CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA

Metal–Olefin Compounds. V. The Reactions of Cycloheptatriene with Platinum(IV) Bromide, Hexabromoplatinic Acid, and Hexachloroplatinic Acid[1]

BY C. R. KISTNER, J. R. DOYLE, N. C. BAENZIGER, J. H. HUTCHINSON, AND P. KASPER

Received April 27, 1964

The reaction of cycloheptatriene with platinum(IV) bromide, hexabromoplatinic acid, or hexachloroplatinic acid yields a mixture of compounds. The mixture consists of the cycloheptatrienylium salt of the platinum(IV) acid and the dihalo(cycloheptatriene)platinum(II) olefin complex in approximately a 1:2 mole ratio. Attempts to form carbonium ion species, bonded directly to platinum, *via* hydride ion abstraction or protonation of dichloro(cycloheptatriene)platinum(II) were unsuccessful.

Introduction

The reaction of cycloheptatriene and platinum(IV) bromide in glacial acetic acid has been reported[2] to yield an orange diamagnetic solid which decomposed at 154–155°. Analytical data indicated the formula $C_7H_{7-8}PtBr_2$ and the infrared spectrum displayed absorption bands at 3017, 1473, 989, and 638 cm.$^{-1}$ characteristic of the $C_7H_7^+$ ion.[3,4] On the basis of this evidence and a series of chemical reactions, a cycloheptatrienylium ion configuration was assigned to the organic moiety and a molecular formula $(C_7H_7PtBr_2)_2$ (I) was proposed.

A previous investigation from this laboratory reported[5] the isolation of dichloro(cycloheptatriene)platinum(II) (II) from the reaction of cycloheptatriene and *sym-trans-μ*-di-chloro-bis[chloro(ethylene)platinum(II)], $(C_2H_4PtCl_2)_2$. The infrared spectrum of II displayed a remarkable number of coincident bands with the spectrum reported for I, and the only major difference noted was the absence of the bands associated with $C_7H_7^+$ in compound II.

Further interest in this report was engendered since a number of recent investigations[6,7] have been concerned with the formation of cycloheptatrienylium ion from cycloheptatriene in the presence of metal halides and possible mechanisms for these reactions.[8] Also, the preparative method reported for the isolation of I has previously been reported[9] as a method for the isolation of platinum(II) olefin compounds. Finally, since compound I appeared to be the first example of a complex containing a carbonium ion bonded in coordinate fashion to platinum and one of the few instances involving rearrangement of an olefin upon coordination to platinum, it was of interest to explore further the chemistry of this unique species.

Experimental

Cycloheptatrienylium Salts.—Cycloheptatrienylium chloride,[10] cycloheptatrienylium bromide,[3] 7-cyano-1,3,5-cycloheptatriene,[3] and cycloheptatrienylium hexachloroplatinate[11] were prepared as described in the literature.

***sym-trans-μ*-Di-chloro-bis[chloro(ethylene)platinum(II)].**—This compound was prepared according to the procedure described by Chatt and Searle.[12] The final recrystallization of the product from methylene chloride yielded orange tablets.

Anal. Calcd. for $(C_2H_4PtCl_2)_2$: Pt, 66.34. Found: Pt, 66.10.

Platinum(IV) Compounds.—Reagent grade chloroplatinic acid was obtained from Matheson Coleman and Bell. Bromoplatinic acid and platinum(IV) bromide were prepared by previously described procedures.[13]

Cycloheptatriene.—A commercial sample[14] of this olefin, analyzed *via* gas chromatography, consisted of a mixture of approximately 87% cycloheptatriene, 5% toluene, 2% norbornadiene, and several other compounds whose individual concentrations did not exceed 1%.

Samples for spectral studies and a few selected preparations were purified by passing the olefin through a column of acid-washed alumina followed by vacuum distillation. The colorless distillate contained less than 5% impurities, chiefly toluene, as indicated by gas chromatographic analysis.

Reaction of Cycloheptatriene with Bromoplatinic Acid.—A 2-ml. sample of cycloheptatriene was added to a solution containing 1.53 g. of hydrated hexabromoplatinic acid in 25 ml. of glacial acetic acid at the boiling point of the mixture. The orange solid, which precipitated immediately upon the addition of the olefin, was separated by filtering, washed with anhydrous ether, and dried in air overnight. The recovered product weighed 1.057 g.

Anal. Calcd. for $(C_7H_7)_2PtBr_6 \cdot 2C_7H_8PtBr_2$: C, 19.21; H, 1.73; Pt, 33.24. Found: C, 19.52; H, 1.81; Pt, 33.35.

A 0.575-g. sample of the above product was extracted with 125 ml. of methylene chloride and the insoluble deep orange solid, 0.272 g., was separated and dried; it decomposed at 191–194°.

Anal. Calcd. for $(C_7H_7)_2PtBr_6$: C, 19.63; H, 1.65; Pt, 22.77. Found: C, 19.99; H, 1.84; Pt, 23.20.

The methylene chloride solution was concentrated until crystallization commenced and, after cooling, the product was separated and recrystallized from a methylene chloride–carbon tetrachloride mixture. The pure product, in the form of light orange needle-

---

[1] For the previous paper in this series see: *Inorg. Chem.*, **2**, 1255 (1963).

[2] E. O. Fischer and H. P. Fritz, *Z. physik. Chem.* (Frankfurt), **17**, 135 (1958).

[3] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

[4] W. G. Fately, B. Curnette, and E. R. Lippincott, *J. Chem. Phys.*, **26**, 1491 (1957).

[5] R. J. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960).

[6] D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962); (b) D. Bryce-Smith and N. A. Perkins, *ibid.*, 2320 (1961), and references cited therein.

[7] J. Holmes and R. Pettit, *J. Org. Chem.*, **28**, 1695 (1963).

[8] K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

[9] M. S. Kharasch and T. A. Ashford, *ibid.*, **58**, 1733 (1936).

[10] H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson *J. Am. Chem. Soc.*, **79**, 4557 (1957).

[11] F. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

[12] J. Chatt and M. L. Searle, *Inorg. Syn.* **5**, 210 (1957).

[13] A. G. Sharpe, *J. Chem. Soc.*, 3444 (1950).

[14] This sample was kindly furnished by the Shell Chemical Corp.

shaped crystals, weighed 0.2401 g. and decomposed at 154–155°.

Anal. Calcd. for $C_7H_8PtBr_2$: C, 18.81; H, 1.80; Pt, 43.64; mol. wt., 450.2. Found: C, 18.69; H, 1.99; Pt, 43.04; mol. wt., 444.6.

The reaction of cycloheptatriene with platinum(IV) bromide in glacial acetic acid also gave a mixture of products. The mixture was separated as in the above procedure to yield dibromo(cycloheptatriene)platinum(II) and the cycloheptatrienylium hexabromoplatinate in approximately a 2:1 mole ratio.

Reaction of Cycloheptatriene with Chloroplatinic Acid.—A 2-ml. sample of cycloheptatriene was added to 10 ml. of boiling glacial acetic acid containing 1.196 g. of hexachloroplatinic acid hexahydrate. A yellow-green solid precipitated immediately, and after cooling the mixture to room temperature the solid product was separated by filtering through a fritted glass crucible. The crude product, after drying in air, weighed 0.878 g.

Anal. Calcd. for $(C_7H_7)_2PtCl_6 \cdot 2C_7H_8PtCl_2$: C, 25.74; H, 2.31; Pt, 44.79. Found: C, 25.79; H, 2.45; Pt, 46.95.

A 0.478-g. sample of the above mixture was extracted with 125 ml. of methylene chloride. The light yellow residue was separated, and after drying in air it weighed 0.168 g.

Anal. Calcd. for $(C_7H_7)_2PtCl_6$: C, 28.50; H, 2.39; Pt, 33.06. Found: C, 28.78; H, 2.64; Pt, 33.81.

The methylene chloride solution was decolorized with charcoal and filtered, and the filtrate was evaporated until crystallization commenced. The product was separated and recrystallized from a methylene chloride–carbon tetrachloride mixture to yield 0.191 g. of light yellow needle-shaped crystals that decomposed at 177–179°.

Anal. Calcd. for $C_7H_8PtCl_2$: C, 23.48; H, 2.25; Pt, 54.47. Found: C, 23.08; H, 2.36; Pt, 53.82.

Dichloro(cycloheptatriene)platinum(II).—This compound was prepared by displacing the ethylene in 0.089 g. of *sym-trans-μ*-dichloro-bis[chloro(ethylene)platinum(II)], dissolved in 10 ml. of boiling methylene chloride, by the addition of 0.2 ml. of cycloheptatriene. The light yellow solution from the reaction was evaporated at room temperature, and the yellow residue was recrystallized from a methylene chloride–carbon tetrachloride mixture. The yellow crystalline product, 0.11 g., decomposed at 174–176°.

Anal. Calcd. for $C_7H_8PtCl_2$: C, 23.48; H, 2.25. Found: C, 24.42; H, 2.64.

Glacial acetic acid or ethanol can be used as the solvent in the above reaction with essentially identical results. Dichloro(cycloheptatriene)platinum(II) was the only product isolated in an attempt to prepare *sym-trans-μ*-di-chloro-bis[chloro(cycloheptatriene)platinum(II)], $(C_7H_8PtCl_2)_2$, *via* the displacement of ethylene from Zeise's acid, $H(C_2H_5PtCl_3)$, in a methylene chloride medium.

Dibromo(cycloheptatriene)platinum(II).—To an acetone solution containing 1.23 g. (3.4 mmoles) of dichloro(cycloheptatriene)platinum(II) was added 0.75 g. (8.62 mmoles) of lithium bromide, and the mixture was evaporated at ambient temperature. The brown gummy residue was extracted with methylene chloride and the solution decolorized with charcoal, filtered, and evaporated. The orange crystalline product, 0.69 g. (theory, 0.94 g.), decomposed at 154–155°. The infrared spectrum of this compound was identical with the spectrum of the compound isolated from the methylene chloride soluble fraction in the reaction of cycloheptatriene with bromoplatinic acid.

Cyanide Displacement Reactions.—To approximately 25 ml. of an aqueous solution, containing 1.0 g. of potassium cyanide, was added 10 ml. of carbon tetrachloride and 5.0 mmoles of the appropriate platinum compound. This mixture was stirred at room temperature for several hours and the carbon tetrachloride layer was then separated and dried. A comparison of the infrared spectrum of the carbon tetrachloride solution with the spectrum of cycloheptatriene or 7-cyano-1,3,5-cycloheptatriene in carbon tetrachloride was used to identify the products of the reaction.

TABLE I

PRODUCTS FROM THE CYANIDE DISPLACEMENT REACTIONS

Reactant	Product
$C_7H_8PtCl_2$	Cycloheptatriene
$(C_7H_7)_2PtCl_6$	7-Cyano-1,3,5-cycloheptatriene
$C_7H_8PtBr_2$	Cycloheptatriene
$(C_7H_7)_2PtBr_6$	7-Cyano-1,3,5-cycloheptatriene
$H_2PtCl_6 + C_7H_8$ or $H_2PtBr_6 + C_7H_8$	A mixture of cycloheptatriene + 7-cyano-1,3,5-cycloheptatriene

Reaction with Concentrated Hydrochloric Acid.—Neither the dichloro nor dibromo derivative of cycloheptatrieneplatinum(II) was soluble in or reacted with concentrated hydrochloric acid to any noticeable extent. Both cycloheptatrienylium hexabromoplatinate and cycloheptatrienylium hexachloroplatinate are soluble in concentrated hydrochloric acid, but they can be recovered unchanged from the solution by slow evaporation. The cycloheptatrienylium hexabromoplatinate was recrystallized by this procedure to yield deep ruby red monoclinic prisms.

The cycloheptatrienylium salts are also soluble in water and the slow hydrolysis of the cycloheptatrienylium ion was evidenced by an increase in the conductivity and acidity of the solution. The equilibrium constant for the hydrolysis of cycloheptatrienylium ion was approximately determined from the equilibrium pH, 3.00, of a 7.00×10^{-4} *M* solution of cycloheptatrienylium hexabromoplatinum(IV). The value obtained from our study was 4.5×10^{-5}, which is of the same order of magnitude as previously observed[13,15,16] for this system.

Pyridine Displacement Reactions. (1).—The following compounds were prepared according to previously reported procedures[17]: *cis*-dichlorobis(pyridine)platinum(II), *trans*-dichlorobis(pyridine)platinum(II), and tetrakis(pyridine)platinum(II) chloride.

(2) **Reaction of Pyridine with Dibromo(cycloheptatriene)platinum(II).**—To approximately 10 ml. of benzene, containing 0.053 g. (0.80 mmole) of pyridine, was added 0.4 mmole of dibromo(cycloheptatriene)platinum(II). The mixture was stirred for 2 hr. and then evaporated at room temperature. The residue was recrystallized from a methylene chloride–benzene mixture. The yellow needle-like crystalline product was identified as *cis*-dibromobis(pyridine)platinum(II) by comparison of the infrared spectrum with the spectrum of *cis*-dichlorobis(pyridine)platinum(II) in the region 4000–400 cm.$^{-1}$.

Anal. Calcd. for $(C_5H_5N)_2PtBr_2$: C, 23.35; H, 1.95. Found: C, 23.81; H, 2.11.

(3) **Reaction of Dibromo(cycloheptatriene)platinum(II) with Excess Pyridine.**—A 0.4-mmole sample of dibromo(cycloheptatriene)platinum(II) was dissolved in 25 ml. of boiling pyridine and the colorless solution was evaporated to one-half its original volume. Upon cooling colorless crystalline tetrakis(pyridine)platinum(II) bromide separated and was identified by comparison of the infrared spectrum with the spectrum obtained from an authentic sample of tetrakis(pyridine)platinum(II) chloride in the region 4000–400 cm.$^{-1}$.

The reaction of tetrakis(pyridine)platinum(II) bromide with an excess of concentrated hydrobromic acid yielded *cis*-dibromobis(pyridine)platinum(II) rather than the expected *trans* isomer. The configuration was established by comparison of the infrared spectrum with that of the previously prepared compound.

Anal. Calcd. for $(C_5H_5N)_2PtBr_2$: C, 23.35; H, 1.95; N, 5.44; Pt, 37.45. Found: C, 22.82; H, 1.94; N, 5.25; Pt, 37.54.

(4) **Reaction of Pyridine with Dichloro(cycloheptatrienr) platinum(II).**—This reaction was conducted following the method used in procedure (2). The yellow needle-like product obtained was identified as *cis*-dichlorobis(pyridine)platinum(II)

---

(15) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

(16) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *ibid.*, **84**, 3349 (1962).

(17) G. B. Kauffman, *Inorg. Syn.*, **7**, 249 (1963).

TABLE II

INFRARED ABSORPTION SPECTRA[a] (IN CM.$^{-1}$) OF PRODUCTS FROM THE REACTION OF PLATINUM(IV) COMPOUNDS AND CYCLOHEPTATRIENE

$(C_7H_7)_2PtBr_6$	Reaction mixt.[b] of $C_7H_8PtBr_2$ + $(C_7H_7)_2PtBr_6$	Reported[c] compd.	$C_7H_8PtBr_2$	$(C_7H_7)_2PtCl_6$	Reaction mixt.[d] of $C_7H_8PtCl_2$ + $(C_7H_7)_2PtCl_6$	$C_7H_8PtCl_2$
	3420[e] m		3440		3420[e]	3420[e] m
		3032 w				
		3017 m	3020 w		3020 s	3020 m
	3005 s			2990 m		
2980 m						
2860 vw						2900 vw
2330 vw	2330 vw		2340 vw	2330 w	2325 vw	2330 vw
2070 vw	2080 vw			2080 w	2080 vw	2010 vw
						1933 vw
1895 vw	1895 vw			1900 w	1900 vw	1830 vw
1770 vw					1695 vw	1695 vw
	1620 m	1611 w	1615 m		1618 w	1613 w
1524 vw				1528 vw		
1470 vs	1473 w	1473 vs		1472 vs	1476 vs	
			1457 w			
			1438 m		1440 m	1435 sh
			1424 m		1427 m	1425 m
1399 vw						
	1385 s	1387 w	1389 s		1388 s	1389 s
		1376 w	1376 m		1374 m	1374 m
			1323 w		1323 w	1321 w
1272 s	1272 s	1277 m	1276 s	1272 s	1275 s	1276 s
1216 w	1213 vw	1215 w		1217 w	1215 vw	
	1183 vw	1187 w	1187 m		1186 w	1186 w
			1169 vw			
			1164 vw			
	1143 vw		1146 vw		1145 vw	1144 w
1099 w	1090 vw			1099 w	1099 w	
				1055 vw		
1024 w	1028 w	1030 w	1032 w	1026 vw	1031 w	1031 w
			997 m			995 m
			992 m			
988 m	989 w	989 w		990 s		
	950 vw		950 w		951 w	952 w
	912 m	914 m	914 vs		913 s	914 s
881 w				882 m		
863 m				865 s	864 w	
854 w				857 m		
	848 w	851 w	850 m		852 m	851 m
	835 m	839 m	838 vs	779 w	840 s	838 s
	744 vs	744 s	744 vs		748 vs	744 vs
	716 vw			723 vw		
	686 w		687 w		690 sh	688 w
672 s	666 m	672 m		673 vs	668 m	
647 vs		646 w		649 vs	645 s	
633 s	642 s	638 m		635 vs		
		626 m		554 vw		
	514 m	507 m	515 s		516 m	551 m
	473 vw		467 w			475 w
	445 m	438 m	444 s		451 s	452 s

[a] vw, very weak intensity; w, weak intensity; m, medium intensity; s, strong intensity; vs, very strong intensity; sh, shoulder. [b] Product from reaction of bromoplatinic acid or platinum(IV) bromide. [c] Data from ref. 2. [d] Product from reaction of chloroplatinic acid. [e] Water band from KBr.

by comparison of the infrared spectrum with the spectrum obtained from an authentic sample of *cis*-dichlorobis(pyridine)-platinum(II).

(5) **Reaction of Dichloro(cycloheptatriene)platinum(II) with Excess Pyridine.**—This reaction was conducted according to the method used in procedure (3). The white needle-like compound obtained was identified as tetrakis(pyridine)platinum(II) chloride by comparison of the infrared spectrum with the spectrum obtained from an authentic sample of tetrakis(pyridine)platinum-(II) chloride.

The reaction of this product with an excess of concentrated hydrochloric acid yielded *trans*-dichlorobis(pyridine)platinum-(II). The product was identified by comparison of the infrared spectrum with that of the previously prepared compound.

(6) **Reaction of Pyridine with Cycloheptatrienylium Hexahaloplatinates.**—A mixture of 50 ml. of pyridine and 0.15 mmole of the appropriate cycloheptatrienylium hexahaloplatinate was refluxed for 8 hr., cooled, and evaporated at room temperature to approximately 25 ml. The white crystalline product was separated by filtering and recrystallized from pyridine. The products were identified as tetrakis(pyridine)platinum(II) chloride and tetrakis(pyridine)platinum(II) bromide by comparison of

the infrared spectra of previously prepared compounds. Recrystallization of tetrakis(pyridine)platinum(II) chloride from nitromethane yielded *trans*-dichlorobis(pyridine)platinum(II).

(7) **Reaction of Pyridine with Hexachloroplatinic Acid.**—A suspension of dipyridinium hexachloroplatinate, prepared by mixing 1.4 g. (3.6 mmoles) of chloroplatinic acid hexahydrate with 25 ml. of pyridine, was refluxed for 2 hr. and the hot solution filtered. The filtrate was cooled and evaporated at room temperature to approximately 10 ml. to yield the white crystalline tetrakis(pyridine)platinum(II) which upon recrystallization from nitromethane gave *trans*-dichlorobis(pyridine)platinum(II), identified by comparison of its infrared spectrum with that of an authentic sample.

Molecular Weight.—The molecular weights were determined by use of a Mechrolab vapor phase osmometer.

Infrared Spectra.—The infrared spectra of the solid products were determined in potassium bromide pressed disks and the region from 400 to 4000 cm.$^{-1}$ was examined for absorption bands. The spectra of liquid samples were observed by use of a 0.1-mm. sodium chloride cell in the region 750–4000 cm.$^{-1}$.

X-Ray Diffraction Studies.—X-Ray diffraction data were collected photographically using a conventional powder camera, 114 mm. in diameter, and filtered copper radiation.[18]

Discussion

The reaction of dichloro(cycloheptatriene)platinum(II) with lithium bromide in acetone yields dibromo(cycloheptatriene)platinum(II) (III). This dibromo derivative decomposes at 154–155° and corresponds in certain other details to the product (I) isolated from the reaction of platinum(IV) bromide and cycloheptatriene. The major difference in the properties of I and III, as in the case of the previously mentioned chloro derivative, was the lack of infrared absorption bands in III due to the $C_7H_7^+$ moiety.

An examination of the spectrum of the crude product from the reaction of cycloheptatriene and platinum(IV) bromide or bromoplatinic acid disclosed the presence of infrared bands associated with the cycloheptatrienylium ion and also all the major infrared bands present in the spectrum of dibromo(cycloheptatriene)platinum(II); see Table I. In the process of purification, the crude reaction product was extracted with methylene chloride and separated into a methylene chloride soluble fraction and an insoluble orange fraction.

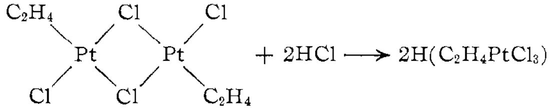
Analysis of the insoluble fraction indicated the formula $(C_7H_7)_2PtBr_6$ (IV). The reaction of IV with aqueous potassium cyanide yielded 7-cyano-1,3,5-cycloheptatriene, a reaction characteristic of cycloheptatrienylium ion.[15] A comparison of the infrared spectrum of IV with the spectrum of a sample of $(C_7H_7)_2PtCl_6$, prepared from cycloheptatrienylium chloride and chloroplatinic acid, indicated nearly identical spectra in the region 400–4000 cm.$^{-1}$ and the presence of all major bands associated with the cycloheptatrienylium ion.

The product isolated from the methylene chloride fraction decomposed at 154–155° and the analysis and molecular weight measurements indicated the formula $C_7H_8PtBr_2$. This product liberated cycloheptatriene upon reaction with an aqueous potassium cyanide solution, and the infrared spectrum of this fraction was identical with the spectrum of dibromo(cycloheptatriene)platinum(II) (III).

A comparison of the X-ray powder diagram of the crude product from the reaction of platinum(IV) bromide or bromoplatinic acid with cycloheptatriene and the X-ray powder diagrams of pure cycloheptatrienylium hexabromoplatinate and dibromo(cycloheptatriene)platinum(II) indicated that the crude material was primarily a mixture of these two compounds and no chemical transformation had occurred during the extraction with methylene chloride.

A similar reaction occurs when cycloheptatriene is mixed with an acetic acid solution of chloroplatinic acid. X-Ray powder diagrams and infrared spectra again indicate that the crude product from this reaction consists of a mixture of cycloheptatrienylium hexachloroplatinate and dichloro(cycloheptatriene)platinum(II).

The chemical evidence used to support the proposed structural assignment of I is at best ambiguous. The reaction of hydrochloric acid with platinum–olefin compounds is not characteristic of all of the compounds of this class. It is true that dimeric species such as *sym-trans-μ*-di-chloro-bis[chloro(ethylene)platinum(II)] do react with hydrochloric acid as shown below, however the group of platinum–olefin compounds containing chelated diolefins is extremely resistant to the displacement of an olefinic linkage by a halide ion in a strongly acidic medium. In the present work we found that both the chloro and bromo derivatives of the platinum–olefin complexes containing cycloheptatriene can be refluxed with concentrated aqueous solutions of the appropriate hydrogen halide for prolonged periods and the platinum–olefin compound can be recovered unchanged. The cycloheptatrienylium salts are soluble in concentrated solutions of the hydrogen halides and can also be recovered unchanged by evaporation of these solutions.



The reaction of the platinum–olefin compounds containing cycloheptatriene with pyridine in a 1:2 mole ratio results in the displacement of the olefin and the formation of *cis*-dihalobis(pyridine)platinum(II). In the presence of excess pyridine the complexes reacted to form tetrakis(pyridine)platinum(II) halide salts which were converted to the *trans*-dihalobis(pyridine)platinum(II) for identification and characterization.[17]

The cycloheptatrienylium platinum(IV) salts are soluble in hot pyridine and prolonged refluxing of the solutions followed by cooling to room temperature produces colorless crystalline tetrakis(pyridine)platinum(II) halide. A similar reaction occurs upon mixing and refluxing the chloroplatinic acid and excess pyridine. The initial step of the reaction of pyridine with chloroplatinic acid appears to be the formation of the yellow-brown dipyridinium hexachloroplatinate which

---

[18] Copies of the X-ray powder photographs may be obtained from J. R. D.

is then partially converted to the tetrakis(pyridine)-platinum(II) salt upon continual refluxing in the presence of excess pyridine.

Analysis of the crude products and extraction procedures with methylene chloride indicated an approximate mole ratio of 2 moles of platinum–olefin complex to 1 mole of cycloheptatrienylium compound were formed when cycloheptatriene reacted with platinum-(IV) bromide, bromoplatinic acid, or chloroplatinic acid. The equations below represent the stoichiometry of these reactions.

$$4C_7H_8 + 3PtBr_4 \longrightarrow (C_7H_7)_2PtBr_6 + 2C_7H_8PtBr_2 + 2HBr$$

$$4C_7H_8 + 3H_2PtX_6 \longrightarrow (C_7H_7)_2PtX_6 + 2C_7H_8PtX_2 + 8HX$$

The reactions of cycloheptatriene with the platinum-(IV) compounds in boiling acetic acid occur rapidly, and the product isolated about 1 min. after addition of the olefin did not differ materially in composition or quantity from a similar product separated 3 hr. after the addition of the olefin to a solution of the platinum(IV) compound.

Although a clear insight into the mechanism of the reaction between platinum(IV) and 1,3,5-cycloheptatriene is not possible from our limited study of the system, it appears that the initial step involves the abstraction of hydride ion from the olefin and the concomitant reduction of platinum from a +4 to a +2 oxidation state. The subsequent coordination of the platinous ion to the olefin and the simultaneous formation of the cycloheptatrienylium compound occur with extreme rapidity.

Recently Chatt and Guy reported[19] an unsuccessful attempt to prepare a triphenylcyclopropenium ion derivative in which this ion was bonded covalently to platinum. In view of the known ability of cycloheptatriene to undergo protonation[20] and hydride ion abstraction reactions[21] while coordinated in certain metal carbonyl complexes, similar reactions were examined as possible methods for obtaining carbonium ion species attached to platinum.

The reaction of dichloro(cycloheptatriene)platinum-(II) with tritylium tetrafluoroborate generated *in situ*[22] or in a dichloromethane medium[23] did not produce the desired cycloheptatrienylium ion species *via* hydride ion abstraction, but instead a nearly quantitative recovery of starting material was realized. The attempted protonation of dichloro(cycloheptatriene)platinum(II) with tetrafluoroboric acid in an acetic anhydride medium also yielded starting material upon purification of the reaction mixture.

In summary, neither the present investigation nor previous reports has yielded any evidence for carbonium species bonded in a coordinate fashion to a platinum atom.

Acknowledgment.—We wish to acknowledge the support of the Army Research Office (Durham), Grant DA-ARO(D)-31-124-G26.

[19] J. Chatt and R. G. Guy, *Chem. Ind.* (London), 212 (1963).

[20] (a) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961); (b) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).

[21] H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).

[22] H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

[23] J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3959 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA

Metal–Olefin Compounds. VI. The Crystal Structure of Catena-μ-chloro-(cyclooctatetraene)copper(I)

BY N. C. BAENZIGER, G. F. RICHARDS, AND J. R. DOYLE

Received April 27, 1964

A single crystal, three-dimensional X-ray study of catena-μ-chloro-(cyclooctatetraene)copper(I) has been carried out. The structure consists of continuous chains formed by the copper and chlorine atoms extending through the crystal in the *a* direction with one olefinic bond closely bound to each copper atom. The carbon atoms of the bonded olefinic group are approximately coplanar with the copper and adjacent chlorine atoms of the chain, and the coordination about the copper(I) may be described as a distorted trigonal arrangement. The bond distances and the bond angles associated with the closely bound atoms are: Cu–Cl, 2.288 ± 0.002 Å., 2.284 ± 0.002 Å.; Cl–Cu–Cl, 106.4 ± 0.1°; Cl–Cu–(C_1–C_2 center), 123.1 ± 0.2°, 130.1 ± 0.2°; Cu–C_1, 2.073 ± 0.010 Å.; Cu–C_2, 2.097 ± 0.007 Å. A variety of weighting schemes was used in the least-squares data refinement procedures to test the sensitivity of the resulting interatomic distances to the weighting scheme and thus provide a test for systematic errors.

Introduction

By means of a new method of preparation of copper-(I)–olefin compounds,[1] a number of well-crystallized complexes have recently become available for structural studies. A preliminary report has been made on the structure of one of these compounds, di-μ-chloro-bis-(1,5-cyclooctadiene)dicopper(I),[2] in which the co-

[1] H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).

[2] J. H. van den Hende and W. C. Baird, *J. Am. Chem. Soc.*, **85**, 1009 (1963).