Journal of Organometallic Chemistry, 172 (1979) 193—199

REACTIONS OF SOME ELECTROPHILIC OLEFINS WITH (CARBONATO)BIS(TRIPHENYLPHOSPHINE)- AND (CARBONATO)BIS(TRIPHENYLARSINE)-PLATINUM COMPLEXES

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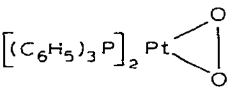
(Received November 30th, 1978)

Summary

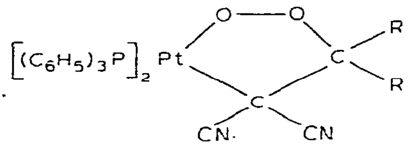
Carbonato complexes L_2PtCO_3 (L = PPh_3 or $AsPh_3$) react with certain electrophilic olefins, such as 1,1-dicyanoolefins, under mild conditions to liberate CO_2. The reaction of L_2PtCO_3 with tetracyanoethylene at room temperature is solvent dependent, and in alcoholic solvents, in contrast to an earlier report, the dicyano complexes, $L_2Pt(CN)_2$, and tricyanoethenolato complexes, $L_2Pt(CN)[OC(CN)=C(CN)_2]$ have been isolated and identified.

Introduction

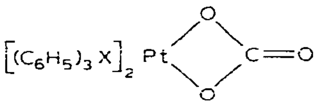
Peroxybis(triphenylphosphine)platinum (I) reacts rapidly at room temperature with electrophilic olefins, such as tetracyanoethylene and 1,1-dicyano-2-methylpropene [1]. The products of these reactions are stable five-membered ring adducts, IIa and IIb. On treatment with trifluoroacetic acid these adducts produce a 1/1 mixture of the original olefin and the corresponding epoxide.



(I)



(IIa, R = CN;
IIb, R = CH_3)



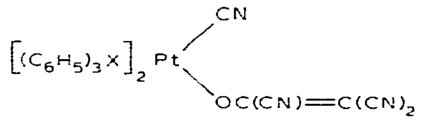
(III, X = P;
IV, X = As)

It appeared to us that carbonato complexes, like III and IV, could react with electrophilic olefins releasing carbon dioxide with formation of epoxide. This reaction, however, involves reductive elimination and stabilization of zerovalent platinum species, a reaction not readily encountered under mild reductive conditions.

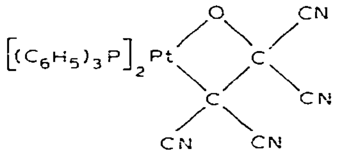
Hacker et al. [2] reported the reactions of electrophilic olefins with IV, but identified the obtained products as either zerovalent platinum olefin complexes or vinyl complexes, Pt(CR=CR$_2$). We reexamined the reactions of olefins with (carbonato)bis(triphenylphosphine)platinum (III) and (carbonato)bis(triphenylarsine)platinum (IV) and wish to report our results, which differ from the earlier published work.

Results

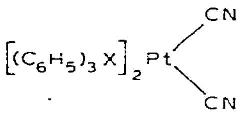
Tetracyanoethylene (TCNE) reacts rapidly and quantitatively at room temperature with III in a wide range of solvents. Carbon dioxide is generated and depending upon the solvent any of three stable products can be identified. These are the tricyanoethenolato complex V, the cyclic tetracyanoethylene oxide (TCNEO) adduct VI and the dicyano complex VII. The distribution of products depends on the solvent used in the reaction.



(V, X = P;
VIII, X = As)



(VI)



(VII, X = P;
IX, X = As)

In isopropanol the tricyanoethenolato complex V is isolated as the major product and the dicyano complex VII as a minor product. In methanol and ethanol the reaction yields predominately the dicyano complex VII and some V. In methylene chloride and tetrahydrofuran a rapid reaction is observed, but no pure products could be isolated from the reaction mixture, although spectroscopic and chromatographic data indicate the presence of products V and VI.

The products V, VI and VII are identified by spectroscopic and chromatographic comparison with authentic materials. In the IR the tricyanoethenolato complex V shows absorptions at 2210, 2185 and 2140 cm^{-1} assignable to cyano groups and an olefinic absorption at 1590 cm^{-1}. The cyclic adduct VI has no olefinic absorption and only one C≡N stretch at 2220 cm^{-1}, as well as a strong C—O stretch at 1070 cm^{-1}. The dicyano complex VII has two C≡N stretches at 2135 and 2140 cm^{-1}.

Further proof that the yellow product isolated from the isopropanol reaction contains a coordinated tricyanoethenolate ion is obtained by applying a previously reported displacement reaction [3]. Upon treating this yellow product with KCN, a white precipitate separates which is identified as the dicyano complex VII. Addition of phenyltrimethylammonium chloride to the filtrate precipitates a salt identified as phenyltrimethylammonium tricyanoethenolate (X) by comparison with an authentic sample. These results are interpreted by reactions 1 and 2:

$$\underset{(V)}{[(C_6H_5)_3P]_2Pt(CN)[OC(CN){=}C(CN)_2]} + KCN \rightarrow \underset{(VII)}{[(C_6H_5)_3P]_2Pt(CN)_2} + K^+[OC(CN){=}C(CN)_2]^- \qquad (1)$$

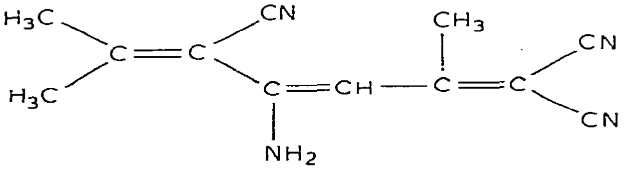
$$K^+[OC(CN){=}C(CN)_2]^- + [(C_6H_5)(CH_3)_3N]^+ Cl^- \rightarrow KCl + \underset{(X)}{[(C_6H_5)(CH_3)_3N]^+ [OC(CN){=}C(CN)_2]^-} \qquad (2)$$

The reaction of TCNE with (carbonato)bis(triphenylarsine)platinum (IV) at room temperature in isopropanol proceeds more slowly than the analogous reaction with III. Nevertheless, CO_2 is generated and a clean yellow solid is isolated with IR bands at 2200, 2185, 2140 and 1585 cm^{-1}. Further reaction of this product with KCN followed by treatment of the filtrate with $[(C_6H_5)(CH_3)_3N]^+$ cation produces first the dicyano complex IX and then yields the tricyanoethenolate salt, $[(C_6H_5)(CH_3)_3N]^+ [OC(CN){=}C(CN)_2]^-$ (X). These results demonstrate that the yellow product is the tricyanoethenolato complex VIII. Apparently the difference in basicity between $(C_6H_5)_3P$ and $(C_6H_5)_3As$ ligands does not affect the course of the reaction.

Hacker et al. [2] reported the reaction of TCNE with IV and identified their product as the zerovalent olefinic complex $[(C_6H_5)_3As]_2Pt[(CN)_2C{=}C(CN)_2]$. This conclusion is unlikely in light of the results of our displacement reaction with KCN and $[(C_6H_5)(CH_3)_3N]^+ Cl^-$. Also, their product, a white solid, gave ν(CN) at 2152 cm^{-1} in the region of ionic CN^-, not coordinated olefin. Under the conditions of their reaction (2 days in ethanol at 40°C) we obtain the white dicyano complex IX with ν(CN) at 2130 cm^{-1}.

The reaction of TCNE with IV in methylene chloride again proceeds very rapidly but pure products could not be isolated. Spectroscopic data give evidence for VIII, but not a compound analogous to VI.

When III is treated stoichiometrically with 1,1-dicyano-2-methylpropene (DCMP) at 35°C in methylene chloride a slow reaction occurs with loss of CO_2. The reaction is followed by IR, which shows a reduction in intensity of the carbonato absorption and complete disappearance of the olefinic stretch at 1600 cm^{-1}. Upon addition of diethyl ether nearly 50% of III is precipitated unreacted. Upon reduction of the filtrate to an oily yellow residue and extraction with n-hexane a white solid product is obtained, which matches identically an authentic sample of the dimer XI of DCMP prepared by literature methods [5]. Identical results are obtained if the reaction is conducted in isopropanol.



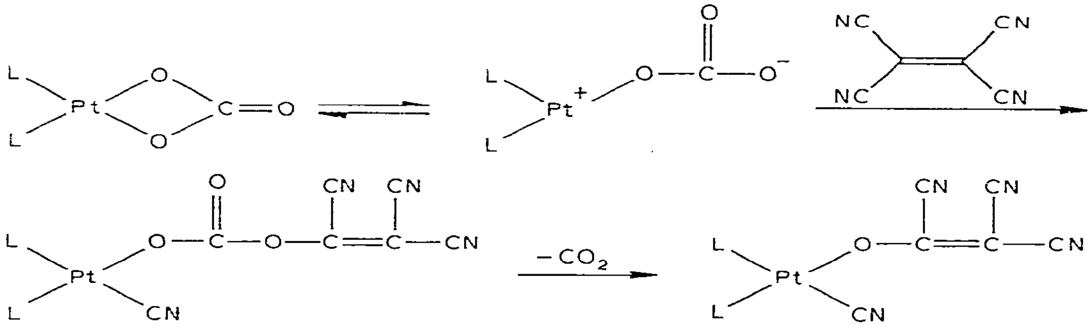
(XI)

A variety of other cyano substituted olefins, such as fumaronitrile, maleonitrile and acrylonitrile, and unactivated olefins such as 1-octene, styrene, cyclohexene and norbornene fail to undergo reaction with III at room temperature.

Discussion

Carbonato complexes of platinum react with electrophilic olefins, but not with non-activated olefins. At least two electron-withdrawing substituents, such as cyano groups, must be present on one olefinic carbon for reaction to occur. Carbon dioxide is released in these reactions, but epoxides are not formed. Stable Pt^{2+} ethenolato complexes are isolated in the reactions of TCNE, while the reactions of DCMP lead to dimerization of the olefin.

The dicyano complexes, which are by-products if the TCNE reaction is conducted in alcohols, are most likely the result of attack of the corresponding alcohol on the electrophilic olefin. In this reaction hydrogen cyanide is generated which converts the reaction product to the dicyano complex. The generation of carbon dioxide most likely occurs after the initial attack of the electrophilic olefin, because the $Pt^{+}—O^{-}$ species formed by loss of carbon dioxide, should undergo cycloaddition to the olefin like an ylide to give the four-membered ring epoxide adduct. This is only observed as a minor by-product if the reaction is conducted in a nonpolar solvent. Furthermore, the carbonato complexes are stable at room temperature in the solvents used in this study. The mechanism of formation of the ethenolato complexes is best explained by the following reaction sequences [*]:



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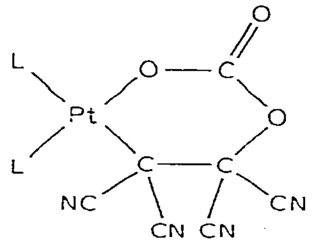
[*] One referee noted that since many electrophiles react with low oxidation state substrates to yield ring compounds, an attractive structure for an initially formed adduct of the carbonato complex and TCNE would be the six-membered ring complex:



Loss of CO_2 would then give the four-membered ring TCNEO complex, VI, which could isomerize to the ethenolato product, V. We found that the TCNEO complex isomerizes under the conditions in ref. 3, but not under the mild conditions in our experiments; and so we prefer the mechanism presented in the text.

The formation of a zerovalent platinum olefin complex as postulated by Hacker et al. [2] involves platinum—carbon bond formation, which is disproved by our displacement reaction with potassium cyanide.

Experimental

I. Materials

The complexes $[(C_6H_5)_3P]_2PtCO_3$ and $[(C_6H_5)_3As]_2PtCO_3$ were prepared by previously reported methods [6, 2]. 1,1-Dicyano-2-methylpropene was prepared according to a literature procedure [7] as was the phenyltrimethylammonium salt of tricyanoethenolate anion, $[(C_6H_5)(CH_3)_3N]^+ [OC(CN)=C(CN)_2]^-$ [8], and $[(C_6H_5)_3P]_2Pt(CN)[OC(CN)=C(CN)_2]$ [3], $[(C_6H_5)_3P]_2Pt(TCNEO)$ [3], $[(C_6H_5)_3P]_2Pt(CN)_2$ [4], $[(C_6H_5)_3As]_2Pt(CN)_2$ [4] and $(CH_3)_2C=C(CN)$-$C(NH_2)=CHC(CH_3)=C(CN)_2$ [5]. Maleonitrile was prepared by photochemical isomerization (100 Watt Hg lamp, 48 h) of fumaronitrile in CH_3CN, followed by fractional distillation; b.p. 110°C/20 mmHg. Tetracyanoethylene was purchased commercially and sublimed freshly before use. Fumaronitrile, acrylonitrile, styrene, 1-octene, cyclohexene and norbornene were purchased commercially and used without further purification.

Infrared spectra were recorded on Beckman Acculab 4 or Perkin—Elmer 621 spectrophotometers using Nujol mulls and KBr for solid state and methylene chloride or chloroform solutions. CO_2 evolved during reaction was identified on a Carbosieve S (100/120 mesh; Supelco) chromatographic column at 120°C in a Hewlett—Packard Model 7620A gas chromatograph. Thin layer chromatograms of products and authentic materials were obtained on silica gel plates (Quanta-Gram) eluted with methylene chloride/acetonitrile solutions ranging from 2 to 20% acetonitrile. Melting points were recorded uncorrected on a Fisher—Jones apparatus.

II. Reactions

A. Cyano substituted olefins with platinum carbonato complexes

All reactions were carried out in a nitrogen atmosphere.

1. Tetracyanoethylene (TCNE) with $[(C_6H_5)_3P]_2PtCO_3$

(a) $[(C_6H_5)_3P]_2PtCO_3$ (0.24 g, 0.3 mmol) was suspended in 5 ml isopropanol. A slight excess TCNE (51 mg, 0.4 mmol) dissolved in 5 ml isopropanol was added and the mixture stirred at room temperature for 2.0 h. Periodic chromatographic analysis of the gases in the reaction flask confirmed the production of CO_2. The yellow product was filtered, washed with isopropanol and diethyl ether and air dried. The product was dissolved in methylene chloride and filtered to remove a white insoluble solid identified as $[(C_6H_5)_3P]_2Pt(CN)_2$ (VII) by comparison with an authentic sample (yield 15%). Ethanol was added to the filtrate to yield yellow crystals identified as $[(C_6H_5)_3P]_2Pt(CN)$ $[OC$-$(CN)=C(CN)_2]$ (V) by comparison with an authentic sample (yield 65%).

(b) When isopropanol was replaced in reaction 1a with methanol or ethanol and the reaction stirred for several hours, a white precipitate was formed.

which was collected, dried in air and identified as $[(C_6H_5)_3P]_2Pt(CN)_2$, VII, by comparison with an authentic sample. Yield 80%.

(c) When isopropanol was replaced in experiment 1a with methylene chloride, CO_2 was rapidly evolved and the initial yellow solution turned dark brown. After stirring $\frac{1}{2}$ h the solution was applied to a silica gel column (Bio-Rad 100—200 mesh) and eluted with 98% methylene chloride/2% acetonitrile. Two fractions were collected, but repeated attempts to precipitate pure materials from these fractions failed.

Comparison of the IR spectra with those of authentic materials gave evidence for the presence of $[(C_6H_5)_3P]_2Pt[TCNEO]$ (VI) in one fraction and $[(C_6H_5)_3P]_2Pt[OC(CN){=}C(CN)_2]$ (V) in the second fraction.

2. Tetracyanoethylene (TCNE) with $[(C_6H_5)_3As]_2PtCO_3$

(a) $[(C_6H_5)_3As]_2PtCO_3$ (0.38 g, 0.4 mmol) was suspended in 5 ml isopropanol. TCNE (50 mg, 0.4 mmol) dissolved in 5 ml isopropanol were added and the reaction stirred overnight at room temperature. Gas analysis confirmed the evolution of CO_2. 10 ml diethyl ether were added whereupon a yellow solid precipitated, which was filtered and dried under vacuum. M.p. 185—190° C dec.; IR (Nujol); ν(CN), 2200, 2185, 2140 cm^{-1}; ν(C=C), 1585 cm^{-1}. Yield: $[(C_6H_5)_3As]_2Pt(CN)\ [OC(CN){=}C(CN)_2]$ (VIII) 75%.

(b) When the reaction in 2a was carried out in ethanol or methanol at 40° C; a white precipitate formed in 2 h. This product was filtered, dried in air and identified as $[(C_6H_5)_3As]_2Pt(CN)_2$ (IX), by comparison with an authentic sample. Yield 90%.

3. 1,1-Dicyano-2-methylpropene (DCMP) with $[(C_6H_5)(CH_3)_3N]^+\ Cl^-$

$[(C_6H_5)_3P]_2PtCO_3$ (0.36 g, 0.5 mmol) was dissolved in 5 ml methylene chloride. 1,1-Dicyano-2-methylpropene (93 mg, 0.9 mmol) was added and the reaction stirred at 35° C overnight. Upon addition of a large excess of diethyl ether approx. 45% of the carbonato complex precipitated unreacted. After separation, the filtrate was concentrated to a yellow-orange residue and treated with n-hexane, whereupon a yellow solid formed. This crude product was recrystallized from chloroform/hexane to give a white crystalline solid which was identified as $(CH_3)_2C{=}C(CN)C(NH_2){=}CHC(CH_3){=}C(CN)_2$ by comparison with an authentic sample. Yield 63%.

B. Displacement reactions of $[(C_6H_5)_3P]_2Pt(CN)\ [OC(CN){=}C(CN)_2]$ (V) and $[(C_6H_5)_3As]_2Pt(CN)\ [OC(CN){=}C(CN)_2]$ with KCN and $[(C_6H_5)(CH_3)_3N]^+\ Cl^-$

Following a reported procedure [3] the products identified as V and VIII (100 mg) were dissolved in 5 ml methylene chloride. A stoichiometric amount of KCN dissolved in 2 ml water/2 ml ethanol was added and the reaction stirred for 30 min. The solution was evaporated to remove methylene chloride and filtered leaving a white solid, which was identified as the dicyano complex VII or IX, by comparison with authentic samples. The filtrate was evaporated to dryness and extracted with diethyl ether leaving a solid identified as $[(C_6H_5)(CH_3)_3N]^+\ [OC(CN){=}C(CN)_2]^-$ (X) by comparison with an authentic sample.

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