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METAL COMPLEXES OF CYANOCARBONS
VIII*. DICYANOACETYLENE COMPLEXES OF PLATINUM

G. L. McCLURE AND W. H. BADDLEY
Coates Chemical Laboratory, The Louisiana State University, Baton Rouge, Louisiana 70803 (U.S.A.)
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SUMMARY

Reactions of the cyanocarbon, dicyanoacetylene, with some Pt^0 and Pt^{II} substrates have been studied under preparative conditions, and several new, very stable complexes have been isolated and characterized. The compound $Pt(Ph_3P)_2(C_4N_2)$ is obtained from the reaction of C_4N_2 with either $Pt(Ph_3P)_4$, $Pt(Ph_3P)_2(PhC{\equiv}CH)$, or $PtHCl(Ph_3P)_2$, and the tertiary arsine analog $Pt(Ph_3As)_2(C_4N_2)$ is obtained from $Pt(Ph_3As)_4$. Reaction of the alkyl phosphine complex $PtHCl(Et_3P)_2$ with C_4N_2 in tetrahydrofuran gives $Pt(Et_3P)_2(C_4N_2)$, but when the reaction is carried out in benzene a dicyanovinyl complex, $PtCl[C(CN){=}CHCN](Et_3P)_2$, is obtained. Also described are reactions of $Pt(Ph_3P)_2(C_4N_2)$ with several reagents, including Br_2 and HX (X=Cl, Br) which give $Pt(Ph_3P)_2(C_4N_2Br_2)$ and $PtX[C(CN){=}CHCN](Ph_3P)_2$ respectively. Analogous chemical characteristics of $Pt(PPh_3)_2(C_4N_2)$ and cyclopropenes are discussed.

INTRODUCTION

Previous papers in this series describing metal complexes of cyanocarbons dealt with some noble metal derivatives of the olefinic cyanocarbon, tetracyanoethylene[2-6]. The exceptional stability of tetracyanoethylene complexes of platinum, rhodium, and iridium relative to analogous ethylene complexes prompted us to attempt the preparation of some dicyanoacetylene complexes of transitional metals since such compounds had not been previously prepared**. This paper describes the preparation and characterization of some dicyanoacetylene complexes of platinum, and some of the reactions which these complexes undergo with common reagents.

EXPERIMENTAL

I. Materials

Dicyanoacetylene was prepared by a slight modification of the method of Moureu and Bongrand[10]. Literature methods were used to prepare the following

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* For Part VII, see ref. 1.

** During the course of the work described herein, several complexes of dicyanoacetylene were reported[7-9].

platinum complexes: $Pt(Ph_3P)_4$[11], $Pt(Ph_3As)_4$[11], $Pt(Ph_3P)_2(PhC{\equiv}CH)$[12], *trans*-$PtHCl(Ph_3P)_2$[13,14], and *trans*-$PtHCl(Et_3P)_2$[15]. Thiophene-free benzene was dried over sodium wire. Tetrahydrofuran was refluxed over sodium, treated with $LiAlH_4$ and distilled, and stored over molecular sieves. All other chemicals needed were reagent-grade materials, and were used without further purification.

Due to the sensitivity of C_4N_2 to oxygen, all reactions were carried out in a nitrogen atmosphere, but work-up of reaction mixtures was usually done in the open atmosphere.

II. Preparation and characterization of some dicyanoacetylene complexes of platinum

A. Bis(triphenylphosphine)(dicyanoacetylene)platinum, $Pt(Ph_3P)_2(C_4N_2)$. This compound was prepared by three different methods.

To a benzene solution (100 ml) of $Pt(Ph_3P)_2(PhC{\equiv}CH)$ (4.04 g, 5 mmoles) at room temperature was added 0.8 ml (10 mmoles) of C_4N_2, and immediately the color of the solution changed from pale yellow to dark red. After the solution had stood for 24 h, solvent was removed with a rotary evaporator until a dark paste was obtained. The paste was treated with 100 ml of hot methanol, and a dark brown solid was collected on a filter. Several recrystallizations of the solid from benzene/methanol were carried out, and a final recrystallization from benzene/hexane gave large orange needles of $Pt(Ph_3P)_2(C_4N_2)$, m.p. 233–235°(dec.). (Found: C, 60.60; H, 4.00; N, 3.49; P, 7.97; mol. wt. in $CHCl_3$, 780. $C_{40}H_{30}N_2P_2Pt$ calcd.: C, 60.38; H, 3.80; N, 3.52; P, 7.70%; mol. wt., 795.) The infrared spectrum* in a Nujol mull includes bands at 1683 (m, br), 2177 (m), 2185 (s), and 2196 (m).

Another method of preparation of $Pt(Ph_3P)_2(C_4N_2)$ utilized $Pt(Ph_3P)_4$ as a starting material. Addition of excess C_4N_2 (0.3 ml, 4.25 mmoles) to 30 ml of 1/2 benzene/tetrahydrofuran containing $Pt(Ph_3P)_4$ (0.8 g, 0.67 mmoles) at room temperature resulted in a dark red solution from which solvent was removed under reduced pressure to give a red tar. The red tar was washed well with methanol until the washings were pale red in color. The residue was collected on a filter and washed further with methanol to give a dark tan solid, which was recrystallized several times from benzene/methanol to give orange needles of $Pt(Ph_3P)_2(C_4N_2)$. The infrared spectrum was identical to that described above. (Found: C, 60.64; H, 3.97%.)

A third procedure for preparing $Pt(Ph_3P)_2(C_4N_2)$ was as follows: The complex *trans*-$PtHCl(Ph_3P)_2$ (0.5 g, 0.67 mmoles) was dissolved in 100 ml of tetrahydrofuran, the solution was cooled to −78° in a dry ice/acetone mixture, and C_4N_2 (0.12 ml, 1.5 mmoles) was added to the cold solution. The resulting dark purple solution was allowed to warm to room temperature, the volume was reduced with a rotary evaporator, and ethanol (30 ml) was added. Further concentration of the solution caused tan crystals to form, and these were collected on a filter to give 0.38 g (70%) of $Pt(Ph_3P)_2(C_4N_2)$. (Found: C, 60.15; H, 4.32%.)

When *trans*-$PtHCl(Ph_3P)_2$ and C_4N_2 were allowed to react in THF at room temperature, the complex $Pt(Ph_3P)_2(C_4N_2)$ was also obtained. However, when the reaction was carried out in benzene or toluene at room temperature, the only platinum-containing compound obtained was the starting material.

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* Abbreviations used in this paper to describe infrared band intensities and widths are: s, strong; vs, very strong; m, medium; w, weak; sp, sharp; and br, broad. All band positions are given in cm^{-1}.

Reactions of *trans*-PtHX$(Ph_3P)_2$ (X=I, CN) with C_4N_2 in either THF or benzene resulted in recovery of PtHX$(Ph_3P)_2$; highly colored solids which contained cyanide groups but no platinum, and which were soluble in ethanol, were also obtained but were not further investigated.

B. Bis(triphenylarsine)(dicyanoacetylene)platinum, $Pt(Ph_3As)_2(C_4N_2)$. This compound was prepared by allowing $Pt(Ph_3As)_4$ (2.84 g, 2 mmoles) in 40 ml of benzene at room temperature to react with C_4N_2 (0.32 ml, 4 mmoles). Treatment of the resulting dark solution with a small amount of charcoal, followed by filtration, gave a yellow-orange solution from which was obtained by addition of an equal volume of ethanol dark orange needles of $Pt(Ph_3As)$ (C_4N_2), m.p. 177–179° (dec.). Recrystallization from benzene/hexane gave an analytically pure sample. (Found: C, 54.39; H, 3.70; As, 16.62; N, 3.09; mol.wt. in CH_2Cl_2, 885. $C_{40}H_{30}As_2N_2Pt$ calcd.: C, 54.35; H, 3.42; As, 16.96; N, 3.17%; mol.wt., 884.) The infrared spectrum in Nujol mull includes bands at 1695 (m, br), 2172 (w), 2194 (s, sp), and 2201 (w).

C. Bis(triethylphosphine)(dicyanoacetylene)platinum, $Pt(Et_3P)_2(C_4N_2)$. This compound was obtained when *trans*-PtHCl$(Et_3P)_2$ (0.69 g, 1.5 mmoles) in 30 ml of tetrahydrofuran at −78° was allowed to react with C_4N_2 (0.24 ml, 3 mmoles). After the mixture had stood for 25 h at −78°, the reaction flask was warmed to room temperature, the solvent was removed with a rotary evaporator, and the dark residue was dissolved in 50 ml of methanol. A small amount of activated charcoal was added to the dark solution, and when it was filtered an orange solution resulted. Water (20 ml) was added, and the solution was concentrated until a cloudiness appeared, whereupon orange crystals precipitated after the mixture was refrigerated for several days. Collection of these crystals on a filter gave 0.44 g (55%) of $Pt(Et_3P)_2(C_4N_2)$, m.p. 105–107°. (Found: C, 37.51; H, 6.09; N, 5.33. $C_{16}H_{30}N_2P_2Pt$ calcd.: C, 37.87; H, 5.97; N, 5.52%.) The Nujol mull spectrum includes bands at 1656 (m, br), 2167 (w), 2176 (s, sp), and 2191 (w).

D. trans-Chloro(dicyanovinyl)bis(triethylphosphine)platinum(II), $PtCl[C(CN){=}CHCN](Et_3P)$. This compound was synthesized from the reaction of *trans*-PtHCl$(Et_3P)_2$ (0.94 g, 2 mmoles) in benzene (20 ml) at room temperature with C_4N_2 (0.24 ml, 3 mmoles). The reaction mixture was allowed to stand for 20 h, then solvent was removed under reduced pressure, and the residue was dissolved in 30 ml methanol. Treatment of the dark solution with activated charcoal gave a pale yellow solution after filtration, to which water was added until a cloudiness appeared. After standing several days in a refrigerator, the solution deposited yellow needles of $PtCl[C(CN){=}CHCN](Et_3P)_2$, m.p. 119–121°. (Found: C, 35.28; H, 5.96; Cl, 6.49; N, 5.33; P, 11.44; mol.wt. in benzene, 540. $C_{16}H_{31}ClN_2P_2Pt$ calcd.: C, 35.33; H, 5.73; Cl, 6.53; N, 5.16; P, 11.38; mol.wt., 544.) A Nujol mull spectrum includes bands at 1533 (m), 2188 (s), and 2205 (m). The ^1H NMR spectrum in $CDCl_3$ shows the methyl protons of the phosphine groups at τ 8.8 in a five line pattern with relative intensities 1/4/6/4/1. The vinyl proton is centered at τ 3.2 relative to TMS with the integrated ratio of signal intensities being 30/1 relative to the ethyl protons. The vinyl resonance consists of a triplet due to coupling with ^{31}P and is flanked by satellites due to coupling with 33% abundance of ^{195}Pt [J(P–H) 2 Hz; J(Pt–H) 148 Hz].

III. Some reactions of $Pt(R_3P)_2(RC{\equiv}CR)$

A. Displacement reactions. To a benzene solution (70 ml) of $Pt(Ph_3P)_2(C_4N_2)$

(0.56 g, 0.7 mmoles) at room temperature was added a ten-fold excess of tetracyanoethylene (0.9 g, 7 mmoles). The progress of the reaction was monitored by measuring infrared spectra of withdrawn samples and observing the decrease in intensity of the 1683 cm^{-1} band [$\nu(C{\equiv}C)$] as a function of time. After 2 h the intensity had decreased slightly, but after 6 h the intensity had decreased appreciably, and after 24 h the band had disappeared. The reaction mixture was taken to dryness and the residue was recrystallized from benzene/hexane. The analysis, infrared spectrum, and melting point indicated that $Pt(Ph_3P)_2(TCNE)$ was the product, and it was obtained quantitatively.

Attempts were made to displace C_4N_2 from $Pt(Ph_3P)_2(C_4N_2)$ by adding large excesses of fumaronitrile, hexafluorobutyne, and CS_2 at room temperature, but in each case $Pt(Ph_3P)_2(C_4N_2)$ was recovered almost quantitatively.

B. Addition reaction with bromine. Pyridinium bromide perbromide ($C_5H_5NH^+Br_3^-$) (0.25 g, 0.8 mmoles) was added to the complex (0.5 g, 0.6 mmoles) in 50 ml of tetrahydrofuran at room temperature and the mixture was stirred for 2 days. Treatment of the resulting dark solution with activated charcoal followed by filtration gave a pale yellow solution to which ethanol was added. The volume was reduced until white crystals separated. These were collected (0.52 g, 77% yield) and characterized as bis(triphenylphosphine)(dibromodicyanoethylene)platinum, $Pt(Ph_3P)_2(C_4N_2Br_2)$, m.p. >250° (dec.). (Found: C, 50.30; H, 3.45; Br, 17.37; N, 2.40; P, 5.99; mol.wt. in $CHCl_3$, 975. $C_{40}H_{30}Br_2N_2P_2Pt$ calcd.: C, 50.28; H, 3.17; Br, 16.73; N, 2.93; P, 6.48%; mol.wt., 956.) The Nujol mull spectrum of the product showed no absorptions in the 1500–2000 cm^{-1} region, but included bands at 2195 m and 2207 sh due to $\nu(C{\equiv}N)$.

Another experiment was carried out using liquid bromine as the brominating agent. Bromine (0.5 ml in 10 ml CH_2Cl_2) was added to 0.4 g complex in 10 ml CH_2Cl_2 and after several minutes the mixture was taken to dryness. Recrystallization of the residue from CH_2Cl_2/ethanol gave a solid which is probably $PtBr_2(Ph_3P)_2$. (Found: C, 49.20; H, 3.44. $C_{36}H_{30}Br_2P_2Pt$ calcd.: C, 49.03; H, 3.42%.) The infrared spectrum shows no absorptions due to cyanide in the 2000–2300 cm^{-1} region.

C. Reactions with hydrogen halides. (1). When HCl gas was bubbled through a benzene solution (200 ml) of $Pt(Ph_3P)_2(C_4N_2)$ (0.8 g, 1 mmole) for several minutes at room temperature, the initial pale orange color faded and a white solid precipitated. The identical white solid was also obtained when a tetrahydrofuran solution of the complex was treated with concentrated hydrochloric acid. This white solid was found to be very insoluble in water, $CHCl_3$, CH_2Cl_2, CH_3CN, benzene, THF, and other common solvents with the exception of pyridine, DMF, and DMSO (*vide infra*). The analytical data fit a formulation corresponding to a 1/1 adduct of $Pt(Ph_3P)_2(C_4N_2)$ and HCl. (Found: C, 57.74; H, 4.02; Cl, 4.13; N, 3.28; P, 6.91. $C_{40}H_{31}ClN_2P_2Pt$ calcd.: C, 57.80; H, 3.76; Cl, 4.27; N, 3.37; P, 7.45%.) The amorphous solid melts with decomposition above 250°. A Nujol mull spectrum includes bands at 1553 (m), 2187 (vs), and 2215 (s). Reaction of $Pt(Ph_3P)_2(C_4N_2)$ with DCl gas in tetrahydrofuran gave a white solid whose infrared spectrum was identical with that above.

A small amount of the insoluble 1/1 adduct (0.72 g) was suspended in 20 ml of pyridine and warmed on a steam bath for 15 min during which time the solid dissolved to give a pale yellow solution. Ethanol (30 ml) was added, and after standing several days in a refrigerator the solution deposited pale yellow crystals, which were collected, washed with ethanol, and dried overnight *in vacuo* to give *trans*-chloro(dicyanovinyl)-bis(triphenylphosphine)platinum(II), $PtCl[C(CN)=CHCN](Ph_3P)_2$, m.p. >250° (dec.). (Found: C, 57.78; H, 4.05; Cl, 4.04; N, 3.79; P, 7.21; mol.wt. in $CHCl_3$, 870. $C_{40}H_{31}ClN_2P_2Pt$ calcd.: C, 57.80; H, 3.76; Cl, 4.27; N, 3.37; P, 7.45%; mol.wt., 832.) The Nujol mull spectrum includes bands at 1544 m, 2196 w, and 2213 s,sp. The ^1H NMR spectrum in $CDCl_3$ shows a triplet at τ 4.9 flanked by satellite triplets arising from ^{195}Pt coupling as well as the intense signal of the aromatic protons; the ratio of the integrated intensities of the aromatic and vinyl protons is 30/1. Coupling constants are: J(Pt–H) 91 Hz; J(P–H) 1.6 Hz.

When the insoluble 1/1 adduct was warmed in dimethylformamide, *trans*-$PtCl[C(CN)=CHCN](Ph_3P)_2$ was also obtained. The 1/1 adduct also dissolved in DMSO, but the solid which was isolated from this solution did not contain cyano groups and was not characterized. Triethylamine and piperidine did not dissolve the 1/1 adduct.

(2) A hydrobromic acid solution (1 ml of concentrated HBr and 10 ml of THF) was added to $Pt(Ph_3P)_2(C_4N_2)$ (0.4 g, 0.5 mmoles) in 25 ml of THF at room temperature, and after standing overnight the yellow solution deposited white microcrystals. These were collected, washed with CH_3OH and recrystallized from CH_2Cl_2/CH_3OH to yield 0.2 g of bromo(dicyanovinyl)bis(triphenylphosphine)platinum(II), $PtBr[C(CN)=CHCN](Ph_3P)_2$, m.p. >250° (dec.). (Found: C, 54.29; H, 3.85. $C_{40}H_{31}BrN_2P_2Pt$ calcd.: C, 54.80; H, 3.56%.) A mull spectrum includes bands at 1549 m [ν(C=C)], 2189 m [ν(CN)], and 2219 s [ν(CN)].

(3). The triethylphosphine complex, $Pt(Et_3P)_2(C_4N_2)$ (0.25 g, 0.5 mmoles) was dissolved in 5 ml of THF and a hydrochloric acid solution (1 ml concentrated acid in 10 ml THF) was added at room temperature. Over a several day period the solution lightened in color and was then taken to dryness to give off-white crystals whose infrared spectrum was identical to that of $PtCl[C(CN)=CHCN](Et_3P)_2$ obtained from the reaction of *trans*-$PtHCl(Et_3P)_2$ and C_4N_2 as described in II(D) above.

(4). The hexafluorobutyne complex $Pt(Ph_3P)_2(CF_3C\equiv CCF_3)$ (0.1 g, 0.11 mmoles) was dissolved in 10 ml of THF, a hydrochloric acid solution (5 ml of concentrated acid and 5 ml of THF) was added at room temperature, and after 20 h the white crystals which had formed were collected, washed with CH_3OH, and dried overnight *in vacuo*. The white crystals, which are soluble in CH_2Cl_2 and $CHCl_3$, are formulated as chloro[1,2-bis(trifluoromethyl)vinyl]bis(triphenylphosphine)platinum(II), $PtCl[C(CF_3)=CH(CF_3)](Ph_3P)_2$, m.p. 263–266° (dec.). (Found: C, 52.42; H, 3.73; Cl, 4.01. $C_{40}H_{37}ClF_6P_2Pt$ calcd.: C, 52.33; H, 3.40; Cl, 3.86%.) The mull spectrum shows ν(C=C) at 1627 as a medium intensity band.

D. Miscellaneous reactions. Acetyl chloride (2 ml, 28 mmoles) was added to 50 ml of THF containing 0.8 g (0.5 mmoles) of $Pt(Ph_3P)_2(C_4N_2)$. After two days the white solid which had formed was collected and its insolubility, analysis and infrared spectrum indicate that it is the same 1/1 adduct of $Pt(Ph_3P)_2(C_4N_2)$ and HCl as was obtained above in III(C). This same compound was also obtained when benzyl chloride and $Pt(Ph_3P)_2(C_4N_2)$ were allowed to react in benzene.

Reactions of $Pt(Ph_3P)_2(C_4N_2)$ with acetone, phenyldiazomethane, formaldehyde, acetaldehyde, benzonitrile oxide, and *N*-bromosuccinimide were attempted. With acetone no reaction occurred after 4 days of refluxing, and with the other reagents reactions occurred but well characterized complexes have not been isolated.

IV. Analyses and instrumentation

Analyses for carbon, hydrogen, and nitrogen were carried out by Mr. R. Seab of the Department of Chemistry, Louisiana State University. Other analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

Infrared spectra in the NaCl region were measured on a Beckman IR-7 spectrophotometer in Nujol or hexachlorobutadiene mulls, KBr pellets, and dichloromethane solutions.

Molecular weights were measured using Mechrolab osmometer, Model 302A, with a 37° probe. Chloroform or benzene was used as a solvent and concentrations of the solutions were in the $5–15 \times 10^{-3}$ M range.

Nuclear magnetic resonance experiments were carried out with a Varian A-60 instrument using $CDCl_3$ as solvent and tetramethylsilane as an internal standard.

RESULTS

New complexes of platinum derived from the reactions of various Pt^0 and Pt^{II} substrates with dicyanoacetylene, and the reactions of one of these complexes, $Pt(PPh_3)_2(C_4N_2)$, with several reagents, are shown in Fig. 1.

Dicyanoacetylene is most reactive, and combines immediately at room temperature in benzene solution with either $Pt(PPh_3)_2(PhC{\equiv}CH)$ or $Pt(PPh_3)_4$ to give, after work-up, pale orange crystals of $Pt(PPh_3)_2(C_4N_2)$ (Ia), and the same compound

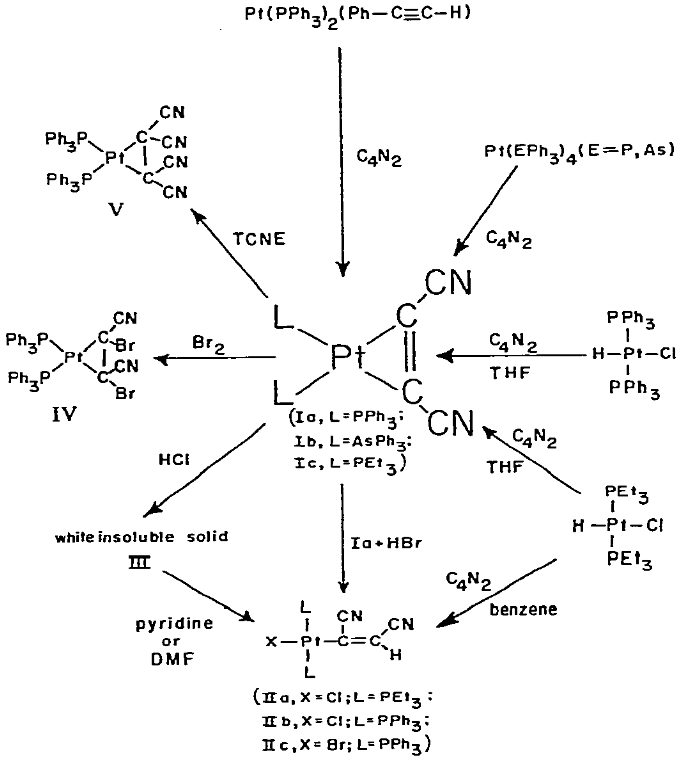
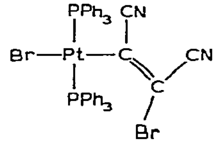


Fig. 1. Preparations and reactions of some dicyanoacetylene (C_4N_2) complexes of platinum.

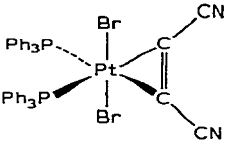
is also obtained from the reaction of *trans*-$PtHCl(PPh_3)_2$ with C_4N_2 in tetrahydrofuran. The compound $Pt(PPh_3)_2(C_4N_2)$ is the most stable platinum–acetylene complex yet prepared if thermal decomposition temperatures are a reliable indicator of stability. However, dicyanoacetylene itself is very unstable thermodynamically; the vapor takes fire spontaneously[10] in air at 110°, and the combustion of C_4N_2 with oxygen or ozone produces temperatures in the 5000–6000°K range[16]. Although $Pt(PPh_3)_2(C_4N_2)$ is stable both in solution and solid state, and is formed in good yields by the several preparative routes, ready isolation of the compound is hindered by side reactions which form dark colored, tarry materials; these side reactions presumably involve polymerization[17] of dicyanoacetylene and/or reaction with triphenylphosphine to give a 1,6-diphosphorane[18].

In the reactions of dicyanoacetylene with hydridoplatinum(II) complexes, the nature of the solvent is important in determining the course of the reaction. While (Ia) is the product of the reaction of *trans*-$PtHCl(PPh_3)_2$ and C_4N_2 in tetrahydrofuran, no product could be isolated from several attempts of the reaction in benzene. Also, the triethylphosphine complex *trans*-$PtHCl(PEt_3)_2$ and C_4N_2 gave (Ic) in THF, but in benzene a different product, (IIa), *trans*-chloro(dicyanovinyl)bis(triethylphosphine)platinum(II) is obtained. The *trans* arrangement of the phosphine groups in (IIc) is evident from the ^1H NMR spectrum where the typical[19] 1/4/6/4/1 pattern of the methyl protons is observed. For compound (IIa) of Fig. 1, the stereochemistry around the carbon–carbon double bond is arbitrarily drawn. The NMR data for the vinyl proton [τ 3.2(t); J(P–H) 2 Hz; J(Pt–H) 148 Hz] are consistent with the formation of only one isomer, but do not establish whether the cyano groups are *cis* or *trans* to one another.

Reaction of bis(triphenylphosphine)(dicyanoacetylene)platinum with several reagents have been studied. The C_4N_2 moiety is not displaced by fumaronitrile, hexafluorobutyne, or CS_2 when benzene solutions of the complex are treated at room temperature with large excesses of the reagents. However, tetracyanoethylene does displace dicyanoacetylene from (Ia) over a several hour period to give (V). The coordinated C_4N_2 in (Ia) undergoes an addition reaction as well as a displacement reaction. Treatment with the mild brominating agent[20] pyridinium bromide perbromide, $C_5H_5NHBr_3$, gives white crystals of a compound believed to be the olefin complex (IV) on the basis of its elemental analysis and infrared spectrum. The absence of absorption bands in the 1500–2000 cm^{-1} region rules out structures such as (VI) and (VII). If excess liquid bromine is used as the brominating agent the C_4N_2 moiety is lost and $PtBr_2(PPh_3)_2$ is obtained.



(VI)

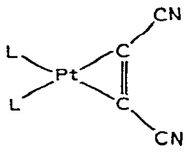


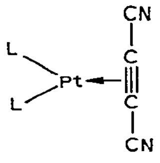
(VII)

Reaction of (Ia) with HBr gives the dicyanovinyl complex (IIc). This product is soluble in CH_2Cl_2, $CHCl_3$, THF, and the infrared spectrum shows a band at ca. 1550 cm^{-1} as expected for a vinyl complex. When HCl is allowed to react with (Ia), however, a white solid is obtained which is quite insoluble in the above mentioned solvents as well as in water, benzene, acetonitrile, and other common solvents. Aside from this highly insoluble nature which may be indicative of a polymeric structure, the compound appears to be analogous to the vinyl complex (IIc) in stoichiometry. Also, there is an infrared band at 1553 cm^{-1}. Compound (III) does dissolve in pyridine and DMF, and from these solutions pale yellow crystals of the monomeric vinyl complex (IIb) may be isolated. Reaction of the hexafluorobutyne complex $Pt(PPh_3)_2(CF_3C{\equiv}CCF_3)$ with HCl gave the monomeric vinyl complex $PtCl[C(CF_3){=}CH(CF_3)](PPh_3)_2$, but well characterized compounds could not be isolated from the reactions of HCl with $Pt(PPh_3)_2(PhC{\equiv}CH)$ or $Pt(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)$.

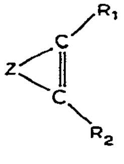
DISCUSSION

Complexes of the type $PtL_2(R_1C{\equiv}CR_2)$ have been known since 1957[21], and there has recently been a resurgence of interest in the structure and bonding of these and related complexes[22-28]. Structural studies of one of the compounds reported herein, $Pt(PPh_3)_2(NCC{\equiv}CCN)$, are underway and preliminary results[29] show the molecule to be almost planar with the $C{\equiv}C$ bond lengthened to ca. 1.40 Å from the 1.19 Å distance in free dicyanoacetylene[30]. In the infrared spectrum the decrease in $\nu(C{\equiv}C)$ of ca. 436 cm^{-1} for the complex relative to uncoordinated C_4N_2 is consistent with the substantial increase of the bond length. While the bonding in $Pt(PPh_3)_2(NCC{\equiv}CCN)$ is most realistically viewed in terms of molecular orbitals, as has been discussed for the related tetracyanoethylene complexes[31-33], valence bond formulations as (VIIIa) and (VIIIb) are useful for pictorial representations. We prefer (VIIIa) as it more nearly approximates to the structural and infrared data, and particularly since there are certain analogies in reactivity between these complexes and cyclopropenes (*vide infra*).

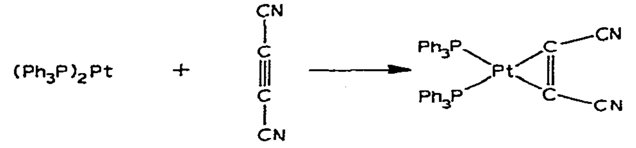

(VIIIa)

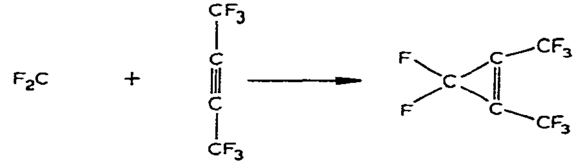

(VIIIb)

Compounds of type (IX) are well known in organic chemistry, and these are characterized structurally by a rigid three-membered ring. Included in this group are cyclopropenes ($Z{=}CH_2$), 2-azirines ($Z{=}NH$), oxirenes ($Z{=}O$), thiirenes ($Z{=}S$) and others. Formally, compounds of the type $PtL_2(R_1C{\equiv}CR_2)$, which by analogy may be called "platinirenes" (IX, $Z{=}PtL_2$) are also members of this class, and it is inter-

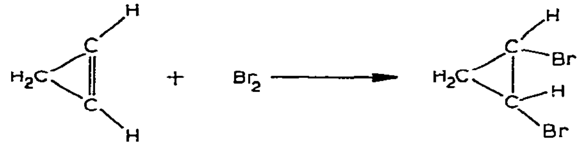

(IX)

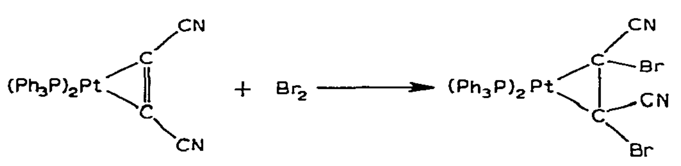
esting to inquire as to whether the chemical characteristics of $PtL_2(R_1C{\equiv}CR_2)$ compounds are consistent with this formal classification. On the basis of mechanistic studies[34-36] which showed that displacement reactions of $Pt(PPh_3)_2$(olefin) and $Pt(PPh_3)_2$(acetylene) proceeded via formation of the coordinatively unsaturated intermediate $Pt(PPh_3)_2$, the synthesis of $Pt(PPh_3)_2(NCC{\equiv}CCN)$ from reaction of dicyanoacetylene with either $Pt(PPh_3)_2(PhC{\equiv}CH)$ or $Pt(PPh_3)_4$ most likely involves generation of $Pt(PPh_3)_2$ as an intermediate which then adds via cycloaddition to C_4N_2. Thus this synthesis (eqn. 1) is quite analogous to a well known synthesis of cyclopropenes from carbenes and acetylenes[37], *cf.*, the preparation of perfluoro-1,2-dimethylcyclopropene (eqn. 2).


(1)


(2)

Important reactions of cyclopropenes are those involving (1) addition to the double bond with preservation of the three-membered ring and (2) reactions leading to ring opening or ring enlargement. Included in the former category is halogenation as exemplified by bromination[38] of cyclopropene to give the 1,2-dibromo compound (eqn. 3). This reaction is to be compared with the bromination of $Pt(PPh_3)_2(NCC{\equiv}CCN)$ reported herein (eqn. 4). Reactions of $Pt(PPh_3)_2(NCC{\equiv}CCN)$ with the hydrogen halides HCl and HBr leads to opening of the three-membered ring with formation of vinyl derivatives* (eqn. 5), and this behavior of course is very similar to the reactions of cyclopropenes with strong acids (eqn. 6). Thus, when 1,3,3-trimethylcyclopropene


(3)


(4)

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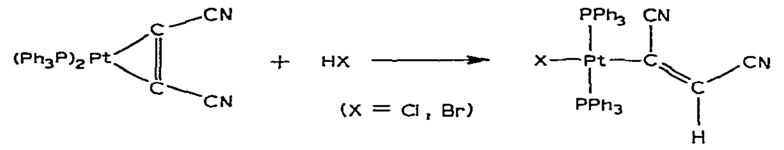
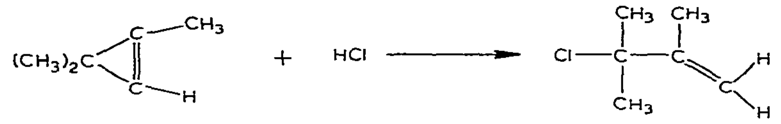
* During the course of this work the reaction of $Pt(PPh_3)_2(CF_3C{\equiv}CCF_3)$ with trifluoroacetic acid to give the vinyl complex $Pt(OCOCF_3)[C(CF_3){=}CHCF_3](PPh_3)_2$ was reported[39].


(5)


(6)

and anhydrous HCl react at −50°, two products are obtained[37], and the less predominant one has a structure analogous to the product of the reaction of $Pt(PPh_3)_2$-(C_4N_2) and HX. The mechanism of the reaction corresponding to eqn. (5) can only be conjectured, but it is an interesting question as to whether a platinum–hydrogen bond is formed by oxidative addition or whether HX adds directly to the coordinated C_4N_2 moiety to give a "platinirane" which could subsequently rearrange to a vinyl complex. Maitlis *et al.*[23] have predicted that metal–acetylene complexes in which the acetylene bears electron-withdrawing substituents should be susceptible to electrophilic attack at the carbon atoms and complexes of the type $Pt(PPh_3)_2$(olefin) are known to rearrange, both in the solid state and in polar solvents, to vinyl complexes[40–42].

While the above-mentioned comparisons of reactivity of cyclopropenes and $Pt(PPh_3)_2(R_1C{\equiv}CR_2)$ complexes are fragmentary, they do suggest that a three-membered ring conception of the bonding in these complexes may be of more utility than the Dewar–Chatt–Duncanson π-bonding model in discussing reactivity patterns.

Finally, the behavior of dicyanoacetylene toward *trans*-$PtHCl(PEt_3)_2$ in different solvents can be understood in terms of a mechanism previously proposed[43] for the reaction of tetracyanoethylene with the same substrate where the platinirane $Pt(PEt_3)_2TCNE$ is obtained in either benzene, dichloromethane, or tetrahydrofuran.

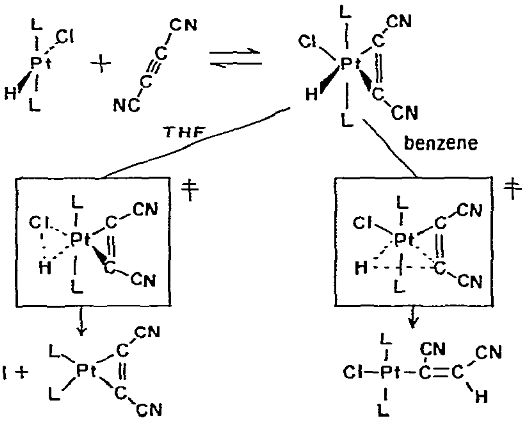


Fig. 2. The effect of solvent on the mechanism and type of product obtained in the reaction of dicyanoacetylene with *trans*-$PtHCl(PEt_3)_2$ ($L = PEt_3$).

In the present case of dicyanoacetylene, a platinirene $Pt(PEt_3)_2(C_4N_2)$ is obtained in THF and a dicyanovinyl complex, $PtCl[C(CN){=}CHCN](PEt_3)_2$, is gotten from reaction in benzene. These results can be explained by assuming that, analogous to the reaction of TCNE with $PtHCl(PEt_3)_2$, a 1/1 adduct is formed initially as an intermediate (Fig. 2) which then decomposes via a three center transition state. Reductive elimination occurs in THF where solvation of HCl assists in its removal. In benzene, where there is less solvent assistance, hydrogen is instead transferred to the C_4N_2 moiety in the usual way for reactions of olefins or acetylenes with hydrido complexes. The contrasting behavior toward $PtHCl(PEt)_2$ in the solvent benzene of dicyanoacetylene (where a dicyanovinyl complex is gotten) and tetracyanoethylene (where a platinirane is obtained) may imply that TCNE is more strongly bonded to platinum than dicyano acetylene. A result of this would be to make the Pt–H and Pt–Cl bonds weaker in the TCNE complex, and, therefore, solvent assistance for reductive elimination of HCl need not be invoked.

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REFERENCES

1 J. S. Ricci, J. A. Ibers, M. Shirley Fraser and W. H. Baddley, *J. Amer. Chem. Soc.*, 92 (1970) 3489.
2 W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, 5 (1966) 33.
3 W. H. Baddley, *J. Amer. Chem. Soc.*, 88 (1966) 4545.
4 W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 3705.
5 C. Panattoni, G. Bombieri, U. Belluco and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 798.
6 P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 5446.
7 M. E. Kimball, J. P. Martella and W. C. Kaska, *Inorg. Chem.*, 6 (1967) 414.
8 R. S. Dickson and D. B. Yawney, *Aust. J. Chem.*, 21 (1968) 1077.
9 M. I. Bruce and M. Z. Iqbal, *J. Organometal. Chem.*, 17 (1969) 469.
10 C. Moureu and J. C. Bongrand, *Ann. Chim. (Paris)*, 14 (1920) 5.
11 L. Malatesta and C. Cariello, *J. Chem. Soc.*, (1958) 2323.
12 J. Chatt, B. L. Shaw and A. A. Williams, *J. Chem. Soc.*, (1962) 3269
13 J. C. Bailar and H. Itatani, *Inorg. Chem.*, 4 (1965) 1618.
14 F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.*, 5 (1966) 1128.
15 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1962) 5075.
16 A. D. Kirshenbaum and A. V. Grosse, *J. Amer. Chem. Soc.*, 78 (1956) 2020.
17 M. Benes, J. Peska and O. Wichterle, *Chem. Ind. (London)*, (1962) 562.
18 M. A. Shaw, J. C. Tebby, R. S. Ward and D. H. Williams, *J. Chem. Soc. C*, (1968) 1609.
19 F. J. Hopton, A. J. Rest, D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, (1966) 1326.
20 L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, N.Y., 1967, p. 967.
21 J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, (1957) 208.
22 J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 89 (1967) 844.
23 E. D. Greaves, C. J. L. Lock and P. M. Maitlis, *Can. J. Chem.*, 46 (1968) 3879.
24 A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, 90 (1968) 5749.
25 J. O. Glanville, J. M. Stewart and S. O. Grim, *J. Organometal. Chem.*, 7 (1967) P9.
26 A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova and Yu. T. Struchkov, *J. Chem. Soc. D*, (1969) 277.
27 R. Mason, *Nature*, 217 (1968) 543.
28 J. H. Nelson, K. S. Wheelock, L. C. Cusachs and H. B. Jonassen, *J. Amer. Chem. Soc.*, 91 (1969) 7005.

29 C. Panattoni and R. Graziani, in M. Cais (Ed.), *Proceedings of the XIth I.C.C.C.*, Elsevier, New York, N. Y. ,1968, p. 310.
30 R. B. Hannan and R. L. Collins, *Acta Crystallogr.*, 6 (1953) 350.
31 W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 3705.
32 C. Panattoni, G. Bombieri, V. Belluco and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 798.
33 J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, (1968) 235.
34 A. D. Allen and C. D. Cook, *Can, J. Chem.*, 41 (1963) 1235.
35 J. P. Birk, J. Halpern and A. L. Pickard, *J. Amer. Chem. Soc.*, 90 (1968) 4491.
36 J. P. Birk, J. Halpern and A. L. Pickard, *Inorg. Chem.*, 7 (1968) 2672.
37 G. L. Closs, in H. Hart and G. J. Karabatsos (Eds.), *Advances in Alicyclic Chemistry*, Vol. I, Academic Press, New York, N.Y., 1966, p. 58.
38 K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, 82 (1960) 6375.
39 D. M. Barlex, R. D. W. Kemmitt and G. W. Littlecott, *J. Chem. Soc. D.*, (1969) 613.
40 M. Green, R. B. L. Osborn, A. J. Rest and F. G. A. Stone, *J. Chem. Soc.*, *A*, (1968) 2525.
41 W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc. A*, (1968) 1278.
42 W. J. Bland, J. Burgess and R. D. W. Kemmitt, *J. Organometal. Chem.*, 14 (1968) 201.
43 P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 5446.