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PLATINUM(0) COMPLEXES OF CYCLOPROPENES

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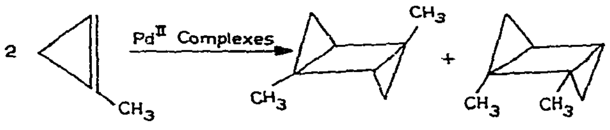
SUMMARY

Cyclopropene and its 3-methyl, 3,3-dimethyl, 1,2-dimethyl, 1,3,3-trimethyl and 1,2,3-trimethyl derivatives have been coordinated to platinum by replacement of ethylene in $Pt(C_2H_4)(PPh_3)_2$. The complexes have been identified by NMR spectroscopy and X-ray analysis.

INTRODUCTION

Cyclopropenes, in particular the lower homologues, are known to have only a limited stability. For example, cyclopropene itself polymerizes, even when stored at −80°. Since unstable unsaturated hydrocarbons can be stabilized by coordination to transition metals[1], we decided to ascertain whether such stabilization can also be achieved for cyclopropenes[★].

Only a few reports have been published in the literature on the interaction between cyclopropenes and metal salts and complexes. Fe^0, Cu^I, Hg^{II}, Tl^{III}, Pb^{IV} and Pt^{II} are known to react with cyclopropenes to give insertion products[3], and Pd^{II} complexes have been reported to catalyse the dimerization of 1- and 3-methylcyclopropenes to dimethyltricyclohexanes[4]. However, none of these accounts provided information to indicate whether the reactions mentioned are preceded by coordination of the cyclopropene to the metal.



RESULTS AND DISCUSSION

Our first experiments were aimed at coordinating 3-methylcyclopropene to the monovalent and divalent metal in the complexes $IrCl(CO)(PPh_3)_2$, $[Rh(CO)_2Cl]_2$, $PdCl_2(PhCN)_2$ and $(C_2H_4)(Py)PtCl_2$ in toluene as the solvent. They all yielded

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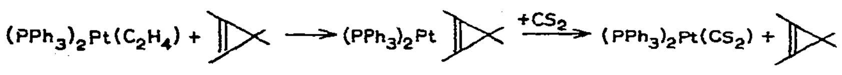
[★] Preliminary results of this investigation have been reported elsewhere[2].

small amounts of the cyclodimerization product 3,6-dimethyl[3.1.0.0^{2,4}]tricyclohexane together with polymeric material. The dimerization product was identical to that reported in ref. 11.

Experiments with the zerovalent platinum complex $(PPh_3)_2Pt(C_2H_4)$, which is known to exchange ethylene quite readily for other unsaturated hydrocarbons, were more successful: addition of stoichiometric amounts of cyclopropenes to a solution of the complex in solvents such as chloroform, benzene, toluene or tetrahydrofuran at ambient temperature induced complete replacement of the coordinated ethylene by the cyclopropene within in a few minutes. Upon addition of ethanol the new complexes precipitated as off-white crystals. Alkyl substituents at C_1 and C_2 appeared to reduce the reaction rate. Elemental analysis (see Experimental) gave satisfactory results.

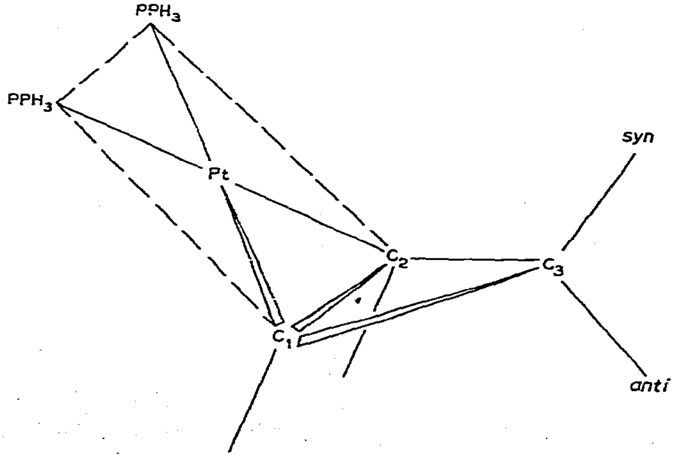


Whereas carbon disulphide was found to liberate all the cyclopropenes investigated from their complexes (see Table 1), triphenylphosphine was able to replace only those cyclopropenes which carried vinylic methyl groups [*i.e.* complexes (IV), (V) and (VI) and not (I), (II) and (III)]. Furthermore, the temperature required to effect the replacement of cyclopropene by carbon disulphide was higher for (I) and (V) than for their 3-methyl-substituted homologues (II) and (VI). We can therefore conclude that:

(*a*). The strength of the platinum–cyclopropene bond is decreased by alkyl substituents;

(*b*). Substitution at the double bond has a more pronounced effect than substitution on C_3.

X-ray structure determinations on the complexes of 3-methylcyclopropene (II) and 1,2-dimethylcyclopropene (V) have been carried out by De Boer and Bright[5].



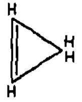
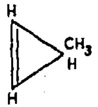
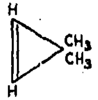
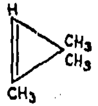
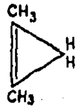
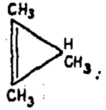
The most important features of the structures are:

(*a*). The cyclopropene ring remains intact on complexation. This contrasts

TABLE 1

NMR DATA OF BIS(TRIPHENYLPHOSPHINE)-CYCLOPROPENE-PLATINUM(0) COMPLEXES IN $CDCl_3$ AT AMBIENT TEMPERATURE

Chemical shifts in ppm downfield from TMS (extern.), coupling constants in Hz.

X in $[P(C_6H_5)_3]_2PtX$		C_1/C_2								C_3											
		H	CH_3	J_{Pt-H}	J_{Pt-CH_3}	J_{P-H} cis	trans	J_{P-CH_3} cis	trans	H syn	anti	CH_3 syn	anti	$J_{(Pt-H)}$ syn	anti	$J_{(Pt-CH_3)}$ syn	anti	$J(H_{anti}-H_{1,2})$	$J(H_{syn}-P)$	$J(H_{syn}-H_{anti})$	$J(H_{syn}-CH_3)$
(I)		2.86		13		6				1.93	2.30			114	236			6^b			
(II)		2.70		15		6.3				2.28			1.62	86			0	^{b}			5
(III)		3.02		14		7						1.97	1.62			4.5					
(IV)		2.56	2.08	0	36	4.5	8.5	0	8			2.06	1.60			0	6				
(V)			1.80		33			8^a		≈1.8	2.15			<41	98				2	2	
(VI)			1.88		37			7.5^b		2.36			1.40	114			7.5				5.5

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[a] This is an example of an $A_3XX'A'_3$ system; the observed coupling constant is the sum of J_{AX} and $J_{AX'}$ (V) or $J_{A'X}$ and $J_{A'X'}$ (VI)[8]. [b] $J(H_{syn}-H_{1,2})=0$.

with the behaviour of cyclopropane in $PtCl_2(C_5H_5N)_2(C_3H_6)$, where the metal becomes part of the ring. Nevertheless, from this complex the cyclopropane can still be set free by stronger coordinating ligands[6].

(*b*). The phosphorus atoms form a distorted square plane with the atoms C_1 and C_2 of the cyclopropene.

(*c*). The cyclopropene ring and the plane defined by the platinum and phosphorus atoms are at an angle of 116°. The distance between platinum and C_3 is 2.83 Å, hence no interaction is likely.

(*d*). Vinylic methyl groups are bent out of the plane of the cyclopropene ring. In complex (V) the angle between the plane of the ring and the best plane fitted through C_1, C_2 and their methyl groups is 112°.

(*e*). The C=C double bond is lengthened from 1.30 Å in the free ligand[7] to 1.50 Å in the complex. A similar bond length (1.52 Å) has been found for the coordinated double bond in $(PPh_3)_2Pt((CN_2)C{=}C(CN)_2)$[8]. Both the bending of the methyl groups out of the plane of the ring and the lengthening of the double bond are indicative of rehybridization of the carbon atoms from sp^2 to sp^3 with considerable σ character of the metal–olefin bond.

(*f*). In complex (II) the methyl group on C_3 is found *anti* to the metal, which is plausible considering the small Pt–C_3 distance (*vide supra*).

Table 1 gives the ^{1}H-NMR data of the complexes prepared in this work. Comparison of the chemical shifts of the vinylic hydrogens of cyclopropene (δ 7.65 ppm) with those of coordinated cyclopropene (δ 2.86) shows that coordination effects a high-field shift of the vinylic protons by approx. 4.8 ppm.

X-ray structure determination (*vide supra*) allows us to assign the NMR spectrum of the 3-methylcyclopropene complex unambiguously. Since the methyl group is *anti* to the metal it is reasonable to assume that the analogous signals in the spectra of the 3,3-dimethylcyclopropene complexes (III) and (IV) also belong to *anti*-methyl groups. Consequently, the signal at lower field has to be assigned to the *syn*-methyl group. This assignment of the low-field signal to the *syn*-methyl group is remarkable since the *syn*-methyl group is closer to the metal than the *anti*-methyl group and might, therefore, be expected to show a larger upfield shift. The observed anomaly is most probably due to the anisotropy of the phenyl group in the triphenylphosphine ligands, which can cause a downfield shift of the signal of the *syn*-methyl group. Apparently, this shift is greater than the upfield shift caused by the metal.

TABLE 2

ELEMENTAL ANALYSES OF COMPLEXES (I)–(VI)

Complex	*Found* (%)		*Calcd.* (%)	
	C	*H*	*C*	*H*
(I)	61.9	4.8	61.7	4.51
(II)	62.5	5.0	62.1	4.70
(III)	62.8	5.0	62.9	5.04
(IV)	62.7	4.9	62.5	4.86
(V)	62.6	5.0	62.5	4.86
(VI)	62.6	5.3	62.9	5.04

Since the signals of the *syn* hydrogens in complexes (II) and (VI) appear at 2.28 and 2.36 ppm, respectively, and the secondary hydrogens absorb at a higher field than tertiary ones, we can assign the higher-field absorptions of the hydrogens on C_3 in complexes (I) and (V) [1.93 *vs.* 2.30 ppm in (I) and 1.8 *vs.* 2.15 ppm in (V)] to the hydrogens *syn* to platinum. Additional support for this assignment is provided by the coupling constants between the vinylic hydrogens and the hydrogens on C_3: $J(H_{3\text{-}anti}{-}H_{1,2})$ 6 Hz and $J(H_{3\text{-}syn}{-}H_{1,2})$ 0 Hz, which is in agreement with the vicinal coupling constants in a cyclopropane or bicyclobutane (the structure of the complex being similar to the latter).

The coupling constants between ^{195}Pt and the hydrogens on C_3 are—if the Karplus plot is applicable here—in line with our assignment: the dihedral angle between $Pt/C_{1(2)}$ and C_3/H is 12° for the *anti*-H and 49° for the *syn*-H, the respective coupling constants being 236 and 114 Hz for (I), 98 and $\leqslant 41$ Hz for (V).

CONCLUSION

Cyclopropenes can be coordinated in a *reversible* manner to zerovalent platinum. In comparison with the free hydrocarbons, the coordinated cyclopropenes show a greatly enhanced thermal stability.

EXPERIMENTAL

All cyclopropenes were prepared by known methods[10].

Preparation of complexes (I)–(VI). General procedure

An excess (1.5 equiv.) of the cyclopropene (in an inert solvent or undiluted) was added to a solution of bis(triphenylphosphine)(ethylene)platinum(0)* in chloroform**, benzene or THF. Cyclopropene and 3-methylcyclopropene were added at −60° and the other cyclopropenes at room temperature. Addition of diethyl ether or ethanol afforded the crystalline products (I)–(VI) in 50–80% yield. They were recrystallized from toluene or chloroform by addition of ethanol and subsequent cooling.

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* With cyclopropene and 3-methylcyclopropene, tetrakis- and tris-(triphenylphosphine)platinum were also used successfully.

** Non-chlorinated solvents are to be preferred since Pt^0 is capable of being inserted into a C–Cl bond.

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