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REACTIONS OF PLATINUM(0) AND PALLADIUM(0) COMPLEXES INVOLVING INSERTIONS INTO CARBON—CARBON BONDS OF ELECTRONEGATIVELY-SUBSTITUTED CYCLOPROPANES

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Summary

1,1,2,2-Tetracyanocyclopropane and its 3-alkyl derivatives react with Pt^0 and Pd^0 complexes of the type $Pt(PPh_3)_2(C_2H_4)$ or ML_n (n = 3,4, M = Pd or Pt, L = phosphines or triphenylarsines) to give metallocyclobutane derivatives, which undergo exchange reactions of the neutral ligand L The structures of these products have been assigned on the basis of the IR and NMR spectra.

Introduction

Much of the current interest in the chemistry of cyclopropane relates to its similarity with propene. For example, both these compounds undergo addition reactions with hydrogen and hydrogen bromide. This correspondence in chemical behaviour is believed to originate from the strain energy of the three membered ring, and larger rings such as cyclopentane bear little chemical resemblance to cyclopropane.

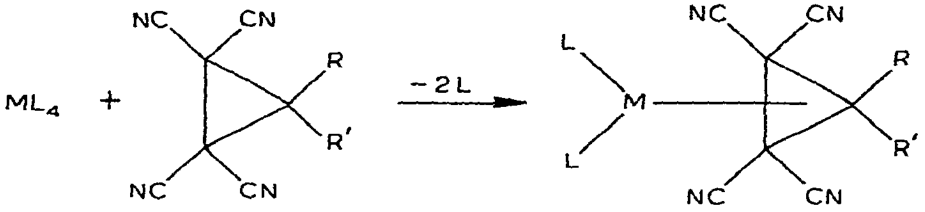
For strained carbocyclics, one would expect chemical properties characteristic of the carbon—carbon double bond [1]. For example, in the presence of Rh^I [2] and Ag^I [3] compounds, the skeletal rearrangement of highly strained ring systems such as bicyclo[1 1.0]butane occurs under mild conditions

Electronegatively substituted cyclopropanes such as 1,1,2,2-tetracyanocyclopropane (TCCP) react under mild conditions with zerovalent platinum and palladium complexes to give metallocyclic derivatives [4]. In the case of the insertion of the $PtCl_2$ moiety into the carbon—carbon bond of cyclopropane [5] and aryl- or alkyl-substituted cyclopropanes [6] an electrophilic attack on the organic ring has been proposed [6].

We describe below the reactions of zerovalent platinum and palladium arsine and phosphine complexes of the type $Pt(PPh_3)_2(C_2H_4)$ or ML_4 (M = Pd or Pt; L = substituted arsine or phosphine) with electronegatively-substituted cyclopropane derivatives, in which insertion of the ML_2 moiety into a carbon—carbon σ-bond occurs.

Results and Discussion

Some new platinum and palladium complexes of the type ML_2 (TCCP derivative) (TCCP = tetracyanocyclopropane) have been synthesised under very mild conditions, by the general reaction represented in eqn. (1).



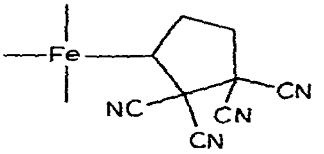
(1)

[$R = R' = H, CH_3, R = CH_3, R' = C_2H_5; R = R' = (CH_2)_5, M = Pd, Pt, L = PPh_3, PMePh_2, PEt_3, PMe_2Ph$, and $AsPh_3$.] (See Experimental.)

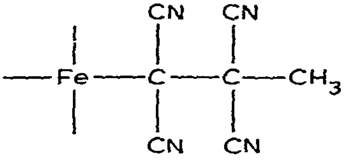
An analogous reaction occurs with $Pt(PPh_3)_2(C_2H_4)$.

The structures of the reaction products have been assigned on the basis of the spectral data shown in Table 1.

As Table 1 shows, the ν(CN) stretching frequencies depend slightly on the nature of the complex: ν(CN) values are shifted toward lower frequencies in comparison to those of the free ligands For complexes of structure (I),



(I)

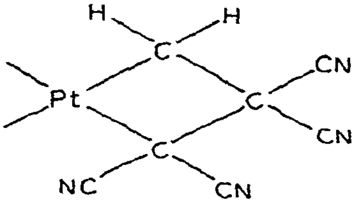


(II)

ν(CN) has been reported at 2250 cm^{-1}, very close to that in organic cyanides [7]. On the other hand, in compounds of type (II), the values of ν(CN) for the cyanide groups bonded to carbon atoms α to the iron fall at 2205 cm^{-1} [8]

The final products of reaction (1) exibit only one band in the IR spectrum in solid or in solution, at about 2220 cm^{-1} for the platinum and at 2200 cm^{-1} for the palladium complexes, values which are relatively far from those for the free ligands, as they are in the case of compounds of type (II) This might be taken as an indication that the cyano groups are bonded to the carbon atoms symmetrically and α to the metal atom The NMR spectra of these products provide evidence for such a symmetrical structure in solution Thus, free 1,1,2,2-tetracyanocyclopropane shows the CH_2 resonance as a singlet at δ 3.47 ppm, whereas upon coordination the signal of the methylene group is shifted by ca. 1 ppm downfield in the case of platinum complexes and by ca. 0.5 ppm for palladium complexes. The smaller deshielding in the latter case is probably attributable to the smaller ability of palladium than of platinum to accept electrons from the cyclopropane ring. This is in agreement with the lower stability of the olefinic complexes of palladium in comparison with that of the analogous platinum derivatives. It should be noted, incidentally, that in complexes of the type $Pt(Py)_2(RC_3H_5)Cl_2$, the chemical shift of the protons bonded to the carbon atoms of the ring are shifted by two or more ppm downfield in comparison to the parent free organic ligand [6] The smaller difference in the chemical shift between free and coordinated organic ligand found in our case can be attributed to the different oxidation state of the platinum atom and/or to the presence of the four cyano groups, which exert a levelling effect

The methylene resonance in complexes of the type ML_2(TCCP) (Table 1) appears as a singlet, and although it displays fine structure when L is a phosphine ligand, it was impossible to resolve the spectra because of the very low coupling to the ^{31}P atom, which indicates that the protons are not bonded to the carbon atom α to the metal [9,10] as they would be in structure (III)*.

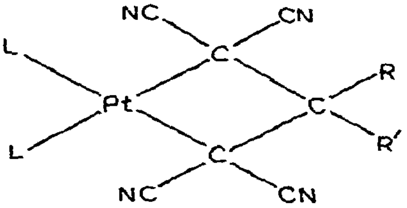


(III)

Moreover, the methylene protons in a structure such as (III) would be expected to have larger coupling constants ^{195}Pt [J(Pt—H) ≈ 65 Hz] [10], than those observed, because of their proximity to the Pt nucleus [J(Pt—H) ≈ 30 Hz]. In complexes having Ph_2MeP or $PhMe_2P$ as ligands, the phosphine methyl resonance appears as a doublet with platinum satellites. Such a pattern is usually associated with *cis* phosphines, with the P—M—P bond angle close to 90° and a small ^{31}P—^{31}P coupling constant The expected pattern for a *cis* derivative has also been found for PEt_3 complexes [10,11a].

Changing the donor atom from P to As causes J(Pt—H) for the methylene group to increase, as would be expected since the *trans*-influence of the phosphine is greater than that of the arsine ligand [11]. For 1,1,2,2-tetracyanocyclopropanes bearing alkyl groups in the 3-position, the NMR absorptions of the carbocyclic moiety are practically identical to those of the free ligand because of the large distance from the metal atom (Table 1).

The NMR and IR data are consistent with the following formulation:



(IV)

(Continued p 412)

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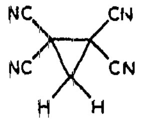
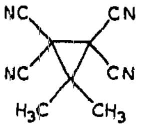
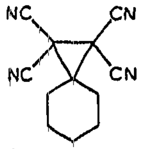
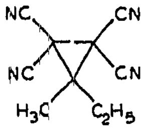
* With PMe_2Ph as ligand a definite triplet was observed [J(P—H) = 1 5 Hz]

TABLE 1

SPECTRAL DATA

Compound	NMR [a]				IR [b]
	δ (ppm)	J (Pt—H) (Hz)	J (P—H) (Hz)	Assignment	ν(CN) (cm^{-1})
 (TCCP)	3 47s [c]			CH_2	2260
 [TCCP(Me)$_2$]	1 81s [c]			CH_3	2260
 [TCCP(CH$_2$)$_5$]	1 8m [c] 2 07 m }			CH_2	2260
 [TCCP) (MeEt)]	1 29t [c] 1 79s 2 05q			$CH_3(CH_3—CH_2)$ CH_3 CH_2	2260
$(Ph_3P)_2Pt(TCCP)$	4 38s [d] 7 34m	38	< 1 5	CH_2 C_6H_5	2220
$(Ph_2MeP)_2Pt(TCCP)$	1 87d 4 4s 7 35m	32 30	9 < 1 5	$CH_3(P—CH_3)$ CH_2 C_6H_5	2216

$(PhMe_2P)_2Pt(TCCP)$	1.57d	31	10	CH_3 $(P—CH_3)$	2215
	4.49t	26	1.5	CH_2	
	7.35m			C_6H_5	
$(Et_3P)_2Pt(TCCP)$	1.18m 2.0m			C_2H_5 $(P—C_2H_5)$	2215
	4.34s	28	1.5	CH_2	
$(Ph_3As)_2Pt$ (TCCP)	4.39s	44		CH_2	2218
	7.25m			C_6H_5	
$(Ph_3P)_2Pt$ $[TCCP(Me)_2]$	1.53s			CH_3	2220
	7.29m			C_6H_5	
$(Ph_2MeP)_2Pt[TCCP(Me)_2]$	1.48s			CH_3	2220
	1.9d	31	10	$CH_3(P—CH_3)$	
	7.31m			C_6H_5	
$(Ph_3As)_2Pt[TCCP(Me)_2]$	1.52s			CH_3	2218
	7.24m			C_6H_5	
$(Ph_3P)_2Pt$ [TCCP(MeEt)]	0.79t			CH_3 $(CH_3—CH_2)$	2220
	1.70s[e]			CH_3	
	1.77q[e]			CH_2	
$(Ph_3P)_2Pt[TCCP(CH_2)_5]$	1.60m 1.97m			$(CH_2)_5$	2220
	7.32m			C_6H_5	
$(Ph_3P)_2Pd(TCCP)$	3.96s[d]		< 1.5	CH_2	2200
	7.3m			C_6H_5	
$(Ph_2MeF)_2Pd(TCCP)$	1.79d		9	CH_3	2200
	4.0s		< 1.5	CH_2	
	7.35m			C_6H_5	

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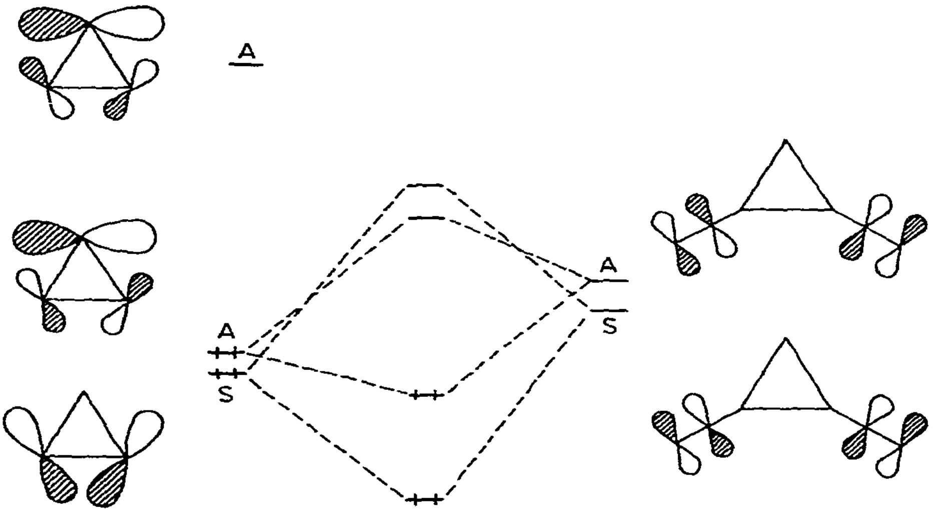
[a] $CDCl_3$ solution (TMS as internal standard). [b] Hexachlorobutadiene or nujol mull. [c] $(CD_3)_2CO$ solution (TMS as internal standard). [d] These figures were misprinted in ref. [4]. [e] Partially overlapped.

The bond between the three-membered ring and platinum has been interpreted on the basis of Walsh orbitals [12] as intermediate between a σ-alkyl and a π-olefin system [6], and this model appears to be the most helpful. It is noteworthy that with our complexes variation in the basicity of the phosphines and arsines ligands do not significantly change the chemical shift of the methylene protons

As for the reaction mechanism, reaction (1) proceeds probably via a nucleophilic attack of the ML_3 moiety on the carbon atom bearing the cyano groups. This mechanism gains some support from our observation that under the same conditions $Pt(PPh_3)_4$ does not react with 1,2-dicyanocyclopropane

Products of type (IV) were proposed as intermediates in the ring opening reactions of cyclopropane derivatives in the presence of palladium metal [13].

The weakening of the C(1)—C(2) bond in the 1,2-dicyanocyclopropane has been interpreted on the basis of the interaction of a symmetric and antisymmetric acceptor orbital combination with the Walsh orbitals of cyclopropane [14].



The interaction of symmetric levels will decrease the 1—2 bond order, whereas the interaction of antisymmetric levels will increase it But the symmetric Walsh orbital has more electron density than its antisymmetric counterpart at the two carbons bearing the π-acceptor substituents. Thus the symmetric interaction should be stronger, resulting in a net decrease of the 1—2 bond order. This effect should be much greater in the tetracyanoderivative, and the C(1)—C(2) bond order would be even smaller The presence of a positive charge on C(1) and C(2) atoms in TCCP has been confirmed by ESCA measurements and theoretical calculations [15].

An alternative mechanism involves a possible dissociation of tetracyanocyclopropane to give a biradical. It has been reported that three-membered rings are to some extent present in open forms, such as a resonating π-biradical, and these might contribute in some way to the reactivity of the cycle [16].

Experimental

The complexes $Pt(PPh_3)_4$ [17], $Pt(PPh_2Me)_4$ [18], $Pt(AsPh_3)_4$ [19], $Pt(PPh_3)_2(C_2H_4)$ [20], $Pd(PPh_3)_4$ [21] and $Pd(PPh_2Me)_4$ [21] were prepared by methods previously described, as were also 1,1,2,2-tetracyanocyclopropane [23] (TCCP), 1,1,2,2-tetracyano-3,3-dimethylcyclopropane [24] [$TCCP(Me)_2$], 1,1,2,2-tetracyano-3-methyl-3-ethylcyclopropane [25] [TCCP(MeEt)], and 1,1,2,2-tetracyano-3,3-pentamethylenecyclopropane [25] [$TCCP(CH_2)_5$]. Infrared spectra were recorded on a Perkin—Elmer Model 457 instrument. Proton NMR spectra were recorded on a Varian HA-100 spectrometer Molecular weights were determined with a Mechrolab osmometer Microanalyses were performed by Dornis und Kolbe-Mulnheim (Germany). Analytical data are listed in Table 2. Three methods were used to prepare the metallocyclic derivatives reported in Table 2, and these are described below.

Method A

Reaction of ML_4 complexes with the appropriate carbocycle

1 *$Pt(PPh_3)_2$(TCCP)*. TCCP (0.142 g, 1 mmole) was dissolved in 25 ml of anhydrous THF, and to this solution was added 1.244 g (1 mmole) of $Pt(PPh_3)_4$ dissolved in the minimum quantity of the same solvent The resulting solution was stirred under nitrogen, and after ½ h the white, air-stable solid product $Pt(PPh_3)_2$(TCCP) began to precipitate The complex was filtered off, dried under vacuum, and recrystallized from $CHCl_3/CH_3OH$ Yield 80%

2 *$Pt(PPh_2Me)_2$(TCCP)*. The same procedure gave a pale yellow solid in 50% yield

3. *$Pt(AsPh_3)_2$(TCCP)* Equimolar amounts of $Pt(AsPh_3)_4$ and TCCP were stirred under nitrogen at room temperature in anhydrous benzene for 2 h. The solution was concentrated under reduced pressure and the white air-stable product was obtained by addition of CH_3OH, and recrystallization from $CHCl_3/CH_3OH$. Yield 50%.

4 *$Pt(AsPh_3)_2[TCCP(Me)_2]$* Equimolar amounts of $Pt(AsPh_3)_4$ and $TCCP(Me)_2$ were stirred under nitrogen at room temperature in THF, as for complex (I), to give an off-white air-stable compound in 50% yield.

5 *$Pt(PPh_2Me)_2[TCCP(Me)_2]$* Equimolar amounts of $Pt(PPh_2Me)_4$ and $TCCP(Me)_2$ were stirred in THF under N_2 The solution became dark red, and on addition of methanol a pale yellow solid separated. Recrystallization from CH_2Cl_2/CH_3OH give white solid in 20% yield.

6. *$Pd(PPh_3)_2$(TCCP)* This was made as described for complex (1), and was isolated as a yellow solid on treatment of the THF solution with methanol. Yield 50%

7. *$Pd(PPh_2Me)_2$(TCCP)* The procedure used for complex (1) was followed, but with benzene as solvent. After 10 min an off-white precipitate was obtained in 80% yield.

TABLE 2

ANALYTICAL DATA FOR THE COMPLEXES

Complex	Analyses found (calcd.) (%)			M.p.	Mol.wt. [b]		Synthetic method
	C	H	N	(°C) [a]	found	calcd.	
$(Ph_3P)_2Pt(TCCP)$	59.9 (59.93)	3.75 (3.74)	6.5 (6.50)	220—225	840	861	A
$(Ph_2MeP)_2Pt(TCCP)$	52.9 (53.73)	3.9 (3.82)	7.6 (7.59)	243—245	748	737	A
$(PhMe_2P)_2Pt(TCCP)$	44.9 (45.03)	3.97 (3.94)	9.2 (9.13)	215—220	622	613	C
$(Et_3P)_2Pt(TCCP)$	40.0 (39.79)	5.6 (5.62)	9.8 (9.77)	202—205	579	573	C
$(Ph_3As)_2Pt(TCCP)$	55.1 (54.38)	3.2 (3.40)	5.8 (5.90)	245—246	934	949	A
$(Ph_3P)_2Pt[TCCP(Me)_2]$	60.4 (60.74)	4.3 (4.08)	6.3 (6.29)	258—260	836	889	B
$(Ph_2MeP)_2Pt[TCCP(Me)_2]$	55.1 (54.90)	4.3 (4.21)	7.4 (7.32)	255—260	781	765	A
$(Ph_3As)_2Pt[TCCP(Me)_2]$	55.1 (55.28)	3.6 (3.71)	5.8 (5.73)	185—187	958	977	A
$(Ph_3P)_2Pt[TCCP(MeEt)]$	60.5 (61.12)	4.4 (4.24)	6.3 (6.20)	265—266	911	903	B
$(Ph_3P)_2Pt[TCCP(CH_2)_5$	61.6 (62.00)	5.0 (4.33)	6.0 (6.02)	255—258	940	929	B
$(Ph_3P)_2Pd(TCCP)$	66.9 (66.80)	4.1 (4.17)	7.3 (7.25)	170—173	754	773	A
$(Ph_2MeP)_2Pd(TCCP)$	59.7 (61.07)	4.5 (4.35)	8.2 (8.63)	165—170	654	648	A

[a] All the complexes decompose on melting. Decomposition temperatures are uncorrected. [b] 1,2-dichloroethane solution 10^{-2} *M*.

Method B

Reaction of $Pt(PPh_3)_2(C_2H_4)$ with the appropriate carbocycle.

This method was found to be better than method A for alkyl substituted tetracyanocyclopropanes. In the case of all the complexes described below, method A gave red solutions because of a side reaction between the free phosphine and the organic ligand.

1 $Pt(PPh_3)_2[TCCP(Me)_2]$ $Pt(PPh_3)_2(C_2H_4)$ (0.747 g; 1 mmole) dissolved in 25 ml of anhydrous THF was added to 0.170 g (1 mmole) of $TCCP(Me)_2$ dissolved in the minimum amount of the same solvent. The mixture was stirred under nitrogen for 0 5 h, and a white air stable solid separated This was filtered off and recrystallized from $CHCl_3/CH_3OH$. Yield 80% The same procedure gave the air stable white complexes

2 $Pt(PPh_3)_2[TCCP(Me, Et)]$ and 3. $Pt(PPh_3)_2[TCCP(CH_2)_5]$

Method C

Exchange of the neutral ligand·

$Pt(AsPh_3)_2(TCCP) + 2L \rightarrow PtL_2(TCCP) + 2AsPh_3$

This method gave very pure complexes in almost quantitative yield.

1. $Pt(PPh_2Me_2)_2(TCCP)$ $Pt(AsPh_3)_2(TCCP)$ (0.949 g, 1 mmole) suspended in anhydrous ethyl ether was treated with a 10-fold excess of $PPhMe_2$ and the mixture was stirred under nitrogen for 48 h The white solid was filtered off, washed with n-hexane, and dried under vacuum.

2 $Pt(PEt_3)_2(TCCP)$ This was made similarly.

Acknowledgements

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