shows to exist as *syn-* and *anti-*isomers at −60° in deuteriochloroform. At 0°, however, the two resonance patterns have merged, corresponding to a rapid interconversion of the *syn-* and *anti-*isomers. The very insoluble $[PtCl(C_3H_5)]_x$ possibly has both bridging chlorines and allyl groups and its structure is being investigated.

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