Journal of Organometallic Chemistry, 90 (1975) 235—248

REACTIONS OF ACETYLENES WITH NOBLE-METAL CARBONYL HALIDES

I. THE REACTION OF 3-HEXYNE AND 2-BUTYNE WITH DICHLORODICARBONYLPLATINUM

F. CANZIANI and M.C. MALATESTA

Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei bassi Stati di Ossidazione del C.N.R., Istituto di Chimica Generale ed Inorganica, Università di Milano, Via Venezian, 21, 20133 Milano (Italy)

(Received November 18th, 1974)

Summary

$Pt(CO)_2Cl_2$ reacts in benzene, toluene or tetrahydrofuran with 3-hexyne to give carbonylplatinumbis[di-μ-chloro,chloro(tetraethylcyclobutadiene)-platinum] (I), bis[dichloro(tetraethylcyclopentadienone)platinum] (III), dichloro-(tetraethyl-*p*-benzoquinone)platinum (IV) and dichloro(tetraethylcyclobutadiene)platinum (II). This last compound is also obtained by treating I with 1 to 3 moles of triphenylphosphine or *p*-toluidine.

The structure and reactions of III are discussed; the anion exchange reaction gives the iodo-analogue, while treatment with donor ligands gives adducts of formula $[(C_2H_5)_4C_4CO]PtCl_2L$ (L = triphenylphosphine, *p*-toluidine, benzylamine and pyridine) and $[(C_2H_5)_4C_4CO]PtCl_2L_2$ (L = benzylamine, 3-methylpyridine).

2-Butyne reacts with dichlorodicarbonylplatinum to give the methyl analogous of compounds I-III.

Introduction

Cyclobutadiene complexes of the transition metals have been prepared during the past sixty years by various different routes [1], one of which is the reaction of acetylenes with carbonyl metals, which leads to cyclobutadiene derivatives of these metals as well as to many other types of complex and organic compounds [2]. The reaction of $Pt(CO)_2Cl_2$ with diphenylacetylene [3] to give principally hexaphenylbenzene, tetracyclone and dichlorotetraphenylcyclobutadieneplatinum is a clear example of the complexity. In order to clarify the nature of the complexes obtained as by-products in these reactions and to obtain a more complete picture of the reaction of dichlorodicarbonylplatinum with acetylenes, we have examined the reactions of 3-hexyne, 2-butyne and other disubstituted acetylenes such as dimethyl and diethyl acetylenedicarboxylate, and we describe below the reactions of 3-hexyne and 2-butyne to give tetraalkylcyclobutadiene and tetraalkylcyclopentadienone complexes of platinum(II).

Results and discussion

The reaction with 3-hexyne

Dichlorodicarbonylplatinum has been treated in anhydrous benzene, toluene, diethyl ether or tetrahydrofuran with 3-hexyne in molar ratios ranging from 1/2 to 1/8. Monitoring the reaction by use of the IR spectra has shown that the complete transformation of dichlorodicarbonylplatinum requires at least 2.4 moles of 3-hexyne.

The compounds isolated in experiments carried out under the conditions specified in Table 1, are summarized in Scheme 1. It is noteworthy that at the end of the reaction only small traces of 3-hexyne were present in solution, as shown by GLC. Compounds I and III were the major isolated products and only a small amount of IV (less than 6% of the starting platinum) was obtained, while the yield of II, which was always formed, could not be estimated owing to the difficulty in isolating it pure from the oily organic residue.

SCHEME 1

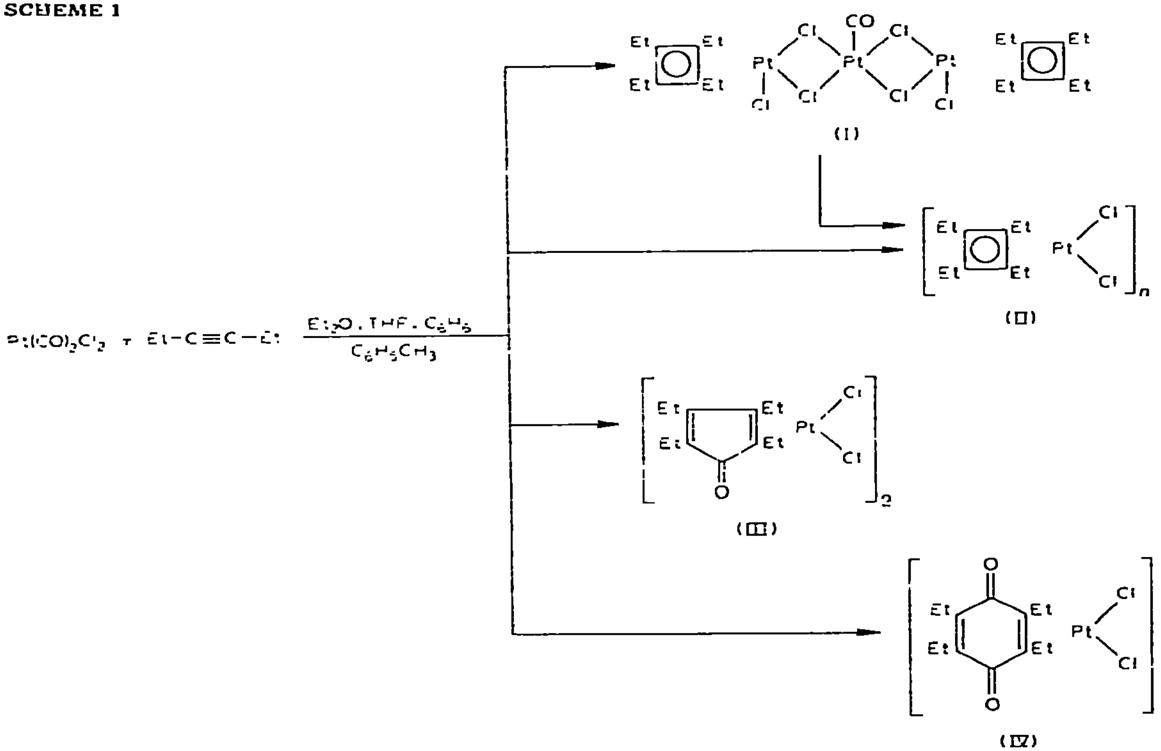


TABLE 1

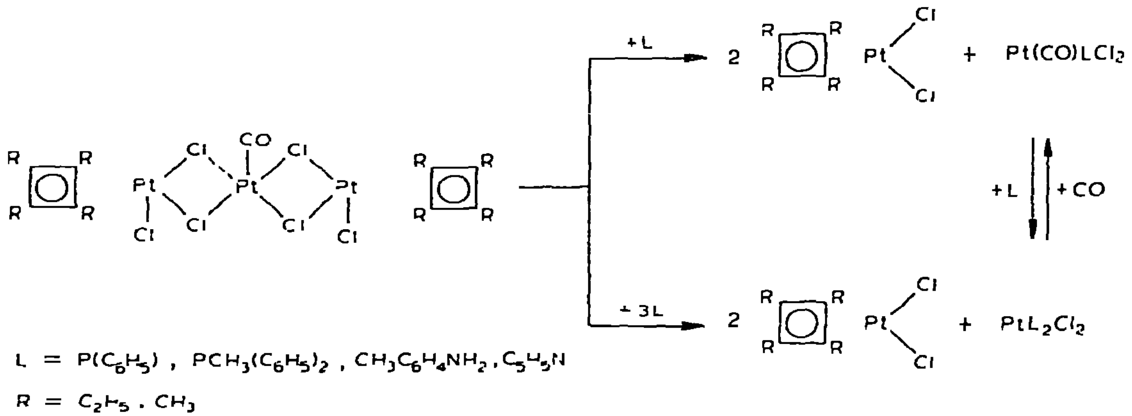
EXPERIMENTAL CONDITIONS AND COMPOUNDS ISOLATED

Solvent	Temperature	Time (h)	Molar ratio $Pt(CO)_2Cl_2$/ 3-hexyne	Products[a]
Benzene	room	24	1/2.4	I(24%) + III(10%) + IV(3%)
Benzene	room	24	1/2.3	I(27%) + III(11%) + IV(2%)
Benzene	room	2	1/5	I(30%) + II + III(15%) + IV(4%)
Benzene	60°	5	1/2.2	I(18%) + III(10%)
Benzene	82°	7	1/2.1	I(15%) + III(9%)
Toluene	room	2	1/5	I(31%) + II + III(18%) + IV(4.5%)
Toluene	room	2	1/8	I(37.5%) + II + III(29.7%) + IV(7%)
Diethyl ether	room	10	1/4.5	I(22%) + III (15%) + IV(1%)
Diethyl ether	37°	24	1/4.6	I(20%) + III(16%) + IV(1%)
THF	50°	18	1/2.5	I(10%) + III(8%)

[a] The yields are referred to pure compounds.

At present it is very difficult to rationalize all the factors which influence the reaction; the data in Table 1 suggest that the major effects are those of temperature and the molar ratio of the reactants. Use of a high temperature and a large excess of 3-hexyne apparently promotes the formation of the cyclobutadiene derivative II, but under these conditions the concurrent formation of organic compounds derived from the oligomerization of 3-hexyne prevents the isolation of any pure organometallic compound in good yield apart from III. The instability of both I and III to carbon monoxide ruled out the possibility of increasing the yield of III and IV by carrying on the reaction between dichlorodicarbonylplatinum and 3-hexyne under CO: with 25% of CO and 75% of N_2 the ratio I/III was effectively unchanged, and no increase in the yield of IV was observed, while with 50% of CO the formation of polynuclear platinum carbonyls drastically lowered the yield of all the organometallic compounds. All attempts to identify the components of the oily residue containing the oligomerization products of 3-hexyne were unsuccessful; column chromatography with alumina, silica-gel and fluorisyl failed, since the formation of platinum metal on the adsorbants prevented any distinction between the initial oligomers and the decomposition products.

The formulation of compound I as carbonylplatinumbis[di-μ-chloro, chloro-(tetraethylcyclobutadiene)platinum], $[Pt_3(CO)Cl_6((C_2H_5)_4C_4)_2]$, was inferred from its elemental analysis, molecular weight, spectroscopic characteristics, and chemical behaviour. The IR spectrum of the solid (nujol mull and KBr disc) showed a strong band in the ν(CO) region, at 2080 cm^{-1} (terminal CO), while the NMR spectrum indicated the presence of equivalent ethyl groups in the molecule, as expected for a cyclobutadiene ring η-bonded to platinum. Moreover the chemical behaviour indicated that the three platinum atoms were in different environments bonded through bridging chlorine atoms. In agreement with this, I reacts under mild conditions with a wide variety of ligands (L) giving IV and species which appear to be derived by extraction of the central carbonyldichloroplatinum group. The course of the reaction depends on the amount of the ligand (L) used as follows:



L = $P(C_6H_5)$, $PCH_3(C_6H_5)_2$, $CH_3C_6H_4NH_2$, C_5H_5N

R = C_2H_5, CH_3

The reaction with triphenylphosphine was carried out in benzene, chloroform, methylene chloride, acetone and tetrahydrofuran: with one mole of ligand the colourless $Pt(CO)[P(C_6H_5)_3]Cl_2$ [4] [ν(CO) 2105 cm^{-1}] was recovered from the solution, while with three moles of phosphine white crystals of $Pt[P(C_6H_5)_3]_2Cl_2$ [5] were formed, the weight of which corresponded satisfactorily to 1/3 of the platinum of the starting compound I. In both cases II was obtained as light-yellow powder, contaminated by secondary or substitution products. Conversely, heating I in benzene in the presence of six moles of triphenylphosphine led to its quantitative transformation into $Pt[P(C_6H_5)_3]_2Cl_2$, while the solution gave on evaporation an oily residue which was shown by GLC to contain high boiling organic substances formed from the acetylene monomer. Similar behaviour was observed on treating I with methyldiphenylphosphine, and with nitrogen donor ligands such as *p*-toluidine, pyridine and 2,2'-bipyridine.

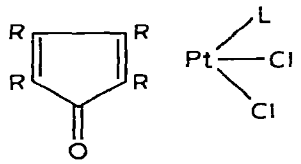
In the preparation of the tetraethylcyclobutadiene complex II, the best results were achieved with *p*-toluidine in benzene, since II could be separated from $Pt(CO)(CH_3C_6H_4NH_2)Cl_2$ [6], [ν(CO) 2110 cm^{-1}], owing to their different solubilities in benzene/hexane. The absence of any significant band in the 2800-1500 cm^{-1} region of the IR spectrum and the presence in the NMR spectrum of signals assigned to a single set of ethyl protons (triplet at τ 8.7, quartet at τ 7.87) strongly support the proposed structure. The molecular weight value found in acetone, in which II is moderately soluble, is very low for a dimer species; this is as expected, since the corresponding tetraphenylcyclobutadiene complexes behave analogously [3].

Compound II is thermally stable and does not react with donor ligands under mild conditions: it is unchanged on standing in solution in the presence of carbon monoxide, unlike I, which was slowly transformed into $Pt(CO)_2Cl_2$ and then into the green-black polynuclear carbonyl $[Pt(CO)_2]_n$, both of which were identified by their IR spectra.

I can be considered as an intermediate in the formation of the more stable II: thus when it is boiled in acetone, it slowly decomposes to give a dark-brown gummy solid consisting of II mixed with an unidentified unstable species containing platinum. When treated with a large excess of 3-hexyne in boiling acetone, I was transformed to II, which was however isolated only in very poor yields owing to the presence of a large amount of unreacted 3-hexyne and of unidentified organic side-products.

The formulation of compound III (isolated as colourless needles) as bis-[dichloro(tetraethylcyclopentadienone)platinum] was inferred from its elemental analysis, molecular weight, spectroscopic properties, and chemical behaviour. The IR spectrum showed two absorption bands at 1680s and 1640m cm^{-1}. The NMR spectrum was not clearly resolved: the methyl protons gave rise to four overlapping triplets, centered at τ 8.58, 8.71, 8.92 and 9.02 [^3J(H—H) = 7 Hz] while the methylene protons appeared as a broad multiplet centered at about τ 7.72. Such a spectrum is consistent with the presence of four non-equivalent ethyl groups on the cyclopentadienone ring, and suggests that the tetraethylcyclopentadienone is not symmetrically 2,3,5,6-η-bonded to platinum, as it is in the analogous rhodium complexes [8]. Further support for structure III comes from the chemical behaviour of the cyclopentadienone complex, which reacts readily with a variety of ligands to give two types of adducts, A and B.

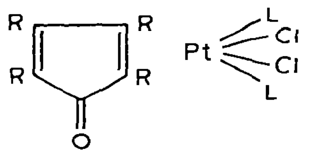
Type A



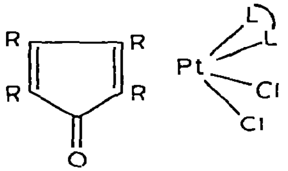
($R = C_2H_5$)

(V) L = triphenylphosphine
(VI) L = p-toluidine
(VII) L = benzylamine
(VIII) L = pyridine

Type B



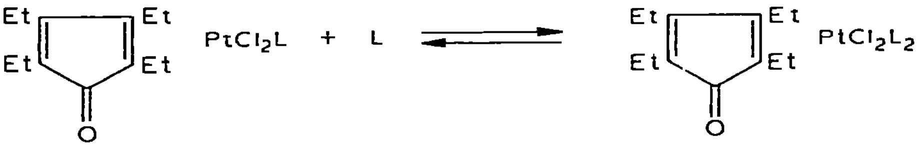
(IX) L = benzylamine
(X) L = 3-methylpyridine



(XI) L = 2,2'- bipyridine

Type A adducts V-VII were obtained by treating 1 mole of III with 2 moles of ligand at room temperature (but pyridine reacted only in boiling benzene to give VIII); use of an excess of ligand leads to the 1/2 adducts, which have been isolated and fully characterized in the case of benzylamine (IX), 3-methylpyridine (X) and 2,2'-bipyridine (XI). Triphenylphosphine gave only the mono adduct V; attempts to obtain the 1/2 species from III or V with an excess of phosphine failed, probably owing to the large steric hindrance of the ligand.

Consistently, benzylamine reacted with VII in the molar ratio 1/1, according to the reaction:



(VII) (IX)

This bis adduct IX is not very stable and reverts to VII in boiling ethanol. The lability of the complexes in which two moles of nitrogen donor ligands are coordinated to the platinum atom as in B, is in agreement with the fact that 1/2 adducts were not isolated from the reaction of III with a large excess of *p*-toluidine or pyridine.

In contrast, chelation promoted the formation of the type B compounds as expected: 2,2′-bipyridine gave the stable derivative XI, which was recrystallized from boiling ethanol without decomposition. The formation of 1/2 ad-

TABLE 2

INFRARED DATA FOR SOLID COMPOUNDS[a]

Compound	Colour	ν(CO) (cm^{-1})	Other bands
I	pale yellow	2080s, 2015w	1320m; 1260m; 1085m; 990m; 785m; 710m
II	yellow		1320s; 1293m; 1255s; 1100m; 1085s; 985m; 720m; 700m; 660m; 610m
III	white	1680s; 1640m;	1280w, 1080w; 852m; 820m; 805m;
IV	yellow	1723vs; 1682(sh)m[b]	1110m; 1050s; 1032m; 860m; 840s; 710s
V	pale yellow	1655s; 1630vs	1090s; 1058m; 1040m; 1000m; 845s; 825s; 755s; 745s; 690s
VI	white	1620vs	3250m; 3170m; 3120m; 1580s, 1510m; 1135s; 860m; 840w; 818m
VII	white	1630vs	3180m; 3120m; 1550s; 1365m; 1190m, 1058m; 980m, 850m; 830m; 812m; 750s; 700s
VIII	white	1640vs; 1605s	1215s; 1070s; 1058ms; 1020m; 857s; 840s; 770s; 700s; 667m; 640s
IX	white	1640vs; 1620s	3310m; 3285m; 3220m; 3140m; 1600(sh); 1580(sh); 1065m; 1040m; 1020m; 995s; 850s; 750m; 737s; 700s; 680m
X	white	1657s ; 1630s	1600w; 1580w; 1210m; 1200m; 1120m; 1060s; 850s; 810s, 803s; 710s, 683s
XI	yellow	1660vs; 1635m	1606m; 1600s; 1315m; 1155m; 1028m; 848m; 832m; 775s; 745m; 735m; 682m
XII	dark-red	1690m; 1650s	1200m; 1170m; 1060m; 1032m; 835m
XIII	white	1680s; 1640m	855m; 830m; 810m
XIV	yellow	1780vs	3260m; 3230m; 3150m; 1590s; 1220w, 1165w; 1070w; 1055w; 980w; 750s; 720w; 700s
XV	white-yellow	2080vs; 2020w	1070w; 1020s
XVI	yellow		1080w; 1020s
XVII	red		1200m; 1065w; 1020s; 1000s; 910m
XVIII	white	1675vs; 1650m	1280w; 1230w; 1090w; 1040m; 1030m; 985m; 950w; 820w; 772w

[a] In nujol mulls. [b] Registered in KBr disc.

TABLE 3

NMR SPECTRA

		Exocyclic alkyl groups[a]			
Compound	Solvent	CH_3	CH_2	Other assignments	
I	CD_3COCD_3	8.67 t	7.94 q		
II	CD_3COCD_3	8.7 t	7.87 q		
III	CD_3COCD_3	8.58; 8.71, 8.92; 9.02 t	7.2-8.12 m		
IV	CD_3COCD_3	8.56, 8.68 t	7.2-7.5 m		
V	$CDCl_3$	8.67; 8.73; 8.9; 9.23 t	6.5-8.5 m	2-3 m	$(C_6\underline{H}_5)_3P$
VI	$CDCl_3$	8.8; 8.95; 9.1, 9.16 t	6.5-8.5 m	8.77 s	$C\underline{H}_3C_6H_4NH_2$
				3 m	$CH_3C_6\underline{H}_4NH_2$[b]
				4.05 s(br)	$CH_3C_6H_4N\underline{H}_2$
VII	$CDCl_3$	9.03; 8.9; 8 85; 8.83 t	6.5-8.5 m	5.9 s	$NH_2C\underline{H}_2C_6H_5$
				2.5-3 m	$NH_2CH_2C_6\underline{H}_5$
VIII	CD_3COCD_3	8.53; 8.67; 8.84; 9.03 t	6.5-8.5 m	0.5-2.5	$C_5\underline{H}_5N$
IX	$CDCl_3$	8.70; 8.75; 8.87; 9 t	6.5-8.5 m	6 s	$NH_2C\underline{H}_2C_6H_5$
				2 5-3 m	$NH_2CH_2C_6\underline{H}_5$
X	CD_3COCD_3	8.7; 8.84, 8.93; 9.07 t	6.5-8.5 m	7.7 s	$C\underline{H}_3C_5H_4N$
				1-3	$CH_3C_5\underline{H}_4N$
XI	not soluble				
XV	CD_3COCD_3	8.32 s			
XVI	CD_3COCD_3	8.4 s			
XVII	CD_3COCD_3	8.55 s			
XVIII	$CDCl_3$	7.84; 7.93 s			

[a] For all compounds containing an ethyl group $^3J(H-H) = 7$ Hz. [b] Collapsed A_2B_2 *p*-toluidine system.

ducts strongly supports the view that the cyclopentadienone ring is asymmetrically η-bonded to the metal, in agreement with the suggestion based on the NMR non-equivalence of the ethyl groups in III, and observed for all its derivatives.

The IR spectra of all the compounds described above (see Table 2) showed that as a consequence of the coordination of the new ligand to platinum, the ν(CO) are lowered as expected, the negative charge brought by the donor atom to the metal being delocalized over the cyclopentadienone ring.

The NMR chemical shifts of the more soluble cyclopentadienone derivatives are listed in Table 3. The methyl and methylene protons of the tetraethylcyclopentadienone in the adducts differ very little in position from those for compound III: this suggests that the entering ligand does not affect significantly the bonding of the unsaturated ring. The appearance of the fairly sharp resonance at about τ 4 assignable to the NH protons in the case of *p*-toluidine adduct VI, and the overlapping of the broad peak due to the amine protons at about τ 7 with the multiplet due to the CH_2 protons of the ethyl groups in the case of the benzylamine compounds VII and IX confirm that the nitrogen atom is strongly bonded to platinum. Furthermore the integration of all proton signals was in agreement with the proposed structure of 1/1 adducts for compounds V-VII and of 1/2 adducts for compounds IX and X.

Compounds V-VII and IX appeared to be monomeric in chloroform and in benzene, and this suggests that the steric hindrance of the tetrasubstituted cyclopentadienone ring, probably bonded to platinum in an unsymmetric fashion as well as of the entering ligands, promotes the breaking of the chloro bridges. The lability of the chloro bridges in compound III has been proved by the exchange

(III) (XII)

(R = C_2H_5)

reaction with iodide ions, which occurred simply on refluxing III with lithium iodide in methanol.

The nature of the entering nucleophile seems to be important in this reaction, since with bromide ions only two chlorine atoms (presumably terminal) are replaced, to give a mixed chlorobromo-derivative XIII, while dibromo-di-μ-bromobis(tetraethylcyclopentadienone)diplatinum was isolated only in traces.

Compound III was unstable in solution under an atmosphere of CO; in tetrahydrofuran it slowly decomposed to give the green-black polynuclear carbonyl compound $[Pt(CO)_2]_n$.

The minor product of the reaction, IV, was characterized as a tetraethylquinone complex. The IR spectrum showed only two carbonyl stretches at 1723 s and 1682 m cm^{-1}, assignable to ketonic groups. The NMR spectrum consisted of two triplets at τ 8.56 and 8.68 and of a poorly resolved system of quartets at τ 7.2-7.5; the fact that the ethyl groups are not equivalent indicated that the tetraethyl-p-benzoquinone is not symmetrically bonded 2,4,5,6-η to platinum but is behaving as an olefin (e.g. 2,3-η). This observation is confirmed by the reaction of IV with benzylamine, which gives a yellow adduct containing two moles of N-donor ligand per atom of platinum of formula $PtCl_2(C_{14}H_{20}O_2)(C_6H_4CH_2NH_2)_2$ (XIV).

The reaction with 2-butyne

The reaction between 2-butyne and dichlorodicarbonylplatinum was performed at 20° in benzene. Monitoring the reaction by recording the IR spectrum revealed the appearance of slowly increasing absorption bands at 2090 s, 1765 s, 1690 s and 1660 w cm^{-1}. At the end of the reaction more than 64% of the platinum had been converted into a yellow crystalline substance which was identified as carbonylplatinumbis[di-μ-chloro,chloro(tetramethylcyclobutadiene)-platinum] (XV), the methyl analogue of I, from its elemental analysis, IR spectrum [ν(CO) 2080 cm^{-1} in nujol mull], and NMR spectrum. The latter shows a sharp singlet at τ 8.32 due to equivalent methyl protons, with two satellite peaks due to the coupling with ^{195}Pt, as expected, [J(Pt—H) = 10.5 Hz].

Compound XV when treated in benzene with 1.5 moles of p-toluidine or methyldiphenylphosphine immediately gave the tetramethylcyclobutadiene derivative $[PtCl_2((CH_3)_4C_4)]_n$ (XVI), by cleavage of the chloro bridges and extraction of the platinum atom bearing the carbonyl group.

Under the same conditions, an excess of ligand, e.g. 5 moles of triphenylphosphine, gave the known $Pt(PPh_3)_2Cl_2$.

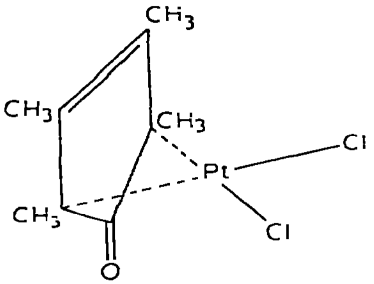
The formation of XVI was observed when XV was refluxed in acetone; a small amount was also obtained from some reactions of $Pt(CO)_2Cl_2$ with 2-butyne in boiling benzene.

When dichloro(tetramethylcyclobutadiene)platinum (XVI) was refluxed in acetone or in methanol containing lithium iodide, the corresponding diiodo(tetramethylcyclobutadiene)platinum complex (XVII) was formed. The IR spectra of XVI and XVII showed no absorption bands between 2500 and 1550 cm^{-1}; their NMR spectra showed a sharp singlet, at τ 8.45 and 8.55 respectively, partially split into a doublet by coupling with ^{195}Pt, [$^3J(Pt—H)$ = 10.5 Hz] as observed for XV.

Definite evidence for the presence of a tetramethylcyclobutadiene ring bonded to platinum was afforded by the transfer of this ring to an iron tricarbonyl moiety on reaction of XVI with pentacarbonyliron in boiling benzene, the tricarbonyl(tetramethylcyclobutadiene)iron being identified from the similarity of its IR spectrum with those of the tetraphenylcyclobutadiene and cyclobutadiene analogues [9].

As in the reaction with 3-hexyne, a ketonic species [ν(CO) 1680 s and 1650 m cm^{-1}] was also obtained; it was isolated from the mother solution as white plates, and found to correspond to dichlorotetramethylcyclopentadienone platinum (XVIII), analogous to III.

Its NMR spectrum was significant; it consisted of two singlets at τ 7.84 and 7.93 associated with two signals at τ 8 and 8.34; the last two peaks were resolved at higher resolution and shown to be poorly defined quartets. The existence of four non-equivalent methyl groups accounts for the unusual bonding situation in the molecule, which can be represented as:



Another ketonic species with an IR absorbance at 1760 cm^{-1} was present in the oily residue of evaporation of the mother solution, but it was not isolated. We suspect that this compound is somewhat similar to the tetraethylquinone derivative (III), although it appears quite different from the duroquinone derivative of rhodium [10].

Conclusions

The results obtained in the reaction of $Pt(CO)_2Cl_2$ with 3-hexyne and with 2-butyne are closely analogous to those reported with diphenylacetylene as far as the formation of the cyclobutadiene derivatives is concerned. The most obvious difference involves the possibility of making stable cyclopentadienone complexes, which were not observed in the diphenylacetylene reactions even though the tetraphenylcyclopentadienone molecule is known to be one of the cyclooligomerization products of the acetylenes [2]. It is reasonable to ascribe the difference in behaviour to the smaller steric hindrance from the alkyl substitutents on the triple bond, which being less rigid than the phenyl groups, may be more readily located to permit coordination to the metal.

However, the NMR spectra of the cyclopentadienone compounds and the formation of 1/2 adducts with donor ligands show the bonding of the tetraalkylcyclopentadienone ring to be unusual and unexpected by comparison with the analogous derivatives of the isoelectronic rhodium(I) compound [8,10] and generally with the previously known cyclopentadienone complexes [3].

In the absence of an X-ray structural analysis, the chemical and physical data provided by this investigation can do no more than indicate that the cyclopentadienone ring is not doubly η-bonded symmetrically to platinum, the bonding situation being like that observed with a strongly polarized olefin.

As for the mechanism of cyclization of acetylene, the system considered was too complicated, in the number and quality of the products to provide any clarification.

Work is in progress with other disubstituted acetylenes and other transition metal carbonylhalides [11].

Experimental

Solvents were purified and dried by standard methods. IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer in Nujol mulls, or in KBr pellets. Molecular weights were determined with a Mechrolab Osmometer Model 301 A, and NMR spectra with a NEVA NV 14 NMR spectrometer.

Reactions of 3-hexyne with dicarbonyldichloroplatinum at 25°

(a). 3-Hexyne (3.7 ml, 31.6 mmol) in 20 ml of benzene was added slowly (1 ml/h) with stirring to a suspension of $Pt(CO)_2Cl_2$ (4.2 g, 13 mmol) in 80 ml of anhydrous benzene under nitrogen. After 48 h, the IR spectrum of the solution no longer showed the characteristic absorption bands of $Pt(CO)_2Cl_2$ at 2170 and 2130 cm^{-1}. A pale yellow solid separated which was filtered off, washed with benzene (20 ml) and dried in vacuo (1.18 g, 24%). It was identified as carbonylplatinumbis[di-μ-chloro,chloro(tetraethylcyclobutadiene)platinum] (I). It is slightly soluble in chloroform, acetone, tetrahydrofuran and diethyl ether, and insoluble in benzene and hexane.

Found: C, 25.30; H, 3.33; Cl, 18.71; O, 1.76; Pt, 51.2; mol. wt. in $CHCl_3$ 980. $C_{25}H_{40}Cl_6OPt_3$ calcd.: C, 25.99; H, 3.49; Cl, 18.43; O, 1.39; Pt, 50.70%; mol. wt. 1154. M.p. 167°(dec.).

The benzene solution was evaporated to dryness and the brown gummy solid so obtained was stirred with hexane (60 ml) to give a light-brown powder, which was filtered off and dried in vacuo. The dry solid was first washed with acetone (30 ml) and then crystallized in a Soxhelet apparatus (40 ml acetone) to give white plates. It was identified as bis[dichloro(tetraethylcyclopentadienone)platinum] (III). It is slightly soluble in acetone, chloroform, benzene, tetrahydrofuran and diethyl ether, and insoluble in hydrocarbons.

Found: C, 34.32; H, 4.42; Cl, 15.17; O, 3.63; Pt, 44.1; mol. wt. in $CHCl_3$ 950. $C_{26}H_{40}Cl_4O_2Pt_2$ calcd.: C, 34.04; H, 4.40; Cl, 15.48; O, 3.49; Pt, 42.6%; mol. wt. 916.

The acetone washings were evaporated to dryness and the residue was crystallized twice from acetone—hexane to give a yellow product which was identified as dichloro(tetraethyl-*p*-benzoquinone)platinum (IV). It is soluble in the common organic solvents except for hydrocarbons. Found: C, 34.98; H, 4.40; O, 6.25. $[C_{14}H_{20}Cl_2O_2Pt]_n$ calcd.: C, 34.55; H, 4.15; O, 6.58%.

(b). 3-Hexyne (4.5 ml, 39.5 mmol) was added to $Pt(CO)_2Cl_2$ (1.6 g, 4.9 mmol) in toluene (40 ml). The suspension was stirred at room temperature under nitrogen for 2-4 h. The yellow precipitate was filtered off, washed with toluene and dried in vacuo. The yellow solid was then treated with benzene in a Soxhlet apparatus: 720 mg of the pale yellow compound I remained undissolved, and this was recrystallized by extraction with chloroform. The benzene solution was evaporated to dryness to give a light-brown solid, from which by extraction with acetone in a Soxhlet apparatus 517 mg of white compound III were obtained.

The toluene mother liquor was evaporated to give a gummy oil: on stirring with hexane (30 ml) a light-brown powder separated which was treated according the procedure described in (a), to give 165 mg of III and 160 mg of IV.

The hexane solution from the treatment of the gummy oil was evaporated in vacuo to give an oily residue which contained a yellowish solid, identified as dichloro(tetraethylcyclobutadiene)platinum (II), by comparison with a pure sample obtained with the procedure described below. Yields of pure compounds: I, 37.5%; III, 29.7%; IV, 7%.

Dichloro(tetraethylcyclobutadiene)platinum (II)

p-Toluidine (142 mg, 1.32 mmol) in benzene (5 ml) was added to a suspension of I (510 mg, 0.44 mmol) in benzene (15 ml). The colourless solution rapidly turned dark-yellow and complete dissolution of I was observed. After 5 h stirring the volume of the solution was reduced to 1/3 by evaporation in vacuo. On addition of hexane, a yellow microcrystalline powder separated, and was crystallized from acetone/hexane.

Found: C, 33.82; H, 4.63; mol. wt. in acetone 383. $C_{12}H_{20}Cl_2Pt$ calcd.: C, 33.47; H, 4.68%; mol. wt. 430. This compound was also obtained by treating I in benzene or chloroform in a similar manner as described above with other ligands such as pyridine, triphenylphosphine, and 2,2'-bipyridine.

Dichloro(tetraethylcyclopentadienone)(triphenylphosphine)platinum (V)

$P(C_6H_5)_3$ (160 mg, 0.61 mmol) was added to III (305 mg, 0.33 mmol) in toluene (40 ml). The solution was kept at room temperature for 1 h and then evaporated to dryness in vacuo. The residue was crystallized from benzene/hexane to give pale-yellow crystals.

Found: C, 50.94; H, 4.90; mol. wt. in benzene, 748. $C_{31}H_{35}Cl_2OPPt$ calcd.: C, 51.59; H, 4.85%; mol. wt. 721.

Dichloro-p-toluidine(tetraethylcyclopentadienone)platinum (VI)

III (300 mg. 0.28 mmol) and *p*-toluidine (60 mg, 0.56 mmol) were stirred for 2 h in toluene (80 ml). On reduction of the volume of the gold-yellow solution to 1/3, a white solid separated, and this was filtered off, and recrystallized from benzene.

Found: C, 42.86; H, 5.12; N, 2.51; mol. wt. in benzene 680. $C_{20}H_{29}Cl_2ON$-Pt calcd.: C, 42.47; H, 5.13; N, 2.47%; mol. wt. 565.

Benzylaminedichloro(tetraethylcyclopentadienone)platinum (VII)

Benzylamine (50 mg, 0.47 mmol) in benzene (5 ml) was added to III (210 mg, 0.23 mmol) in benzene (15 ml). After 2 h of stirring the solution was evaporated to dryness and the residue treated with hexane. The product (a white powder) was recrystallized from ethanol to give white plates.

Found: C, 42.95; H, 5.34; N, 2.33; mol. wt. in benzene 602. $C_{20}H_{29}Cl_2ON$-Pt calcd.: C, 42.47; H, 5.13; N, 2.47%; mol. wt. 565.

Dichloropyridine(tetraethylcyclopentadienone)platinum (VIII)

Compound III (0.268 g, 0.29 mmol) and pyridine (2 ml; 24.8 mmol) were refluxed in benzene for 24 h. Evaporation of the pale yellow solution gave a white powder, which was crystallized from acetone.

Found: C, 40.22; H, 4.54; N, 2.46. $C_{18}H_{25}Cl_2NOPt$ calcd.: C, 40.22; H, 4.65; N, 2.60%.

Bis(benzylamine)dichloro(tetraethylcyclopentadienone)platinum (IX)

(a). Benzylamine (0.3 ml, 2.80 mmol) was added to III (163 mg, 0.17 mmol) in benzene (15 ml). After 2 h stirring the solution was evaporated to dryness, and the residue treated with hexane and dried to obtain a white powder.

Found: C, 47.80; H, 5.41; N, 4.01; mol. wt. in chloroform 478. $C_{27}H_{38}Cl_2$-N_2OPt calcd.: C, 48.2; H, 5.64; N, 4.17%; mol. wt. 672.

(b). VII (100 mg, 0.177 mmol) was dissolved in benzene (10 ml) containing benzylamine (110 mg, 0.37 mmol); the solution was kept at room temperature for 1 h then evaporated to dryness, and the residue treated with hexane (30 ml). The white crystalline powder was washed with hexane (10 ml).

Found: C, 47.45; H, 5.48; N, 4.16%.

Dichlorobis(3-methylpyridine)(tetraethylcyclopentadienone)platinum (X)

3-Methylpyridine (0.25 ml, 2.58 mmol) was added to III (195 mg, 0.213 mmol) in benzene (15 ml). The solution was stirred at room temperature for 2 h and then evaporated to dryness, and the residue treated with hexane. The white powder was recrystallized from benzene/hexane.

Found: C, 46.56; H, 5.10; N, 4.39; $C_{25}H_{34}Cl_2N_2OPt$ calcd.: C, 44.95; H, 5.28; N, 4.35%.

Dichloro-2,2'-bipyridine(tetraethylcyclopentadienone)platinum (XI)

III (161 mg, 0.176 mmol) was refluxed in benzene with 2,2'-bipyridine (120 mg, 0.77 mmol) for 4 h. On addition of hexane, a yellowish solid separated, and this was recrystallized from ethanol.

Found: C, 45.22; H, 4.21; N, 4.51. $C_{23}H_{28}Cl_2N_2OPt$ calcd.: C, 44.95; H, 4.56; N, 4.56%.

Diiodo(tetraethylcyclopentadienone)platinum (XII)

LiI (550 mg, 4.1 mmol) was added to a suspension of III (110 mg, 0.12 mmol) in methanol (20 ml) and stirred for 8 h at 50°. The solution was evaporated to dryness and the red gummy solid was treated with water to remove the lithium halides. The solid residue was washed with methanol and dried in vacuo.

Found: C, 23.50; H, 3.18. $C_{13}H_{20}I_2OPt$ calcd.: C, 24.3; H, 3.12%.

Bromochloro(tetraethylcyclopentadienone)platinum (XIII)

LiI·H_2O (180 mg, 1.7 mmol) was added to a suspension of II (83 mg, 0.09 mmol) in acetone (15 ml) and stirred for 8 h at 50°. The solution was evaporated to dryness and the white solid was treated with water to remove the lithium halides, then washed with methanol and dried in vacuo.

Found: C, 31.21; H, 3.80; Cl, 6.42; Br, 15.59. $C_{13}H_{20}BrClOPt$ calcd.: C, 31.04; H, 4.01; Cl, 7.05; Br, 15.90%.

Bis(benzylamine)dichloro(tetraethyl-p-benzoquinone)platinum (XIV)

Benzylamine (30 mg, 0.28 mmol) was added to III (30 mg, 0.062 mmol) in benzene (10 ml). After stirring for 2 h the solution was evaporated to dryness and the residue treated with hexane. The product (a cream solid) was recrystallized from ethanol to give yellow plates.

Found: C, 50.90; H, 5.80; N, 4.24; $C_{28}H_{38}Cl_2N_2O_2Pt$ calcd.: C, 48.00; H, 5.43; N, 4.00%.

Reaction of 2-butyne with dicarbonyldichloroplatinum in benzene at 20°

2-Butyne (2.5 ml, 31.94 mmol) was added with stirring to a suspension of $Pt(CO)_2Cl_2$ (3.13 g, 9.12 mmol) in anhydrous benzene (50 ml) under nitrogen. After 6 h the IR spectrum of the solution did not show any of the characteristic stretching frequencies of $Pt(CO)_2Cl_2$. A white-yellow solid separated from solution, which was washed with benzene (20 ml) and dried in vacuo. It was identified as carbonylplatinumbis[di-μ-chloro,chloro(tetramethylcyclobutadiene)platinum] (XV) (2.16 g, 64%). It is slightly soluble in acetone, chloroform and tetrahydrofuran and insoluble in benzene and hydrocarbons.

Found: C, 19.90; H, 2.22; O, 1.40; Cl, 20.11; Pt, 55.30. $C_{17}H_{24}Cl_6OPt_3$ calcd.: C, 19.59; H, 2.32; O, 1.53; Cl, 20.41; Pt, 56.15%.

The benzene solution was evaporated to dryness and then stirred with hexane. A dark brown solid was obtained, which was extracted in a Soxhelet apparatus with benzene. The benzene solution was again evaporated to dryness and the solid residue dissolved in 50 ml acetone. Cooling to —20° gave white plates, which were identified as dichloro(tetramethylcyclopentadienone)platinum (XVIII).

Found: C, 26.80; H, 2.86; O, 4.07; Cl, 17.40; Pt, 47.7; $C_9H_{12}Cl_2OPt$ calcd.: C, 26.88; H, 3.01; O, 3.98; Cl, 17.63; Pt, 48.51%.

Dichloro(tetramethylcyclobutadiene)platinum (XVI)

p-Toluidine (0.173 g, 1.62 mmol) was added to XV (1.3 g, 1.13 mmol) in benzene and the suspension was stirred for 12 h at room temperature. On addition of hexane (50 ml) a yellow solid separated, which was crystallized from acetone and hexane (680 mg, 74%).

The presence of the tetramethylcyclobutadiene ring was confirmed by treating XVI with $Fe(CO)_5$ in benzene to give tricarbonyltetramethylcyclobutadieneiron which was identified by comparison of its IR spectrum with the spectra of analogous compounds previously reported.

Found: C, 25.90; H, 3.19; Pt, 50.63. $C_8H_{12}Cl_2Pt$ calcd.: C, 25.66; H, 3.23; Pt, 52.14%.

Compound XVI was also obtained by treating XV with methyldiphenylphosphine.

Bis[diiodo(tetramethylcyclobutadiene)platinum] (XVII)

XVI (1 g, 2.67 mmol) was stirred at 50° in methanol (50 ml) with lithium iodide (2 g, 15 mmol). After 4 h, the dark yellow solid was filtered off, washed with methanol (20 ml), and dried (1 g, 61%). Recrystallisation from acetone gave reddish crystals.

Found: C, 17.69; H, 2.11; I, 43.7; mol. wt. in $CHCl_3$ 1000. $C_{16}H_{24}I_4Pt_2$ calcd.: C, 17.25; H, 2.15; I, 45.5%; mol. wt. 1114.

Acknowledgements

We thank the C.N.R. for financial support. We are also grateful to Dr. P.C. Fantucci for the NMR spectra and helpful discussions, and to Prof. P. Chini and Prof. L. Malatesta for valuable suggestions.

References

1 M.P. Cava and M.J. Mitchell, Cyclobutadiene and Related Compounds, Academic Press, New York, 1967, pp. 88-121.
2 F.L. Bowden and A.B.P. Lever, Organometal. Chem. Rev., 3 (1969) 227, and refs. therein.
3 F. Canziani, P. Chini, A. Quarta and A. Di Martino, J. Organometal. Chem., 26 (1971) 285.
4 A.C Smithies, M. Rycheck and M. Orchin, J. Organometal. Chem., 12 (1968) 199.
5 J.C. Bailar and H. Itatani, Inorg. Chem., 4 (1965) 1618.
6 R.J. Irving and E.A. Magnusson, J. Chem. Soc., (1957) 2018.
7 G. Booth, J. Chatt and P. Chini, Chem. Commun., (1965) 639; G. Booth and J. Chatt, J. Chem. Soc. A, (1969) 2131 and refs. therein.
8 S. McVey and P.M. Maitlis, J. Organometal. Chem., 19 (1969) 169.
9 W. Hubel and E.H. Braye, J. Inorg. Nucl. Chem., 10 (1959) 250; G.P. Emerson, L. Watts and R. Pettit, J. Amer. Chem. Soc., 87 (1965) 131.
10 J.W. Kang, S. McVey and P.M. Maitlis, Can. J. Chem., 46 (1968) 3189.
11 F. Canziani and M.C. Malatesta, to be published.