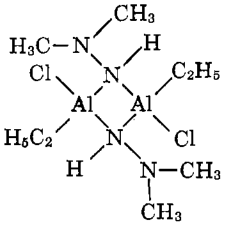
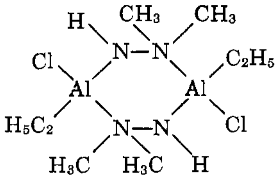
than the frequency separation of the resonance peaks corresponding to the two environments of the methyl groups, then the two peaks would merge into a single one of intermediate chemical shift. It is not possible to make a very good prediction of the expected frequency difference, but it could well be of the order of 10 c.p.s., so that the average lifetime of the bond in the addition compound would then have to be of the order of 0.1 sec. or longer in order for the two peaks to be resolved. Since the rate of any exchange process should be reduced at lower temperatures, a 50% solution of tetramethylhydrazine–triethylaluminum in carbon disulfide was run at −90°. A slight broadening of the resonance of the methyl peaks was observed, but the results were not clear-cut enough to indicate that a chemical shift difference was the cause.

The compound ethylchloro-2,2-dimethylhydrazinoaluminum, $[C_2H_5ClAlNHN(CH_3)_2]_2$, can exist as either a four- or a six-membered ring. The bond angles would favor the six-membered ring as the lowest energy configuration. If we assume that the six-membered ring is formed and assume sp^3 coordination of both nitrogen and aluminum, the ring can exist in either the chair or the boat conformation.





The pyrolysis of ethylchloro-2,2-dimethylhydrazinoaluminum produced a condensed compound which is insoluble in common organic solvents and which has a melting point 160° higher than the parent compound. Since only 85% of the theoretical amount of ethane was evolved it is postulated that the resulting polymer is end stopped with 15% of the parent compound.

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Metal–Olefin Compounds. IV. The Preparation and Properties of Some Aryl and Alkyl Platinum(II)–Olefin Compounds

BY C. R. KISTNER, J. H. HUTCHINSON, J. R. DOYLE,[1] AND J. C. STORLIE

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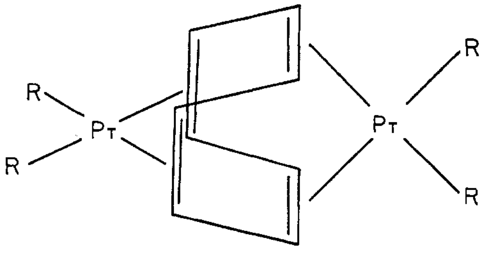
The reaction of alkyl or aryl Grignard reagents with platinum(II)-olefin compounds containing cyclic diolefins yields a series of products in which the halide groups initially present in the platinum(II)-olefin compounds are partially or completely replaced to give compounds of the type (olefin)PtR$_2$ or (olefin)PtRI. The methods of preparation and some physical properties of this series of compounds are reported. The chemical reactivity and spectral data are discussed, and possible structures for the compounds are proposed.

Introduction

Recently Chatt and Shaw[2,3] predicted that platinum(II) alkyl and aryl derivatives could be stabilized by the presence of ligands that produce large crystal field splitting and using a series of substituted phosphines they succeeded in isolating a number of these compounds. They reported[3–5] that the substituted phosphine derivatives of nickel(II), palladium(II), and platinum(II) containing σ-bonded *o*-substituted aryl derivatives had greater stability than the *p*-substituted analogs. The difference in stability of these compounds was believed to be due to a combination of electronic and kinetic effects.

Calvin and Coates[6] have reported the isolation of bismethyl-(1,5-cyclooctadiene)-palladium(II), indicating that cyclic polyolefins can also be used as stabilizing ligands.

In the previous paper in this series[7] the binucle r



R = CH_3 or C_6H_5

I

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[1] To whom communications concerning this paper should be addressed.

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[3] J. Chatt and B. L. Shaw, *ibid.*, 4020 (1959).

[4] J. Chatt and B. L. Shaw, *ibid.*, 1718 (1960).

[5] J. Chatt, *Record Chem. Progr.*, **21**, 147 (1960).

[6] G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).

[7] J. R. Doyle, J. H. Hutchinson, N. C. Baenziger, and L. W. Tresselt, *J. Am. Chem. Soc.*, **83**, 2768 (1961).

TABLE I

COMPOUNDS OF THE TYPE (OLEFIN)PtI_2

Complexed olefin	Compound	mmoles K_2PtCl_6	mmoles olefin	Yield, %	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Cyclooctatetraene	$C_8H_8PtI_2$[a]	20.6	38.5	78	17.36	17.72	1.46	1.38
1,5-Cyclooctadiene	$C_8H_{12}PtI_2$[b]	10.0	41.8	56	17.24	17.10	2.17	2.32
Norbornadiene	$C_7H_8PtI_2$[c]	39.2	160	74				

[a] K. A. Jensen, *Acta Chem. Scand.*, 1, 868 (1953). [b] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957). [c] R. J. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960).

TABLE II

ALKYL AND ARYL PLATINUM(II) OLEFIN DERIVATIVES

Compound	Prepn.	mmoles (olefin)-PtI_2	Recrystn. solvent	Color	Yield, %	Dec. pt., °C.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Cyclooctatetraene										
$C_8H_8Pt(CH_3)_2$	B	. . .	Benzene	Yellow	5	80–90	36.46	37.85	4.28	4.85
$C_8H_8Pt_2(CH_3)_4$[7]	B	10.0	CH_2Cl_2	Yellow	36	168–171	25.98	26.41	3.63	3.81
$C_8H_8Pt_2(C_6H_5)_4$[7]	B	3.6	CH_2Cl_2–hexane	Green	70	155–165	47.86	47.30	3.51	3.56
$C_8H_8Pt(C_2H_5)I$	B	3.6	CH_2Cl_2–hexane	Yellow	4	25–30	26.38	24.24	2.88	3.15
$C_8H_8Pt(p\text{-}CH_3C_6H_4)_2$	B	4.0	CH_2Cl_2–hexane	White	29	137–140	54.86	54.84	4.60	4.71
$C_8H_8Pt(o\text{-}CH_3C_6H_4)_2$	B	9.4	CH_2Cl_2–hexane	White	64	171–174	54.86	54.39	4.60	4.42
$C_8H_8Pt(1\text{-}C_{10}H_7)_2$	B	6.0	CH_2Cl_2	White	65	175–195	60.73	60.17	4.00	4.10
1,5-Cyclooctadiene										
$C_8H_{12}Pt(CH_3)_2$	B	7.1	CH_2Cl_2	Colorless	71	94–95	36.01	36.20	5.44	5.28
$C_8H_{12}Pt(C_2H_5)_2$	B	2.6	Benzene	Yellow	5	25–30	39.86	39.50	6.13	6.15
$C_8H_{12}Pt(C_6H_5)_2$	B	2.2	Benzene	White	94	52	52.49	50.80	4.84	4.93
$C_8H_{12}Pt(p\text{-}CH_3C_6H_4)I$[a]	B	9.0	CH_2Cl_2–hexane	White	70	147	34.55	34.64	3.67	3.62
$C_8H_{12}Pt(o\text{-}CH_3C_6H_4)I$	D[b]	0.4	Benzene	Cream	51	186–187	34.55	34.55	3.67	3.99
$C_8H_{12}Pt(o\text{-}CH_3C_6H_4)_2$[c]	B	9.0	CH_2Cl_2–hexane	White	90	190–192	54.40	54.38	5.39	5.30
$C_8H_{12}Pt(1\text{-}C_{10}H_7)_2$	B	8.0	CH_2Cl_2	Cream	47	214–219	60.29	59.93	4.70	4.76
Norbornadiene										
$C_7H_8Pt(CH_3)I$	B	10.0	CH_2Cl_2	Orange	45	122–124	22.39	22.16	2.58	2.56
$C_7H_8Pt(C_6H_5)_2$	B	5.5	Hexane	Colorless	34	146–152	51.67	51.46	4.10	4.24
$C_7H_8Pt(p\text{-}CH_3C_6H_4)_2$	B	6.6	Hexane	Colorless	5	97–99	53.70	52.35	4.72	4.66
$C_7H_8Pt(o\text{-}CH_3C_6H_4)_2$	B	4.4	Benzene	White	51	160–170	53.70	53.73	4.72	4.91
$C_7H_8Pt(1\text{-}C_{10}H_7)_2$	B	4.1	Acetone	Cream	35	170–190	59.86	60.45	4.09	3.93
Dicyclopentadiene										
$C_{14}H_{12}Pt(CH_3)I$	B[d]	4.1	Ether	Orange	5	25–30	28.14	29.74	3.22	3.73

[a] Mol. wt.: Calcd., 521. Found, 507. [b] Reaction temperature, 115°. [c] Mol. wt.: Calcd., 486. Found, 469. [d] $LiCH_3$ used in place of the methyl Grignard in procedure B.

methyl and phenyl platinum(II)–cyclooctatetraene compounds were reported and a cyclooctatetraene bridged structure (I) was proposed for these compounds. In order to examine the scope of this series of compounds and to provide further chemical evidence for the proposed binuclear bridge structure, the synthesis of a series of alkyl and aryl derivatives of platinum(II) containing cyclic diolefins such as norbornadiene, dicyclopentadiene, and 1,5-cyclooctadiene was carried out. The series involving cyclooctatetraene has been expanded to include other aryl derivatives and the reactivity of this new class of compounds with reagents such as pyridine, triphenylphosphine, and methyl iodide was investigated.

Experimental

Procedure A. The Preparation of Diiodo-(cyclic polyolefin)-platinum(II) compounds.—To a suspension of potassium hexachloroplatinate, K_2PtCl_6, in 250 ml. of water was added the appropriate olefin followed by a solution containing a twofold excess of potassium iodide in 30 ml. of water. The resulting red mixture was treated with a solution containing 2.0 g. of sodium bisulfite in 50 ml. of water until the supernatant solution was colorless. The mixture was stored at ambient temperatures for 3 hr. and then filtered. The crude product was washed with 50 ml. of absolute ethanol followed by 50 ml. of anhydrous ether and finally recrystallized from methylene chloride (see Table I).

Diiodo-(cyclopentadiene)-platinum(II) was prepared by a previously described procedure.[8]

Procedure B. Grignard Reactions.—An excess of Grignard was prepared in the usual manner, filtered, and added to a suspension of diiodo-(cyclic polyolefin)-platinum(II) in anhydrous benzene. The resulting solution was hydrolyzed by use of an ammonium chloride–ice mixture and the benzene–ether layer was separated and dried with anhydrous sodium sulfate. The dried solution was decolorized with charcoal, filtered, and the product was recovered by evaporation of the solvent at room temperature. The product was purified by recrystallization (see Table II).

Procedure C. Olefin Displacement Reactions. (1) Reactions with Triphenylphosphine.—A sample of the platinum(II)–olefin compound was suspended in a solution containing a twofold excess of triphenylphosphine and the mixture was heated. The solution was kept at the reaction temperature for 0.5–2 hr., then it was cooled and evaporated at room temperature. The residue was recrystallized to yield the pure product (see Table III).

(2) **Reactions with Pyridine.**—A sample of the platinum(II)–olefin compound was suspended in a 10–30-fold excess of pyridine and heated. The solution was kept at the reaction temperature for 0.5–2 hr., then it was cooled and evaporated at room

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[8] J. R. Doyle and H. B. Jonassen, *J. Am. Chem. Soc.*, **78**, 3965 (1956).

TABLE III

ALKYL AND ARYL PLATINUM COMPOUNDS CONTAINING TRIPHENYLPHOSPHINE

Compound	Prepn.	Solvent	React. temp., °C.	Recrystn. solvent	Color	Yield, %	Dec. pt., °C.	Carbon		Hydrogen	
								Calcd.	Found	Calcd.	Found
$[(C_6H_5)_3P]_2Pt(CH_3)I$	C	Xylene	138	Benzene	White	55	273–275	51.57	50.82	3.86	3.48
$[(C_6H_5)_3P]_2Pt(CH_3)_2$	C	Xylene	138	Benzene	Colorless	14	206–209	60.86	60.76	4.84	4.95
$[(C_6H_5)_3P]_2Pt(p\text{-}CH_3C_6H_4)_2$[a]	C	Benzene	80	Benzene	White	6.5	161–170	66.57	65.80	4.91	5.01
$[(C_6H_5)_3P]_2Pt(p\text{-}CH_3C_6H_4)I$	C	Xylene	138	CH_2Cl_2	White	52	>230	55.07	54.91	3.98	3.95
$[(C_6H_5)_3P]_2Pt(o\text{-}CH_3C_6H_4)_2$	C	Xylene	138	CH_2Cl_2–hexane	White	11	179–189	66.57	66.52	4.91	4.82
$[(C_6H_5)_3P]_2Pt(CH_3)I_3$	D	CH_3I	115	Benzene	Red	97	215	39.84	39.66	2.98	3.02

[a] Mol. wt.: Calcd., 906. Found, 884.

TABLE IV

ALKYL AND ARYL PLATINUM COMPOUNDS CONTAINING PYRIDINE

Compound	Prepn.	React. temp., °C.	Recrystn. solvent	Color	Yield, %	Dec. pt., °C.	Carbon		Hydrogen		Nitrogen	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
$(C_5H_5N)_2Pt(CH_3)_2$[a]	C	50	CCl_4–CH_2Cl_2	Yellow	5	206–209	...	...	...	...	...	...
$(C_5H_5N)_2Pt(CH_3)I$	C	50	CH_2Cl_2	Yellow	65	127–136	26.67	26.93	2.64	2.91	5.65	6.28
$(C_5H_5N)_2Pt(C_6H_5)_2$	C	80	CH_2Cl_2	White	50	157–165	52.05	51.39	3.97	3.78	5.52	5.52
$(C_5H_5N)_2Pt(p\text{-}CH_3C_6H_4)_2$	C	80	Benzene	White	72	145–152	53.81	52.90	4.51	4.45	5.24	5.33
$(C_5H_5N)_2Pt(p\text{-}CH_3C_6H_4)I$	C	80	Benzene	White	24	132–143	35.74	36.11	3.00	3.30	4.90	5.12
$(C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)_2$	C	80	CH_2Cl_2–benzene	White	87	155–158	53.81	53.76	4.51	4.21	5.24	5.11
$(C_5H_5N)_2PtCH_3(o\text{-}CH_3C_6H_4)I_2$	D	42	CH_2Cl_2	Yellow	15	134–138	30.30	29.86	2.86	2.90	3.93	3.86

[a] Characterized from the infrared absorption spectrum.

temperature. The residue was recrystallized to yield the pure product (see Table IV).

(3) **Reactions with Potassium Cyanide.**—A suspension of 0.1 mmole of the platinum(II)–olefin compound in 4 ml. of carbon tetrachloride was added to a solution containing 0.1 g. (15.4 mmoles) of potassium cyanide in 10 ml. of water. The mixture was stirred for 2 hr., and the layers were separated and dried. The carbon tetrachloride solution was examined *via* gas chromatography and infrared spectroscopy to determine the presence of the unchanged olefin.

Procedure D. Reactions with Methyl Iodide.—A small sample of a bis-(*o*-tolyl)-platinum(II) derivative was added to 25–35 ml. of methyl iodide and heated. The mixture was maintained at the reaction temperature for 6–12 hr., and then it was cooled to room temperature. Evaporation of the solution and recrystallization of the resulting residue yielded the pure product.

Infrared Spectra.—The infrared absorption spectra were determined by use of Perkin-Elmer Model 21 and Infracord spectrophotometers covering the range of 2–25 μ. The spectra of all solids were observed in potassium bromide pressed disk media. The relatively low solubility of the compounds in solvents suitable for infrared spectroscopy precluded the acquisition of reliable solution spectra. The spectra of the pure olefins were determined as smears between potassium bromide plates. The spectra of the products from the potassium cyanide displacement reactions were examined in carbon tetrachloride solutions.

Proton Magnetic Resonance Spectra.—The p.m.r. spectra were recorded on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. The sample of bismethyl-(1,5-cyclooctadiene)-platinum(II) was examined as a 5 wt. % solution and μ-cyclooctatetraene-bis-[bis-(methyl)-platinum(II)] as a 3.5 wt. % solution in deuteriochloroform. The concentrations utilized were approximately saturated solutions of the compounds in deuteriochloroform. The data for these compounds are summarized in Table V.

Molecular Weight.—The molecular weights were determined in chloroform using a Mechrolab "Vapor Phase Osmometer." It was not possible to determine the molecular weight of a number of compounds because of low solubility in suitable solvents.

Gas Chromatography.—The recovery of the cyclic polyolefins by the reaction of potassium cyanide with compounds of the type (cyclic polyolefin)PtR_2 or (cyclic polyolefin)PtRI was determined using an F and M Model 500 programmed temperature gas chromatograph.

Discussion

The crystal structure of μ-cyclooctatetraene-bis-[bis-(methyl)-platinum(II)] is presently being investigated in this laboratory. In our preliminary studies of this structure it became apparent that the presence of two strongly scattering platinum atoms in this molecule presented a major obstacle in the determination of the precise location of the carbon atoms. The structure factor calculations were carried out in the usual fashion and yielded surprisingly low discrepancy factors (R = 9–18%); however, this agreement was achieved with platinum atom contributions and did

TABLE V

Compound	δ, p.p.m.		*J*, c.p.s.	Relative intensity
$C_8H_8Pt_2(CH_3)_4$	CH	5.52 (7 bands)	12	8 (8H)
			26	
			40	
	CH_3	0.78 (triplet)	81	13 (12H)
$C_8H_{12}Pt(CH_3)_2$	CH	4.89 (triplet)	40	4.5 (4H)
	CH_2	2.38 (triplet)	18	9.2 (8H)
	CH_3	0.81 (triplet)	86	8.5 (6H)
$C_8H_8Pt_2(C_6H_5)_4$[a]	$CH(C_8H_8)$	5.85 (7 bands)	14	...
			30	...
			46	...
	CH (phenyl)	6.93		...
	(broad triplet)	7.06		...
		7.16		...

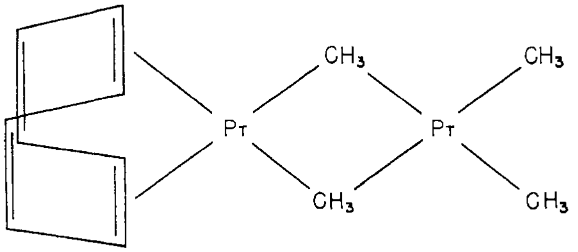
[a] The spectrum of this compound was observed in a methylene chloride solution because of the low solubility of the material in deuteriochloroform. The presence of a relatively strong solvent band at $\delta = 5.80$ p.p.m. masked the downfield bands of the CH peak for cyclooctatetraene. The upfield portion of the spectra appears to be similar to that observed for $C_8H_8Pt_2(CH_3)_4$ with a single strong peak and three weak side bands. The *J* values were calculated by measuring the splitting between the single strong band and side bands and doubling this value. Accurate proton counts could not be obtained because of the low solubility and solvent interference.

not include carbon atom contributions to the structure factors. In addition, one set of Weissenberg data indicated either partial decomposition of the compound or an extremely small contribution to the measured intensities by the carbon atoms present in the molecule. A new set of data using the third crystal setting has now been collected and new series of computer programs to facilitate the structure factor calculations on this compound have been completed. The results of our single crystal studies will be reported upon completion of the calculations on the newly acquired data.

In order to obtain further information concerning the structure of this compound, other possible approaches were examined. In the previous paper[7] in this series the spectral data presented indicated a bridged cyclooctatetraene configuration. Unfortunately, this evidence is not unequivocal and presents no evidence on the conformation of the cyclooctatetraene in the platinum complex.

The present report concerns our efforts to gather further evidence concerning the structure of μ-cyclooctatetraene-bis-[bis-(methyl)-platinum(II)] and similar compounds and to examine the extent to which cyclic olefins stabilize the alkyl and aryl derivatives of platinum(II).

Initially two possible structures, I and II, were considered for this compound; however, the recently determined[9] structure of μ-cyclooctatetraene-bis-(tricarbonyliron) indicates that the cyclooctatetraene may adopt conformations other than its usual "tub" form and consequently several variations of I with the cyclooctatetraene in different conformations are possible.



II

If the cyclooctatetraene derivative had the configuration shown in structure II, then cyclic diolefins such as norbornadiene, dicyclopentadiene, or 1,5-cyclooctadiene, in which the olefinic bonds are oriented in a similar fashion to those in cyclooctatetraene, might be expected to yield similar methyl-bridged derivatives. The reaction of diiodo-(norbornadiene)-platinum(II) with methylmagnesium iodide proceeded smoothly, but the product isolated was an iodomethyl derivative and not the fully methylated derivative expected.

$$C_7H_8PtI_2 + CH_3MgI\text{ (excess)} \longrightarrow C_7H_8Pt(CH_3)I$$

The reaction of diiodo-(dicyclopentadiene)-platinum(II) with methylmagnesium iodide did not occur and the starting material was recovered from this reaction. By the utilization of methyllithium, iodo-(methyl)-dicyclopentadieneplatinum(II) was finally isolated in small yield. Contrary to the preceding reactions, diiodo-(1,5-cyclooctadiene)-platinum(II) reacted readily with methylmagnesium iodide to give a dimethyl derivative of 1,5-cyclooctadieneplatinum(II).

The 1:1 ratio of olefin to platinum in the methyl derivatives containing norbornadiene, 1,5-cyclooctadiene, or dicyclopentadiene precludes a structure for this group similar to the cyclooctatetraene derivatives.

Further evidence in support of the proposed structure I was supplied by the reaction of phenylmagnesium iodide with diiodo-(cyclooctatetraene)-platinum(II) to give the tetra-(phenyl)-diplatinum analog of the methyl compound. The possibility of the phenyl groups bridging in a manner similar to that proposed in structure II is unlikely; no bonding or major steric difficulties would be encountered with a cyclooctatetraene bridged configuration.

The p.m.r. spectrum of $C_8H_8Pt_2(CH_3)_4$ is consistent with structure I in that only two strong bands, δ =

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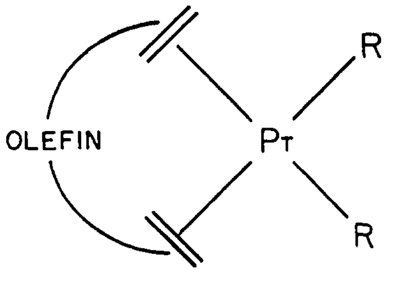
(9) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

0.78 p.p.m. (CH_3) and $\delta = 5.52$ p.p.m. (CH) are observed. The splitting pattern observed in the spectrum of this compound is presumably due to the presence of the magnetically active Pt^{195} isotope or possible interaction of the cyclooctatetraene protons and the methyl group protons. The splitting of the ethylene protons in Zeise's salt by Pt^{195} has been reported[10] with a coupling constant, $J_{Pt^{195}-H}$, of 34 c.p.s. In this investigation coupling constants of 40 and 46 c.p.s. were observed for the C–H protons in coordinated cyclooctatetraene and 1,5-cyclooctadiene. The spectrum of the phenyl analog, $C_8H_8Pt(C_6H_5)_4$, displayed a similar pattern in the C–H resonance region with a single strong band and three weak side bands, on the high field side. The low field spin–spin bands were obscured by a strong solvent band.

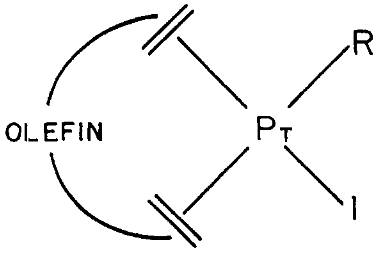
This evidence coupled with previously reported infrared[7] data lends plausibility to the bridged configuration I for the methyl and phenyl derivatives containing cyclooctatetraene, but it does not define the conformation of the cyclooctatetraene ring.

The norbornadiene, 1,5-cyclooctadiene, and dicyclopentadiene methylplatinum derivatives have similar infrared spectra to the parent diiodo compounds, indicating that the chelate structure IIIa or IIIb is retained in the methylated derivatives. In addition, the p.m.r. spectrum of bis-(methyl)-1,5-cyclooctadiene-platinum(II) displays three strong bands, $\delta = 4.89$ p.p.m. (CH), $\delta = 2.38$ p.p.m. (CH_2), and $\delta = 0.81$ p.p.m. (CH_3), consistent with the general structure IIIa.

In an attempt to extend the series of binuclear cyclooctatetraene derivatives by use of Grignard reagents, derived from 1-bromonaphthalene, *o*-bromotoluene, and *p*-bromotoluene, it was found that mononuclear derivatives of type IIIa or IIIb were consistently isolated.



IIIA



IIIB

The reaction of methylmagnesium iodide with diiodo-(cyclooctatetraene)-platinum(II) was re-examined in conjunction with the investigation of cyclopentadienyl derivatives and a yellow crystalline dimethyl-(cyclooctatetraene)-platinum(II) derivative was isolated. This compound decomposed slowly at room temperature. Repeated recrystallization of dimethyl-(cyclooctatetraene)-platinum(II) from benzene or warming of the solid on a steam bath followed by recrystallization of the residue gave the binuclear derivative I. Although the liberation of cyclooctatetraene was not unequivocally established by chemical means, the characteristic odor of this compound was detected when the mononuclear derivative was heated on the steam bath. A possible equation to represent this reaction is

$$2C_8H_8Pt(CH_3)_2 \longrightarrow (CH_3)_2PtC_8H_8Pt(CH_3)_2 + C_8H_8$$

To explore further the scope of the reaction of the iodo derivatives of the chelated platinum–olefin compounds containing cyclooctatetraene, 1,5-cyclooctadiene, and norbornadiene with Grignard reagents, a number of reactions, utilizing a variety of alkyl and aryl Grignard reagents, were examined.

Several general trends were noted in the products isolated from these reactions. First, with the exception of the aforementioned methyl and phenyl derivatives containing cyclooctatetraene, all of the products have a 1:1 ratio of cyclic olefin to platinum and are mononuclear derivatives. Second, the products containing aryl groups are of greater kinetic stability than those derived from the alkyl Grignard reagents with the exception of the methyl derivatives, and within the aryl series the following order of decreasing kinetic stability holds: 1-naphthyl > *o*-tolyl > phenyl > *p*-tolyl. A similar sequence has also been noted[3,5] in the aryl series of platinum compounds containing substituted phosphines. Third, the kinetic stability decreases in the alkyl series with an increase in the size of the alkyl group and only the methyl derivatives display appreciable stability at room temperature. In reactions involving the use of ethylmagnesium iodide only one derivative was fully characterized and this decomposed slowly at room temperature. The reactions of diiodo-(cyclic polyolefin)-platinum(II) compounds with the Grignard reagents derived from *t*-butyl or dihaloalkyls, $Br(CH_2)_xBr$, where $x = 5–8$, led to the decomposition of the olefin complex and no readily isolable product. Finally, no appreciable difference was noted in the stabilizing ability of the various cyclic polyolefins used in this investigation.

Of special interest was the reaction of diiodo-(cyclooctatetraene)-platinum(II) with cyclopentadienylmagnesium iodide and a variety of other metallic cyclopentadienyl compounds. Two products were isolated from these reactions, a yellow crystalline material corresponding closely to a binuclear derivative, $C_8H_8Pt_2(C_5H_5)_4$, and a red crystalline material whose analysis

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[10] D. P. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

corresponded to a mononuclear species, $C_8H_8Pt(C_5H_5)_2$. Approximately 30 reactions were attempted, but only on three occasions were similar products isolated. We are now in the process of evaluating the variables in these reactions to develop a reproducible synthetic method and obtain sufficient quantities of material to carry on structural studies of these species.

In the previous report in this series we indicated that pyridine and triphenylphosphine displaced cyclooctatetraene from the alkyl and aryl platinum(II) derivatives containing this compound. The displacement reaction of pyridine or triphenylphosphine appears to be general for the olefin–platinum alkyl or aryl derivatives and proceeds according to the equations

$$(\text{olefin})PtR_2 + 2py \longrightarrow (py)_2PtR_2 + \text{olefin}$$

$$(\text{olefin})PtR_2 + (C_6H_5)_3P \longrightarrow [(C_6H_5)_3P]_2PtR_2 + \text{olefin}$$

$$(\text{olefin})PtRI + 2py \longrightarrow (py)_2PtRI + \text{olefin}$$

$$(\text{olefin})PtRI + 2(C_6H_5)_3P \longrightarrow [(C_6H_5)_3P]_2PtRI + \text{olefin}$$

A similar displacement reaction occurs upon treating a methylene chloride solution of the olefin–platinum alkyl or aryl compounds with an aqueous potassium cyanide solution. In addition, an examination of the methylene chloride solutions upon completion of the cyanide displacement reaction *via* gas chromatography indicated only the presence of the originally complexed olefin in this phase. Also, a comparison of the infrared spectra of the liberated olefins with authentic samples showed that the olefins had the same configuration as the starting materials.

The reactivity of the olefin–platinum alkyl or aryl derivatives parallels the thermal stability of these compounds. The aryl derivatives generally required prolonged treatment with pyridine or triphenylphosphine to liberate the olefin, whereas the methyl derivatives reacted in comparatively short time at the same temperatures. In all instances a single isomer of the pyridine or triphenylphosphine–platinum(II) alkyl or aryl derivatives was isolated.

In the investigation of compounds of the type $(R_3P)_2Pt(CH_3)_2$, where R is an alkyl group, it was reported[11] that the platinum–carbon stretch frequencies occur in the region of 500–600 cm.$^{-1}$. It was also noted that the absorption band associated with the platinum–carbon stretch frequency occurs as a doublet for the *cis* isomers and a single band for the *trans* isomer. The spectra of bis-(methyl)-1,5-cyclooctadieneplatinum(II) and μ-cyclooctatetraene-bis-[bis-(methyl)-platinum(II)] display a medium-to-strong doublet band of equal intensity at 563, 548 and 564, 548 cm.$^{-1}$, respectively. Compounds of the type $(R_3P)_2Pt(CH_3)I$, where R is an alkyl group, also have infrared bands in this region, but only a single band is noted[11] for both *cis* and *trans* isomers. An examination of the spectrum of iodo-(methyl)-norbornadieneplatinum(II) in this region revealed a strong doublet occurring at 572 and 544 cm.$^{-1}$ with the 572 cm.$^{-1}$ band of greater intensity.

The agreement between the spectral data on the fully methylated platinum–olefin compounds and the previously prepared phosphine derivatives indicates the expected *cis* configuration for this series. The reasons for the observed doublet in iodo-(methyl)-norbornadieneplatinum(II) are obscure, since the parent diiodo-(norbornadiene)-platinum(II) complex does not display any absorption bands in the region 480 to 580 cm.$^{-1}$. Possibly this compound has a different molecular configuration than the fully methylated derivatives, or the assignment of these bands to platinum–carbon stretch frequencies may not be unambiguous.

We examined the region of 1170–1200 cm.$^{-1}$ in the spectra of the methylated platinum–olefin compounds in an attempt to assign bands to the methyl deformation frequencies. Definitive assignments could not be made because of the presence of absorption bands associated with the other ligand molecules, which occur in this region. Similar difficulties precluded the assignments of platinum–carbon stretch frequencies in the region of 500–600 cm.$^{-1}$ for the derivatives containing aryl groups, coordinated pyridine, or triphenylphosphine.

The spectrum of μ-cyclooctatetraene-bis-[bis-(methyl)-platinum(II)] was discussed[7] briefly in a previous publication in this series. The absence of an absorption band at 1635 and 1609 cm.$^{-1}$ assigned to the C=C stretch frequency *possibly* indicates that all of the olefinic bands are involved in coordination to the metal atom. In contrast to this, the absorption spectra of the mononuclear platinum–cyclooctatetraene compounds display a weak band at 1635 cm.$^{-1}$ indicating the presence of uncoordinated olefinic bands in this series. A strong band at 1352 cm.$^{-1}$ appears to be characteristic of the binuclear platinum–cyclooctatetraene derivatives, while the mononuclear series has a strong band at 1372 cm.$^{-1}$.

Norbornadiene has a strong absorption band at 1550 cm.$^{-1}$ which is absent in the spectra of all of the platinum(II)–norbornadiene compounds studied, with the exception of the 1-naphthyl derivatives. In the 1-naphthyl derivatives a band occurring at 1550 cm.$^{-1}$ of weak intensity appears characteristic of this group in this series of compounds. All of the derivatives containing norbornadiene have a characteristic strong band in the region of 1174–1188 cm.$^{-1}$.

Similarly, the band occurring at 1661 cm.$^{-1}$ associated with the C=C stretch frequency in 1,5-cyclooctadiene is absent in all of the platinum–1,5-cyclooctadiene derivatives. A strong band at 1428 cm.$^{-1}$ occurs in the spectra of all of the platinum–1,5-cyclooctadiene derivatives.

Methyl iodide reacts with monomethyl derivatives containing trialkylphosphines, $(R_3P)_2PtCH_3I$, at 100° to yield platinum(IV) compounds of the type $(R_3P)_2Pt(CH_3)_2I_2$.[2] We have found that methyl iodide reacts with bis-(*o*-tolyl)-platinum(II) derivatives containing triphenylphosphine, pyridine, or 1,5-cyclooctadiene according to the equations

$$[(C_6H_5)_3P]_2Pt(o\text{-}CH_3\text{-}C_6H_4)_2 + CH_3I \xrightarrow{115^\circ} \underset{\text{IV}}{[(C_6H_5)_3P]_2Pt(CH_3)I_3}$$

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(11) D. M. Adams, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 2047 (1960).

$$(py)_2Pt(o\text{-}CH_3\text{-}C_6H_4)_2 + CH_3I \xrightarrow{42°} (py)_2Pt(o\text{-}CH_3\text{-}C_6H_4)(CH_3)I_2$$

V

$$C_8H_{12}Pt(o\text{-}CH_3\text{-}C_6H_4)_2 + CH_3I \xrightarrow{115°} C_8H_{12}Pt(o\text{-}CH_3\text{-}C_6H_4)I$$

VI

Each of these reactions is accompanied by the displacement of a tolyl group, and in the reactions involving the triphenylphosphine and pyridine derivatives the addition of methyl iodide yields a platinum(IV) compound. The isolation of VI, in which the platinum has an oxidation number of +2, indicated that these reactions may proceed *via* displacement and subsequent addition of methyl iodide in the presence of the bulky *o*-tolyl group.

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Nuclear Magnetic Resonance Spectra and Stereochemistry of Propenylmercury Compounds[1,2]

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The coupling constants and chemical shifts have been determined from the n.m.r. spectra of di-(*cis*-, *trans*-, and iso-)-propenylmercury. These values and the Hg^{199}–H coupling have been used to determine the absolute configurations of these compounds.

Introduction

Nesmeyanov[3] has synthesized isomers of propenylmercuric bromide and dipropenylmercury by the series of reactions

$$C_3H_5Br \xrightarrow{Li} C_3H_5Li \xrightarrow{HgBr_2} C_3H_5HgBr \xrightarrow{Na_2SnO_2} (C_3H_5)_2Hg$$

He proposed that this series of reactions takes place with complete retention of configuration and has further demonstrated this by a series of metal exchange reactions making use of "odd and even cycles." This conclusion is further substantiated by the proof of the structure of *trans*-β-chlorovinylmercuric chloride from X-ray crystal data[4] and its similarity in reactions to the propenyl derivatives. Dipole moment studies on the organomercuric chlorides were consistent with the stereochemical assignments as were the melting points of all of the derivatives and their infrared spectra. However, the data presented are only indirect proof of isomeric purity since the chemical analysis, melting points, and dipole moments would still be consistent with isomeric mixtures. To date, only the reaction of lithium metal with the propenyl halides has been shown to proceed with complete retention of geometry by direct spectroscopic evidence.[5]

The n.m.r. spectra of these compounds would allow the direct determination of the isomeric form present as well as detect the presence of mixtures of isomers or other impurities. The determination of the magnitude of the proton spin–spin coupling constants allows one to assign the relative steric relationships of the hydrogen atoms to one another since it has been well established[6] that $J_{trans} > J_{cis} > J_{gem}$. This relationship has been substantiated by a valence bond calculation of the vinyl coupling constants by Karplus.[7] The *trans* coupling constants have been shown to take on values from 14 to 20 c.p.s., the *cis* from 5–15 c.p.s., and the *gem* from 0–5 c.p.s.

Naturally occurring mercury is made up of several isotopes, one of which, Hg^{199}, possesses a spin of $I = 1/2$ and is present in a natural abundance of 17%. The mercury spin can couple with the proton spins and give rise to satellite peaks in the proton resonance spectrum. It has been observed that the Hg^{199}–H coupling constants in divinylmercury[8] follow the order $J_{trans} > J_{cis} > J_{gem}$. Since one would expect that the substitution of a methyl group would not change this order, the magnitudes of these Hg^{199}–H couplings can be used to confirm the structural assignments of the propenyl groups.

Experimental

The syntheses of the dipropenylmercury derivatives starting from propenyl bromide were accomplished through the above series of reactions described by Nesmeyanov.[3]

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[1] This work was supported in part by the National Science Foundation, Grant NSF-G-15829.

[2] Based upon a thesis submitted by David Moy in partial fulfillment of the requirements for the Doctor of Philosophy degree.

[3] A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1174 (1959) (English translation).

[4] A. I. Kitaigorodsky, *ibid.*, 170 (1945); *ibid.*, 259 (1947).

[5] N. L. Allinger and R. B. Hermann, *J. Org. Chem.*, **26**, 1040 (1961).

[6] T. Schaeffer, *Can. J. Chem.*, **40**, 1 (1962).

[7] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[8] D. W. Moore and J. A. Happe, *J. Phys. Chem.*, **65**, 224 (1961).