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SYNTHESIS AND CHARACTERIZATION OF 1,2-DIPHENYL-3-PLATINA-4-DISUBSTITUTED METHYLENE CYCLOBUTENE DERIVATIVES

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Summary

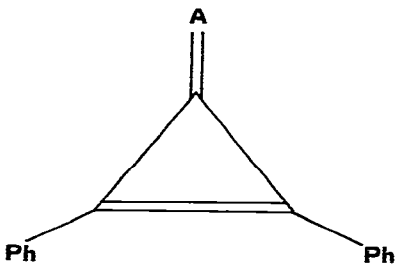
Derivatives of diphenylcyclopropenone react with various platinum(0) complexes to give metal insertion into the carbon—carbon bond. Mononuclear or dinuclear complexes can be isolated depending on the conditions. The bulkiness of the ligand plays an important role in determining the position of the equilibrium between the two species.

Introduction

Reactions of low valent complexes of platinum and palladium with electronegatively-substituted three or four membered rings occur with ring opening and insertion of the metal into the carbon—carbon bond. The presence of a partial positive charge on the carbon atoms appears to be the driving force in these reactions, rather than the strain energy of the small ring [1]. Platinum (0) and palladium(0) complexes react in a similar fashion with diphenylcyclopropenone [2] and cyclobutenedione [3] derivatives. In the last case metal olefin intermediates can be isolated under certain experimental conditions [4]. In order to compare the two modes of reaction: (i) ring opening or (ii) formation of metal-olefin compounds, we have investigated the reactions of platinum(0) complexes with 4,4 dicyano-2,3-diphenyltriafulvene (TRYA) and its derivatives, which could in principle give stable metal-olefin complexes [5], and for which a significant delocalisation of charge onto the $C(CN)_2$ moiety was proposed to account for the high value of dipole moment found (7.89 D in dioxane at 30°C) [6]. A large positive charge is expected to be present on the ring, promoting nucleophilic attack to give insertion of platinum into the carbon—carbon bond.

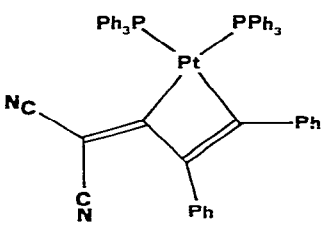
Results and discussion

We have studied the reactions of diphenylcyclopropenone derivatives:

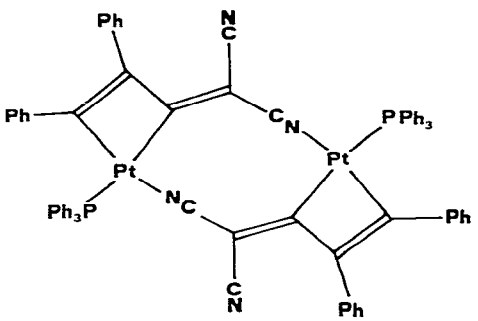


(where A = O (1,2 diphenylcycloprenone DCP); $C(CN)_2$ (4,4-dicyano-2,3-diphenyltriafulvene, TRYA); C(CN)(COOEt) (1,2 diphenyl-3-cyanocarboethoxymethylenecyclopropene, DCCE)) with platinum(0) complexes of the type [Pt-$(PPh_3)_2(C_2H_4)$], and [PtL_4] (L = $PMePh_2$, PMe_2Ph and $AsPh_3$).

In a preliminary account [7] we reported the reaction of [$Pt(PPh_3)_2(C_2H_4)$] with TRYA. The reaction was carried out in benzene and in THF and in the first solvent two products were obtained (**a** and **b**).



a



b

In THF only the dinuclear compound b was obtained. The products were completely characterized by X-ray analysis. The platinacyclo compound **a** has a rather distorted structure, and this can be easily understood in terms of the large steric hindrance exerted by the phosphine ligand on the -$C(CN)_2$ group. In the absence of steric effects we would expect no significant distortion in the platinacyclo in view of the nature of the ligand. These results suggest that compound **a** releases a phosphine ligand to yield a less strained dinuclear species **b**. Thus in THF **a** is completely converted spontaneously to **b** which after addition of an excess of PPh_3 regenerates **a**, showing that there is an equilibrium **a** $\rightleftharpoons$ **b** + PPh_3; the position of this equilibrium can be established by monitoring the IR spectra of the mixture in CH_2Cl_2 solution (see Table 1). The equilibrium depends on the solvent used, and in a coordinating solvent such as THF only dinuclear compounds are obtained, probably because the coordination by the solvent increases the steric hindrance around the metal. To provide better information on this point, we carried out the reaction between [$Pt(PPh_3)_2(C_2H_4)$] and TRYA in a

TABLE 1

INFRARED AND ^1H NMR SPECTRA OF PLATINACYCLO COMPLEXES

Complex	IR		NMR [d]			
	ν(CN) (cm^{-1})	ν(CO) (cm^{-1})	δ(ppm) [e]	J(Pt—H) (Hz)	J(P—H) (Hz)	
$[Pt(PPh_3)_2(TRYA)]$	2220 [a]					
$[Pt(PPh_3)(TRYA)]_2$	2210 [a] 2245					
$[Pt(PPh_2Me)_2(TRYA)]$	2210 [b]		1.35 2.0	25 24	9 8	P—CH_3 P—CH_3
$[Pt(PPhMe_2)_2(TRYA)]$	2210 [c]		1.05 1.85	24 27	10 10	P—CH_3 P—CH_3
$[Pt(AsPh_3)(TRYA)]_2$	2232 [b] 2208					
$[Pt(PPh_3)_2(DCCE)]$	2202 [b]		1.25t; 1.4t 4.25q; 4.35q			CH_3 CH_2
$[Pt(PPh_2Me)_2(DCCE)]$	2200 [b]		complex spectrum [f]			
$[Pt(AsPh_3)(TRYA)(CO)]$	2215 [b]	2080 [b]				
$[Pt(PPh_2Me)_2(DCP)]$		1640 [b]	1.2 1.95	18 30	7 10	P—CH_3 P—CH_3
TRYA	2205 [b] 2218					
DCCE	2202 [b]					

[a] Nujol mull. [b] CH_2Cl_2 solution. [c] in KBr. [d] $CDCl_3$ solution. [e] phenyl protons absorption not reported. [f] complex spectrum due to overlapping of CH_2CH_3 with P—CH_3. TRYA: PhC=C(Ph)C=$C(CN)_2$; DCCE: PhC=C(Ph)C=C(CN)COOEt; DCP: PhC=C(Ph)C=O.

NMR tube in $CDCl_3$ and we followed the change in the ^{31}P NMR spectrum of the solution. The compounds are not very soluble under these conditions and spectra had to be accumulated. The results are schematically shown in Figure 1.

The spectra of the products were compared with those of authentic samples. The results show that the first compound to be formed in the reaction is the dinuclear species. During the reaction, phosphine accumulates and then reacts with the dinuclear species to give compound **a**, according to the following scheme

$$2[Pt(PPh_3)_2(C_2H_4)] + 2TRYA \xrightarrow{-C_2H_4} [Pt(PPh_3)(TRYA)]_2 + 2\,PPh_3 \qquad (1)$$
$$\downarrow$$
$$2[Pt(PPh_3)_2(TRYA)]$$

These results indicate that the monomeric complexes $[Pt(PPh_3)_2(TRYA)]$ in unstable not only in THF, in which solvent molecules coordinated above and below the plane could cause destabilization, but also in non coordinating solvents such as chloroform. These results, when viewed in association with the steric hindrance found in the solid state [7], indicate that bulkiness of ligands play an important role in the reactions.

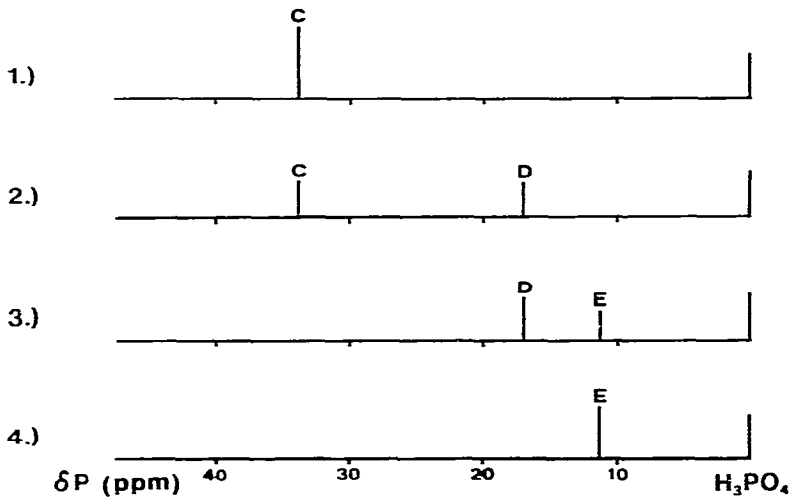


Fig. 1. ^{31}P NMR spectra of the reaction $[Pt(PPh_3)_2(C_2H_4)]$ + TRYA in $CHCl_3$. 1, Spectrum after few minutes; 2, Spectrum after one hour; 3, Spectrum after one day; 4, Spectrum after addition of excess of PPh_3. C: $[Pt(PPh_3)_2(C_2H_4)]$; D: $[Pt(PPh_3)(TRYA)]_2$; E: $[Pt(PPh_3)_2(TRYA)]$; PPh_3 signal not shown.

We then studied the following reactions:

$$[PtL_4] + TRYA \xrightarrow{-2L} [Pt(L)_2(TRYA)] \qquad (2)$$

$L = PMePh_2$, PMe_2Ph

The reactions were carried out in benzene and only mononuclear species were detected. However, the free phosphine present in solution might be responsible for shifting the equilibrium towards the mononuclear compounds. These last species were isolated, but in THF they do not give the dinuclear complexes of type b such as were found for PPh_3 compounds. The monomeric complexes of type a appear to be stable under these conditions because of the smaller steric effect of the coordinated phosphines. In the reaction 3 $[Pt(AsPh_3)_4]$ was treated with TRYA:

$$[Pt(AsPh_3)_4] + TRYA \xrightarrow{-AsPh_3} [Pt(AsPh_3)(TRYA)]_2 \qquad (3)$$

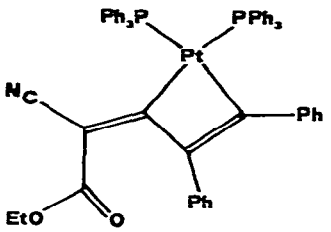
$$[Pt(AsPh_3)(TRYA)]_2 \xrightarrow{+AsPh_3} \text{no reaction}$$

$$[Pt(AsPh_3)(TRYA)]_2 \xrightarrow{+CO} [Pt(AsPh_3)(CO)(TRYA)]$$

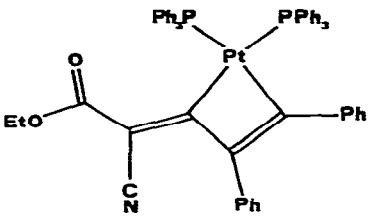
The reaction was carried out in benzene, and only the dinuclear complex was obtained. This was treated with a large excess of $AsPh_3$, but no trace of the mononuclear species $[Pt(AsPh_3)_2(TRYA)]$ was found. Reaction with a much smaller ligand such as CO caused bridge splitting and formation of a mononuclear species $[Pt(AsPh_3)(CO)(TRYA)]$.

Our results prove the steric nature of the driving force in these reactions; thus by varying the size of the ligand we obtain mononuclear species with PMe_2Ph or $PMePh_2$ or dinuclear species with $AsPh_3$. Using PPh_3 both types of complexes could be obtained, and this ligand appears to be on the borderline between the

two types. DCCE also reacts with $[Pt(PPh_3)_2(C_2H_4)]$ to give a mixture of two compounds, which we believe to be the two isomers **c** and **d** in 1/1 ratio. The IR



c



d

spectra show only ν(CN) frequencies attributable to uncoordinated CN groups, the analysis and molecular weight are as expected, and the NMR spectrum appears as two overlapping quartets for CH_2 giving rise to a quintet and detectable triplets for the CH_3 groups. Analogous results were found with platinum complexes with $PMePh_2$ as the ligand. In this case a complex NMR spectrum is obtained due to the presence of P—CH_3. In all cases only mononuclear species were found, and we suspect that this is due to the different steric requirements of the C—COOEt and C—CN entities.

Experimentsl section

Instruments. Infrared spectra were recorded using a Perkin-Elmer 257 or 225 spectrophotometer. The NMR spectra were recorded on a Jeol C60 HL spectrometer.

Materials. Solvents were dried as previously reported [8]. TRYA (4.4-dicyano-2.2-diphenyltriafulvene) was synthesized as by a published method which involves the following sequence of reactions [9].

$$PhCH_2COCH_2Ph + Br_2 \rightarrow PhCHBrCOCHBrPh + 2\ HBr \qquad (4)$$

$$PhCHBrCOCHBrPh \xrightarrow{NEt_3} PhC{=}C(Ph)C{=}O$$

Diphenylcyclopropenone (DCP) was used to prepare TRYA or DCCE (1,2 diphenyl-3-cyanocarboethoxymethylenecyclobutene) by reaction of DCP with dimalononitrile or ethylcyanoacetate, respectively [10].

$$PhC{=}C(Ph)C{=}O + H_2C(CN)_2 \rightarrow PhC{=}C(Ph)C{=}C(CN)_2 + H_2O \qquad (5)$$

Platinum(0) complexes were also prepared by use of literature methods or slight modifications of them: $[Pt(PPh_3)_2(C_2H_4)]$ [11], $[Pt(PMe_2Ph)_4]$ [12], $[Pt(PMePh_2)_4]$ [13], $[Pt(AsPh_3)_4]$ [13].

Reaction of TRYA with $[Pt(PPh_3)_2(C_2H_4)]$

0.254 g (1 mmol) of TRYA are dissolved in 20 ml of benzene under nitrogen. To the solution 0.747 g (1 mmol) of $[Pt(PPh_3)_2(C_2H_4)]$ dissolved in 10 ml of the same solvent are added. The resulting solution is refluxed for 1 h. Crystallization of the crude product from benzene or benzene/methanol gives two products, **a**: $[Pt(PPh_3)_2(TRYA)]$ m.p. 132—135°C: Elemental analysis, found: C,

66.1; H, 4.0; N, 2.9. $C_{54}H_{40}N_2P_2Pt$ calcd.: C, 66.6; H, 4.1; N, 2.9%; M.W. found: 1050; calcd.: 1053. **b**: $[Pt(PPh_3)(TRYA)]_2$ m.p. 286—289°C; Elemental analysis found: C, 61; H, 3.6; N, 3.9. $C_{36}H_{25}N_2PPt$ calcd.: C, 60.7; H, 3.52; N, 3.9%; M.W. in C_6H_6 found: 1501; calcd.: 1522.

The same reaction was carried out in THF and the mixture left overnight at room temperature. Under these conditions only product **b** was obtained. The product **a** was isolated and characterized then dissolved in THF; after 0.5 h the IR spectrum was monitored and showed that only **b** was present (ν(CN) in CH_2Cl_2 2200 cm^{-1}). Addition of excess of PPh_3 very rapidly restored **a** (ν(CN) in CH_2Cl_2 2210, 2245 cm^{-1}).

Synthesis of [Pt(PMePh$_2$)$_2$(TRYA)]

To a hot benzene solution of 90 mg (0.33 mmol) of TRYA was added 340 mg of $[Pt(PMePh_2)_4]$ (0.33 mmol) dissolved in 30 ml of the same solvent. The solution was refluxed under nitrogen for 4 hours. Separation on a silica gel column with ethylacetate as eluent gave the product as the first fraction and it was crystallized from methylene chloride-hexane to give $[Pt(PMePh_2)_2(TRYA)]$. Yield 19%. M.p. 141—143°C. Elemental analysis, found: C, 62; H, 4.3; N, 3.2. $C_{44}H_{36}N_2P_2Pt$ calcd.: C, 61.3; H, 4.56; N, 3.3%. M.W. in C_6H_6 found: 895; calcd.: 909. $[Pt(PMePh_2)_2(TRYA)]$, was dissolved in THF and the solution refluxed for 4 hours. The IR spectrum in CH_2Cl_2 showed no formation of dinuclear species.

Synthesis of [Pt(PMe$_2$Ph)$_2$(TRYA)]

To a degassed solution of TRYA (0.254 g, 1 mmol) in 150 ml of benzene under argon was added solid $[Pt(PMe_2Ph)_4]$ (0.747 g, 1 mmol). The solution was stirred at room temperature for two hours and filtered through active charcoal to remove platinum metal formed during the reaction. The solution was evaporated to small volume and addition of ethanol gave the complex as yellow crystals. Yield 50% M.p. 190—193°C. Elemental analysis, found: C, 53; H, 4.6; N, 4.2; $C_{34}H_{32}N_2P_2Pt$ calcd.: C, 53.2; H, 4.73; N, 4.14%. M.W. found: 897; calcd.: 765. $[Pt(PMe_2Ph)_2(TRYA)]$ was dissolved in THF and the solution refluxed for 4 hours. The IR spectrum in CH_2Cl_2 showed no formation of dinuclear species.

Synthesis of [Pt(AsPh$_3$)(TRYA)]$_2$

0.710 mg (0.5 mmol) of $[Pt(AsPh_3)_4]$ were suspended in dry benzene under nitrogen, and 130 mg (0.5 mmol) of solid TRYA added. After few minutes heating a clear solution was obtained and this was stirred at room temperature for two hours. After evaporation to small volume, methanol was added to precipitate the air-stable yellow $[Pt(AsPh_3)(TRYA)]_2$ Yield 20%. M.p. 210—215°C. Elemental analysis, found: C, 58; H, 3.5; N, 3.7; $C_{54}H_{40}N_2As_2Pt$ calcd.: C, 57.2; H, 3.3; N, 3.71%; M.W. found: 1480; calcd.: 1510. $[Pt(AsPh_3)(TRYA)]_2$ (0.250 mg) was dissolved in 20 ml of CH_2Cl_2, and a five fold excess of $AsPh_3$ was added. The solution was refluxed for two hours, but only starting material was present.

Synthesis of [Pt(AsPh$_3$)(CO)(TRYA)]

$[Pt(AsPh_3)(TRYA)]_2$ dissolved in 20 CH_2Cl_2 was left in a CO atmosphere for 2 hours during which the colour changed from orange to yellow. The solution was evaporated to small volume and after addition of hexane the yellow $[Pt(AsPh_3)(CO)(TRYA)]$ was obtained. Yield 90% M.p. 164—167°C (dec.). Elemen-

tal analysis, found: C, 56.0; H, 3.44; N, 3.6; $C_{37}H_{25}N_2OAsPt$ calcd.: C, 56.7; H, 3.19; N, 3.58%.

Synthesis of [Pt(PPh$_3$)$_2$(DCCE)]

[Pt(PPh$_3$)$_2$(C$_2$H$_4$)] 750 mg, 1 mmol) was dissolved in 50 ml of benzene under nitrogen, and a solution of 300 mg (1 mmol) of DCCE in 50 ml of benzene was added. The mixture was refluxed and the reaction was complete in 3 h. The benzene was evaporated off and the resulting red oil was crystallized from CH_2Cl_2/n-hexane. The product was filtered off and dried under vacuum. Yield: 0.3 g, 29%. Found: C, 65.3; H, 4.64; N, 1.34. $C_{56}H_{45}NO_2P_2Pt$ calcd.: C, 65.9; H, 4.41; N, 1.37%. IR: ν(CN) 2202 cm^{-1}.

Synthesis of [Pt(PPh$_2$Me)$_2$(DCCE)]

In a three neck flask, equipped with a magnetic stirrer, a pressure equalized dropping funnel and a reflux condenser with a N_2 inlet, 0.33 g of [Pt(PPh$_2$Me)$_4$] were dissolved in 30 ml of benzene. The mixture was refluxed for 3 h during which the colour slowly changed from yellow to orange. The solution was evaporated and the product purified by thin layer chromatography (Kiesel gel GF 254, eluent ethyl acetate). The yellow oil obtained was crystallized by evaporating its solution in a mixture of CH_2Cl_2/n-hexane. Yield 75 mg (15%). M.p. 125°C (dec.).

Synthesis of [Pt(PPh$_2$Me)$_2$(DCP)]

To a benzene (20 ml) solution of 0.5 g (0.5 mmol) of [Pt(PPh$_2$Me)$_4$], a solution of 0.1 g (0.5 mmol) of diphenyl cyclopropenone in benzene was added. The mixture was refluxed for 4 h. The solvent was evaporated off and the yellow oil obtained was crystallized from CH_2Cl_2/n-hexane to give a yellow solid. Yield 0.35 g (52%). M.p. 188—192°C. 300 mg of this product were refluxed in dry THF for 4 h. The yellow product precipitated from the solution by the procedure described immediately above was found to have the same spectroscopic properties as the original [Pt(PPh$_2$Me)$_2$(DCP)].

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