Coordination Chemistry Reviews, 16 (1975) 35—50
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

REACTIONS OF PLATINUM(0) AND PALLADIUM(0) COMPLEXES WITH ELECTRONEGATIVELY ACTIVATED SMALL RINGS

M. GRAZIANI, M. LENARDA, R. ROS and U. BELLUCO
Facoltà di Chimica Industriale, The University, Venezia (Italy)

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. As a matter of fact, larger rings such as cyclopentane bear little chemical resemblance to pentene. Therefore, for strained carbocyclics, one would expect chemical properties to be characteristic of the carbon—carbon double bond [1]. Indeed, a variety of transition metals catalyze ring opening and skeletal rearrangement of highly strained ring systems such as bicyclo-[1.1.0]butane [2], quadricyclene [3] and many others.

There has been suggested either a concerted pathway [2] via interaction of appropriate metal *d* orbitals with the carbocycle orbitals, or an oxidative addition [3] involving initial rupture of the carbon—carbon bond in the first reaction step. The oxidative addition pathway finds some support in the preparation and characterization of complexes in which the metal has become inserted across the carbon—carbon bond to give metallocyclobutane derivatives.

PLATINUM(II) SYSTEMS

The reaction of cyclopropane with chloroplatinic acid was first described by Tipper to give $[(C_3H_6)PtCl_2]_n$ [4]. The fact that only cyclopropane was evolved when the complex was treated with cyanide (eqn. 1) suggested that the three-membered ring is intact in the molecule and that the platinum atom is bound equally to all three carbon atoms to form an "edge complex"

$$\begin{tikzcd}
\underset{(I)}{[(C_3H_6)PtCl_2]_n} \arrow[r, "+CN^-"] \arrow[d, "py"] & C_3H_6 + [Pt(CN)_4]^{2-} + 2Cl^- \qquad (1) \\
\underset{(II)}{[(C_3H_6)PtCl_2py_2]} \arrow[ur, "-py", "+CN^-"'] &
\end{tikzcd}$$

NMR and IR studies showed that (I) is polymeric in nature and that both (I) and (II) contain the trimethylene—platinum moiety [5]. The polymeric formulation for (I) was based on the low solubility of the complex in various solvents. Several attempts were made, using a number of methods, to obtain the molecular weight of (I), but they were unsuccessful owing to the low concentration and the easy decomposition of the solution [6]. A cryoscopic method using 2-methyl-naphthalene as the solvent gave results which indicated $M > 1{,}000$. The mass spectrum of (I) showed intense parent *m/e* peaks due to the thermal decomposition product, platinum(II) chloride. Superimposed on the $[PtCl_2]_n$ fragmentation pattern was a low intensity pattern up to *m/e* centered on 1,232. This corresponds to $[(C_3H_6)PtCl_2]_4$ and, as there are no other peaks above this which are not assignable to $[PtCl_2]_n$, it was concluded that it was the parent peak of (I) thereby supporting the tetrameric structure [6].

Upon treatment of (I) with pyridine the complex (II) is obtained in nearly quantitative yield. An X-ray analysis of this complex is shown in Fig. 1.

Table 3 showed a C(1)—C(3) distance of 2.55(10) Å, thereby ruling out the suggestion that there is a significant bond order between these two atoms in the complex [7]. That cyclopropane is released in high yield on treatment of complexes (I) and (II) with bases, could be related to the stereoselectivity of the elimination reaction [7]. Also, on the basis of NMR measurements it has been concluded that the bonding in the ground state of (II) is best represented by the platinum(IV)-trimethylene formation [8]. However, the ^{13}C NMR evidence does suggest that there is some direct interaction between platinum and the carbon atom across the 4-membered ring. Similar conclusions were reached from an interpretation of NMR spectra [9] and X-ray analysis [10]

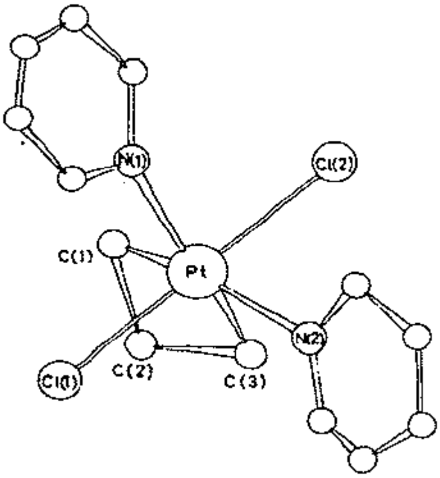
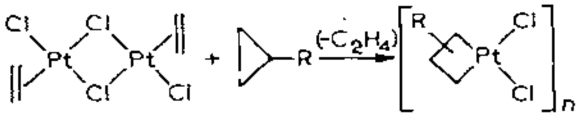


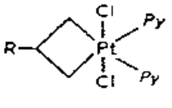
Fig. 1. $[(C_3M_6)PtCl_2py_2]$. Molecular stereochemistry.

of complexes analogous to (II) with substituted cyclopropane, which were synthesized as follows [9]:

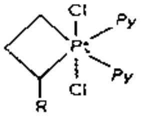


(III)

These products react with pyridine to give (IV) and (V):



(IV)



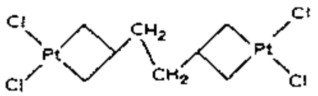
(V)

The changes in reactivity of cyclopropane with changing nature of the substituent group and the relative extent of ring fission along the substituted and unsubstituted bonds would throw useful light on the nature of the insertion process. Monosubstituted cyclopropanes gave a reactivity sequence depending on R in the order R = n-C_6H_{13} > $PhCH_2$ > Ph > o-$NO_2C_6H_4$, whereas cyclopropanes with R = CN, $COCH_3$, CO_2CH_3 failed to react. This sequence shows that the reactivity depends on the electron donor capacity of the substituent in the cyclopropane ring, and that the $PtCl_2$ residue acts as an electrophile [9].

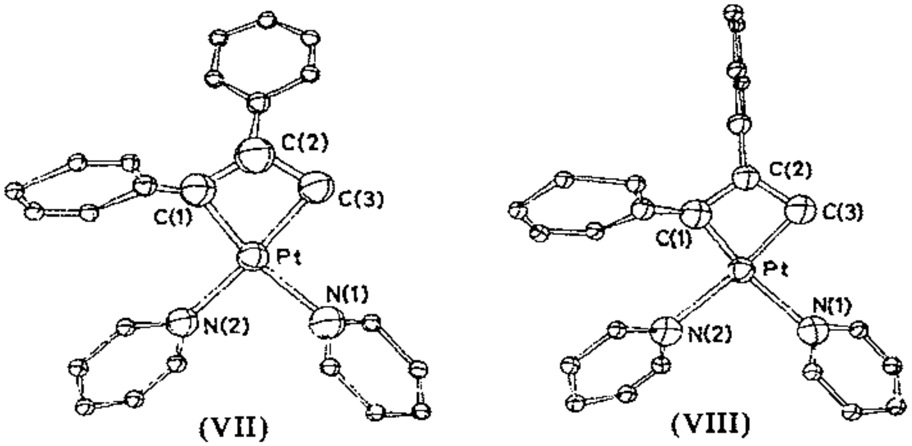
From the ^1H NMR spectra of the bis-pyridine derivatives [$(RC_3H_5)PtCl_2py_2$] it was inferred that the insertion occurs preferentially across the less substituted cyclopropane bond when R = n-C_6H_{13}, $PhCH_2$, o-$NO_2C_6H_4$ or Ph, (IV), whereas for R = p-$CH_3C_6H_4$ the principal product arises from insertion across the more substituted bond (V). In the case of disubstituted cyclopropanes different behaviour was found, depending on the ring substituents. Thus, certainly *trans*-1,2-diphenylcyclopropane, and most probably *trans*-1-methyl-2-*n*-butylcyclopropane undergo fission along the less substituted edge of the cyclopropane ring; *cis*-1-methyl-2-*n*-butylcyclopropane, however, was found to react quite differently. Thus, this cyclopropane derivative reacts by fission of the more substituted 1,2-bond to give a mixture of olefins [9]

(3)

1,2-dicyclopropylethane gave a $PtCl_2$ complex and a bis-pyridine derivative



(VI)



(VII) (VIII)

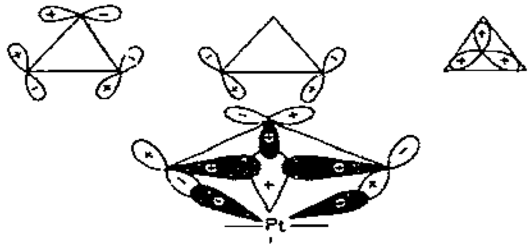
Fig. 2. Drawing of two independent molecules of different geometry of $[(C_3H_4Ph_2)PtCl_2\text{-}py_2]$. The ligands coordinated to platinum in the equatorial plane are shown.

By way of contrast, a compound formulated as an "edge complex" [11] has

(IX)

been reported to be formed by reaction of triasterane(tetracyclo[$3.3.1.0^{2,4}.0^{6,8}$]-nonane) with $K[(C_2H_4)PtCl_3]$ or $[(C_2H_4)PtCl_2]_2$. However, it should be noted that complex (IX) gave no triasterane upon heating.

The bonding mode of the cyclopropane moiety to platinum has been proposed on the basis of both x-ray analysis of the *trans*-1,2-diphenyl derivative (Figure 2) [9] (Table 3) and a detailed interpretation of the NMR spectra [8]. Using the Walsh orbitals picture [12], it is possible to represent the bond as a σ donor interaction from the cyclopropane ring orbitals to the empty orbitals of the metal, together with a π back-donation from the metal to the antibonding orbitals of the ring



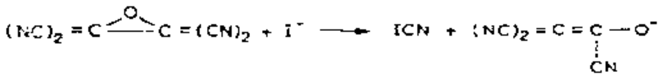
(4)

Such a bonding could rationalise the proton deshielding that is generally observed, and probably also the formation of the cyclopropane by treatment with base or upon heating. These observations indicate that the metallocyclobutane complexes should be looked upon as intermediate between σ-alkyl and π-olefin platinum complexes.

PLATINUM(0) SYSTEMS

The presence of a fractional positive charge on the carbon atom of electronegatively substituted cyclopropanes has been predicted by theoretical calculations and proved by ESCA measurements [13] (Table 1).

The organic chemistry of TCNEO is consistent with these results, TCNEO does not undergo ring opening on electrophilic attack as do most three-membered ring systems [14], but it undergoes nucleophilic attack as follows:

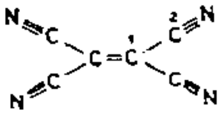


$$(NC)_2=C\overset{O}{\frown}C=(CN)_2 + I^- \longrightarrow ICN + (NC)_2=C=\underset{CN}{C}-O^- \qquad (5)$$

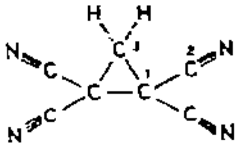
Thus, at variance with cyclopropane where an electrophilic attack by the $PtCl_2$ moiety was proposed [9], tetracyanocyclopropane derivatives and tetracyano-

TABLE 1

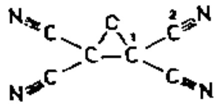
Observed 1*s* core binding energies [a] [13]



TCNE



TCCP



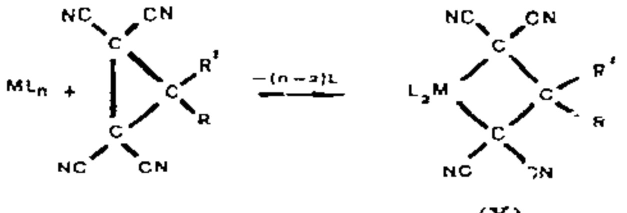
TCNEO

Compound	C_1	C_2	C_3	N	O
TCNE	4.0	3.1		−3.2	
TCNEO	6.0	3.4		−2.8	−3.2
TCCP	4.1	3.1	1.4	−3.2	
Ethylene oxide	1.6				−4.5
Cyclopropane	−0.3				

[a] In eV, with carbon referred to CH_4 (290.7 eV), nitrogen to N_2 (409.9 eV), and oxygen to O_2 (543.1 eV).

ethyleneoxide are expected to be susceptible to nucleophilic attack by complexes of type ML_n (M = Pd or Pt, L = tertiary phosphine or arsine).

Some platinum and palladium complexes of the type [ML_2(TCCP derivative)] have been synthesized under very mild conditions by the following reaction [15]



(6)

(X)

(R = R′ = H, CH_3; R = CH_3, R′ = C_2H_5; R + R′ = $(CH_2)_5$;

M = Pt,Pd; L=PPh_3, PPh_2Me, $AsPh_3$; n = 3,4)

An analogous reaction occurs with [$Pt(PPh_3)_2(C_2H_4)$]. In some cases exchange of the neutral ligand (L) gave very pure complexes in almost quantitative yield:

$$Pt(AsPh_3)_2(TCCP) + 2L \rightarrow PtL_2(TCCP) + 2AsPh_3 \qquad (7)$$

(L = PPh_2Me, PEt_3).

The final products (X) exhibit only one band in the IR spectrum in the solid or in solution, at about 2220 cm^{-1} for platinum and at 2200 cm^{-1} for palladium complexes. These values are relatively far from those for the free ligand (ν(CN) = 2260 cm^{-1}). 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, whereas upon coordination the signal of the methylene group is shifted by ca. 1 p.p.m. downfield in the case of platinum and by 0.5 p.p.m. for palladium complexes. The smaller deshielding in the latter case is probably attributable to the smaller ability of palladium than platinum to accept electrons from the cyclopropane ring. It should be noted that in complexes of the type [$(RC_3H_5)PtCl_2py_2$], the chemical shift of the protons bonded to the carbon atoms of the ring are shifted by two or more p.p.m. downfield in comparison to the parent free organic ligand [9]. The smaller difference in the chemical shift between free and coordinated ligand found for the platinum(0) system 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.

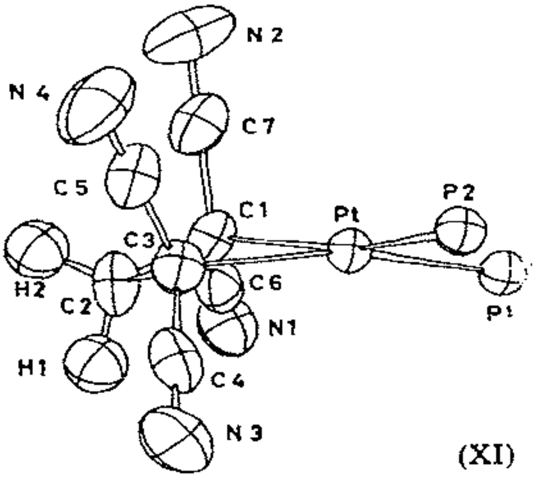
TABLE 2

NMR spectra for TCCP derivatives (CH_2) [a]

Compound	δ	J(Pt—H) (Hz)
TCCP [b]	3.47	
[Pt($PMe_2Ph)_2$(TCCP)]	4.49	26
[Pt($PEt_3)_2$(TCCP)]	4.34	28
[Pt($PMePh_2)_2$(TCCP)]	4.44	31
[Pt($PPh_3)_2$(TCCP)]	4.38	38
[Pt($AsPh_3)_2$(TCCP)]	4.39	44
[Pd($PPh_3)_2$(TCCP)]	3.96	
[Pd($PMePh_2$(TCCP)]	4.00	

[a] TMS as internal standard in $CDCl_3$.
[b] TMS as internal standard in $(CD_3)_2CO$.

Methylene protons appear as a triplet (J(P—H) = 1.5 Hz) showing them to be coupled to two equivalent ^{31}P atoms, as expected for a metallocyclobutane structure [16] (X). Changing the donor atom from P to As causes J(Pt—H) for the methylene protons to increase as expected, since the *trans* influence of the phosphine is greater than that of the arsine ligand [17]. A careful structural investigation of the four-coordinated metallocyclobutane complex $[Pt(PPh_3)_2](C_3H_2(CN)_4)$ has been carried out to elucidate the bonding mode in these types of complexes [18].



(XI)

Fig. 3. Drawing of [Pt($PPh_3)_2$TCCP] molecule.

TABLE 3

Structural data for metallocyclobutane complexes

	(II)	(XII)	(XIII)	(XI)
Intramolecular distances (Å)				
Pt—C(1)	2.04(5)	2.06(3)	2.05(3)	2.137(6)
Pt—C(2)	2.69(4)	2.60(4)	2.62(3)	2.712(6)
Pt—C(3)	2.19(5)	2.11(5)	2.17(3)	2.139(6)
C(1)—C(2)	1.48(8)	1.59(7)	1.59(4)	1.545(9)
C(1)—C(3)	2.55(10)	2.39(7)	2.60(4)	2.404(9)
C(2)—C(3)	1.82(9)	1.48(5)	1.71(4)	1.584(9)
Bond angles (°)				
C(1)—Pt—C(3)	74(2)	70(2)	76(1)	68.4(2)
C(1)—C(2)—C(3)	101(4)	102(3)	104(2)	100.4(5)
Pt—C(1)—C(2)	99(4)	90(2)	91(2)	93.5(4)
L(1)—Pt—L(2)	89(1)	82(1)	92(1)	96.99(6)
Dihedral angles (°)				
C(1)—Pt—C(3) } L(2)—Pt—L(1)	1(1)	4(1)	3(2)	18.0(2)

In Table 3 are reported the main structural data for complexes (II), (VII), (XIII) and (XI).

Structural parameters for the octahedral complexes (II), (VII) and (VIII), indicate that the four equatorial ligands C(1), C(3), L(1) and L(2) are essentially coplanar, whereas complex (XI) is severely distorted by a square-planar arrangement so that the dihedral angle between the planes C(1)—Pt—C(3) and L(1)—Pt—L(2) is 18.0(2)°. The four-coordinated complexes [$Pt(PPh_3)_2$-(TCNE)] [19], [$Pt(PPh_3)_2$(FMN)] [20] and [$Pt(PPh_3)_2(C_2H_4)$] [21], and related complexes are also perturbed from a square-planar arrangement, albeit to a different extent (Table 4).

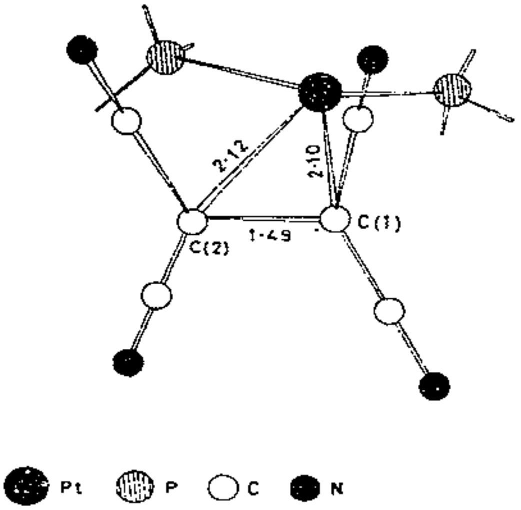
In the complex (XI) the platinum atom is inserted across the carbon—carbon bond (C(1)—C(3) = 2.55 Å) in a metallocyclobutane arrangement. The H—C—H angle of 121.4(30)° in TCCP [26] suggests an sp^2 hybridization at this carbon atom, in agreement with the Walsh [12] bonding scheme for cyclopropane rings [27]. However, in complex (XI) the angle H(1)—C(2)—H(2) is 104.2(51)° indicating an increase in *p*-orbital contribution to the hybrid orbitals interacting with these hydrogens. This implies a reorganization in the bonding scheme of the cyclopropane ring upon metallation to give a bonding mode of the same nature as in cyclobutane.

The model proposed in octahedral metallocyclobutane complexes ((II), (VII), (VIII)) implying a synergic interaction between available metal orbitals

TABLE 4

X-ray structural data for platinum(0) complexes $[Pt(PPh_3)_2X]$

X:	TCNE [19]	FMN [20]	C_2H_4 [21]	$(NC)_2C{=}CCl_2$ [22]	$Cl_2C{=}CCl_2$ [23]	$NC{-}C{\equiv}C{-}CN$ [24]	$Ph{-}C{\equiv}C{-}Ph$ [25]
C(1)—C(2) (Å)	1.49	1.53	1.43	1.42(3)	1.62(3)	1.40	1.32(9)
Pt—C(1) (Å)	2.10	2.05	2.11	2.10(2)	2.02(3)		2.06
Pt—C(2) (Å)	2.12	2.16		2.00(2)	2.05(3)		2.01
$P_2Pt{-}PtC_2$ (degr)	8.3	5.2	1.3	1.9	12.3	8	14
$C_1{-}Pt{-}C_2$ (degr)	41.5	42.6		40.6	47		39



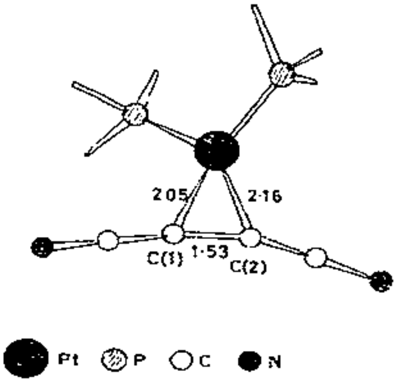


Fig. 4. Details of the molecule [Pt(PPh$_3$)$_2$TCNE].

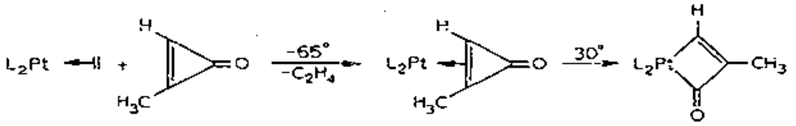
Fig. 5. Details of the molecule [Pt(PPh$_3$)$_2$FMN].

and molecular orbitals of the cyclopropane ring (eqn. 4), does not readily explain the puckering observed, but it rationalizes the general proton deshielding observed in the NMR of these complexes; it must be noted, however, that the chemical shift of the methylene protons of (*XI*) does not change with changing basicity of the neutral ligand L (Table 2). It generally appears that the bonding of a substituted trimethylene moiety to a metal cannot be described in simple σ-bonding terms nor as a π-type interaction. Rather, the true description of the bonding in a particular molecule is intermediate between these two extremes and is influenced by the nature of the trimethylene substituent groups. Interestingly, a structural investigation [26] of 1,1,2,2-tetracyanocyclopropane has shown the 1—2 bond to be lengthened due to the strong electron-withdrawing cyano substituents (1.561(4) Å compared to the average value of 1.503(4) Å for the 1—3 and 2—3 bonds). Moreover, the weakening of the 1—2 bond in 1,2-dicyanocyclopropane has been interpreted on the basis of the interaction of a symmetric and antisymmetric acceptor orbitals combination with the Walsh orbitals of cyclopropane, showing a net decrease in the 1—2 bond order [28].

This effect is even greater in 1,1,2,2-tetracyanocyclopropane. Thus, the chemistry of the insertion reaction of the metal across carbon—carbon bond takes place by nucleophilic attack of the ML$_n$ moiety on the carbon atom bearing the cyano groups. This mechanism gains some support from the observation that under the same experimental conditions [Pt(PPh$_3$)$_4$] does not react with the less electrophilic 1,2-dicyanocyclopropane [15].

Ring opening reactions of cyclopropenone derivatives by [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]

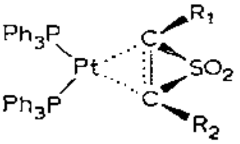
have been found to proceed via coordination of the olefinic bond to the platinum followed by carbon—carbon bond cleavage [29].



(8)

The possibility of trapping the platinum olefin complex depends on the ring substituents. Thus, using dimethyl- or diphenylcyclopropenone only the insertion products were obtained. The same product was obtained on reacting diphenylcyclopropenone with $[Pt(PPh_3)_4]$ [30]. This behaviour — coordination of the olefin followed by metal insertion across the carbon—carbon bond — seems to be a peculiar feature of cyclopropenones: as a matter of fact, from the reaction of cyclopropene derivatives with $[Pt(PPh_3)_2(C_2H_4)]$ only olefinic derivatives could be isolated [31] with no evidence for metal insertion across the carbon—carbon single bond, as shown by the structure in Fig. 6 for the dimethylcyclopropene derivatives [32].

A similar reaction to that proposed for cyclopropenone derivatives has been suggested for the thermal decomposition of a platinum(0)-thiiren-1,1-dioxide (TD) adduct [33]



The thermal decomposition proceeds according to the following equation

$$[PtL_2(TD)] \rightarrow [PtL_2(SO_2)] + R_1C{\equiv}CR_2 \qquad (9)$$

which is also part of a catalytic reaction sequence, by which thiiren-1,1-dioxides decompose into SO_2 and the corresponding acetylenes in the presence

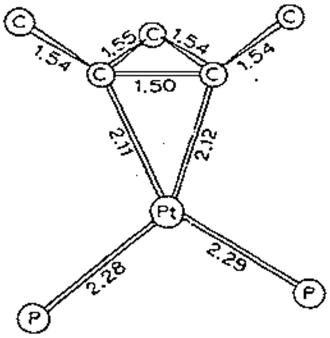
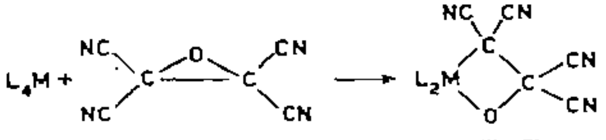


Fig. 6. X-ray structure of dimethylcyclopropene platinum derivative.

of these complexes. Such a reaction has been proposed to proceed via formation of an intermediate in which the metal atom is inserted across the carbon—sulphur bond [34].

The presence of a positive charge on tetracyanoethyleneoxide (TCNEO) as found by ESCA measurements (Table 1) suggested a reactivity similar to or even higher than that of TCCP. Platinum complexes of the type $[PtL_2(TCNEO)]$ ($L = PPh_3$, $AsPh_3$ and $P(p\text{-}CH_3C_6H_4)_3$) have been synthesized according to the reaction [35]



(10)

M = Pt (XII)

Such a structure has been confirmed by X-ray investigation [35] (Fig. 7) for the $AsPh_3$ derivative.

The platinum atom is inserted across the carbon—oxygen bond (C(1)—O = 2.335(9) Å). The metal atom and the four equatorial ones, C(1), O, As(1), As(2) are essentially coplanar. The dihedral angle between the planes C(1)—Pt—O and As(1)—Pt—As(2) is 4.5(2)°, much smaller than in complex (XI) (Table 3) where such angle is 18.0(2)°. The degree of puckering is low, probably an effect of the oxygen in the four-membered ring. For instance, the puckering in cyclobutanes is much more pronounced than in oxacyclobutane, which is instead essentially planar [36]. Complexes involving insertion reaction across the metal—oxygen bond in three-membered ring etherocycles have been proposed as intermediates in the catalytic formation of ethylenecarbonate in the system Ni^0, CO_2, ethyleneoxide [37] or in the rearrangement of cyclooctatetraene-oxide catalyzed by palladium or platinum complexes [38]. The

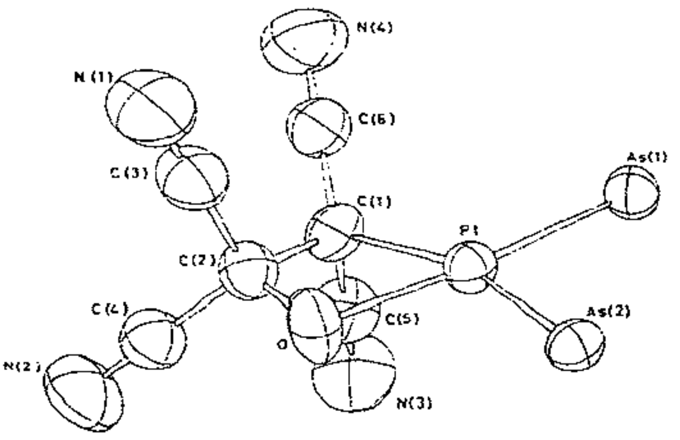
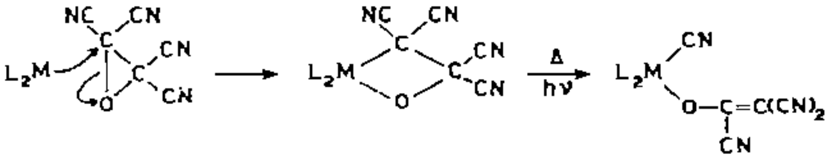


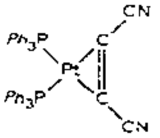
Fig. 7. Drawing of $[Pt(AsPh_3)_2TCNEO]$ molecule.

ring opening reaction probably proceeds via nucleophilic attack by the PtL_n moiety on the carbon atom of the TCNEO ring to give a metallooxacyclobutane complex

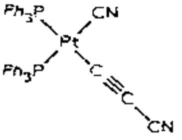


(11)

Metallooxacyclobutane complexes are not thermally stable [39], (eqn. 11) their stability depending on the metal atom (platinum complexes are more stable than their palladium analogs), and on the basicity of the coordinated phosphines. When using basic phosphines such as PEt_3, only the tricyanovinylethanolate complex is obtained [39]. Irradiation at low temperature of metallooxacyclobutane platinum complexes also gives tricyanovinylethanolate complexes in very high yield [40]. Irradiation of platinum complexes involving migration of a cyano group to the metal has been reported for $[Pt(PPh_3)_2(NCC{\equiv}CCN)]$ [41]. Irradiation of an acetone solution of (XIII) with a sun lamp gave a residue of white crystals whose IR spectrum is consistent with the cyanoacetylide complex. A crystallographic [41] study of complex (XIV) showed that coordination around the platinum atom is strictly planar (Fig. 8). Interesting features are the C(1)—C(3) distance of 1.24 Å which is long for a triple bond and the C(3)—C(4) distance of 1.31 Å which is short



(XIII)



(XIV)

(12)

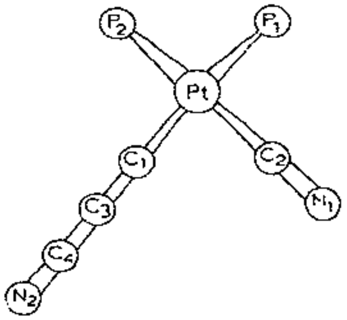
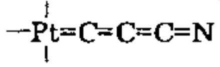


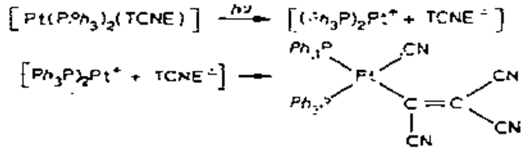
Fig. 8. Drawing of $[Pt(PPh_3)(CN)CCCN]$ complex.

for a single bond. These distances may indicate extensive electronic delocalization in the coordinated cyanoacetylido moiety, as can result in the valence-bond method by the contribution of the canonical form



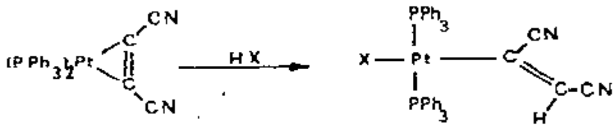
$$-\overset{|}{\underset{|}{\mathrm{Pt}}}=C=C=C=N$$

Since it is reasonable to assume that multiple bonding exists between platinum and C(2), the similar Pt—C(1) (1.96(3) Å), and Pt—C(2) (2.02(3) Å) distances may imply a comparable π-acceptor capacity for the cyano—acetylido and cyano groups. Irradiation [42] of a solution of [Pt$(PPh_3)_2$(TCNE)] in $CHCl_3$ at 313 nm gives a percyanovinyl complex of platinum (II):



(13)

The reaction proceeds stepwise with formation of $TCNE^{\dot{-}}$ as intermediate, as detected by ESR spectroscopy [43] by comparison with an authentic sample. Irradiation at 313 nm of solutions at different concentration showed that (i) the quantum yield (ϕ = 0.01) for the disappearance of [Pt$(PPh_3)_2$-(TCNE)] is independent of the initial complex concentration, and (ii) the quantum yield for the formation of $TCNE^{\dot{-}}$ depends on such concentration. In the presence of radical trapping agents no cyanovinyl—platinum(II) complex was produced during the photoreaction. These results may indicate that the photoreaction proceeds through a dissociative step forming $TCNE^{\dot{-}}$ followed by thermal rearrangement to the final cyanovinyl—platinum(II) complex [eqn. 13]. It must be noted that this type of reaction appears to be markedly affected by the nature of the substituents on the coordinated olefin. Thus, whereas [Pt$(PPh_3)_2$(TCNE)] is recovered unchanged after refluxing in ethanol [42], [Pt$(PPh_3)_2(Cl_2C{=}CCl_2)$] gives, under the same conditions, the perchlorovinylderivative [Pt$(PPh_3)_2(ClC{=}CCl_2)$Cl] [44]. This tendency of platinum complexes with electronegatively substituted olefins or acetylenes to rearrange to Pt^{II} vinyl species is also borne out by their reactivity with electrophilic agents [45] such as HX (X = Cl, Br) and HgX_2, which is reminiscent of cyclopropene derivatives



(14)

These results, combined with structural data (C—Pt—C angle about 40°), indicate that the three-membered ring <u>Pt—C—C</u> is still highly strained, although the decomposition temperatures [46] of complexes of type [Pt$(PPh_3)_2$-

(olefin)] (122° through 218° to 268°C on passing from ethylene through tetrafluoroethylene to tetracyanoethylene) indicate that the strain energy is not so high as structural data would suggest.

ACKNOWLEDGEMENTS

M.G. thanks the C.N.R. (Rome) for partial financial support.

REFERENCES

For a general survey on Platinum Chemistry, see: U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press Inc., London, 1974.

1 P.G. Gassman and K.T. Mansfield, J. Amer. Chem. Soc., 90 (1968) 1517.

2 L.A. Paquette, Accounts Chem. Res., 4 (1971) 280; P.G. Gassman and F.J. Williams, J. Amer. Chem. Soc., 94 (1972) 7733.

3 L. Cassar and J. Halpern, Chem. Commun., (1970) 1082.

4 C.F.H. Tipper, J. Chem. Soc., (1955) 2045.

5 D.M. Adams, J. Chatt, R.G. Guy and N. Sheppard, Proc. Chem. Soc , London, (1960) 179; J. Chem. Soc., (1961) 738.

6 S.E. Binns, R.H. Cragg, R.D. Gillard, B.T. Heaton and M.F. Pilbrow, J. Chem. Soc., (1969) 1227.

7 R.D. Gillard, M. Keeton, R. Mason, M.F. Pilbrow and D.R. Russell, J. Organometal. Chem. 33 (1971) 247.

8 P.W. Hall, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 71 (1974) 145.

9 F.J. McQuillin and K.G. Powell, J. Chem. Soc. Dalton, (1972) 2123.

10 J.A. McGinnety, J. Organometal. Chem., 59 (1973) 429.

11 H.C. Volger, H. Hogeveen and M.M.P. Gaasbeck, J. Amer. Chem. Soc., 91 (1964) 2137.

12 A.D. Walsh, Trans. Faraday Soc., 45 (1945) 179.

13 G.D. Stucky, D.A. Matthews, J. Hedman, M. Klasson and C. Nordling, J. Amer. Chem. Soc., 94 (1972) 8009.

14 W.J. Linn, O.W. Webster and R.E. Benson, J. Amer. Chem. Soc., 87 (1965) 3647.

15 M. Lenarda, R. Ros, M. Graziani and U. Belluco, J. Organometal. Chem., 46 (1972) C29; J. Organometal. Chem., 65 (1974) 407.

16 J.M. Jenkins and B.L. Shaw, J. Chem. Soc., A, (1966) 770; M.J. Church and M.J. Mays, J. Chem. Soc., A, (1968) 3074.

17 H.C. Clark and L.E. Manzer, Inorg. Chem., 11 (1972) 2749.

18 D.J. Yarrow, J.A. Ibers, M. Lenarda and M. Graziani, J. Organometal. Chem., 70 (1974) 133.

19 C. Panattoni, G. Bombieri, U. Belluco and W.H. Baddley, J. Amer. Chem. Soc., 90 (1970) 798; G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani and G. Bandoli, J. Chem. Soc., A, (1970) 1313.

20 C. Panattoni, R. Graziani, G. Bandoli, D.A. Clemente and U. Belluco, J. Chem. Soc., B, (1970) 371.

21 P.T. Cheng, C.D. Cook, S.C. Nyburg and K.Y. Wan, Inorg. Chem., 10 (1971) 2210.

22 A. McAdams, J.N. Francis and J.A. Ibers, J. Organometal. Chem., 29 (1971) 149.

23 J.N. Francis, A. McAdams and J.A. Ibers, J. Organometal. Chem., 29 (1971) 131.

24 C. Panattoni and R. Graziani, in M. Cais (Ed.), Progress in Coordination Chemistry, Elsevier 1968, p. 310.

25 J.O. Glanville, J.M. Stewart and S.O. Grim, J. Organometal. Chem., 7 (1967) P9.

26 Y. Wang and G.D. Stucky, Acta Crystallogr., Sect. B, 29 (1973) 1255.
27 W.A. Bernett, J. Chem. Educ., 44 (1967) 17.
28 R. Hoffman and W.D. Stohrer, J. Amer. Chem. Soc., 93 (1971) 6941.
29 J.P. Visser and J.E. Ramakers-Blom, J. Organometal. Chem., 44 (1972) C63.
30 W. Wong, S.J. Singer, W.D. Pitts, J.F. Watkins and W.H. Baddley, Chem. Commun., (1972) 672.
31 J.P. Visser, A.J. Schipperijn, J. Lukas, D. Bright and J.J. de Boer, Chem. Commun., (1971) 1266.
32 J.J. de Boer and D. Bright, quoted in J. Organometal. Chem., 47 (1973) 433.
33 J.P. Visser, C.G. Leliveld and D.N. Reinhoudt, Chem. Commun., (1972) 178.
34 D.N. Reinhoudt, C.G. Kouwenhoven and J.P. Visser, J. Organometal. Chem., 57 (1973) 403.
35 R. Schlodder, J.A. Ibers, M. Lenarda and M. Graziani, J. Amer. Chem. Soc., 96 (1974) 6893.
36 S.I. Chan, J. Zinn, J. Fernandez and W.D. Swinn, J. Chem. Phys., 33 (1960) 1643.
37 R.J. De Pasquale, Chem. Commun., (1973) 157.
38 G. Strukul, P. Viglino, R. Ros and M. Graziani, J. Organometal. Chem., 74 (1974) 307.
39 M. Lenarda, W.D. Pitts, W.H. Baddley and M. Graziani, to be published.
40 O. Traverso, M. Lenarda, W.H. Baddley and M. Graziani, to be published.
41 W.H. Baddley, C. Panattoni, G. Bandoli, D.A. Clemente and U. Belluco, J. Amer. Chem. Soc., 93 (1971) 5590.
42 O. Traverso, V. Caassiti, M. Graziani and U. Belluco, J. Organometal. Chem., 57 (1973) C22.
43 A. Sotgiu, O. Traverso, M. Lenarda, and M. Graziani, to be published.
44 W.J. Bland and R.D.W. Kemmitt, J. Chem. Soc. A, (1968) 1278.
45 G.L. McClure and W.H. Baddley, J. Organometal. Chem., 25 (1970) 261.
46 W.H. Baddley, Inorg. Chim. Acta Rev., 2 (1968) 7.