Now taking the very high sulfate concentrations, where $(\mathrm{Sn}^{+4}) \cong 0$ then

$$c'' = (C_{\mathrm{Sn}} - c'')(\mathrm{H_2SO_4})K_2$$

and

$$c'' = \frac{C_{\mathrm{Sn}}K_2(\mathrm{SO_4^{=}})}{1 + K_2(\mathrm{SO_4^{=}})} = \frac{C_{\mathrm{Sn}}K_2(\mathrm{H_2SO_4})}{1 + K_2(\mathrm{H_2SO_4})}$$

C_{Sn} = total tin concentration
Then if $D_{\mathrm{obsd}} = e_2c''d$ (*i.e.*, if $e_3 >> e_2$)

$$1/D_{\mathrm{obsd}} = (1/e_3C_{\mathrm{Sn}}d)(1/K_2(\mathrm{H_2SO_4}) + 1) \quad \text{(III)}$$

Thus we plot $1/D_{\mathrm{obsd}}$ against $1/(\mathrm{H_2SO_4})$ and obtain a good straight line, indicating that our reasoning was essentially correct. Then the data indicate that K_2 is quite small, since e_3 is obviously large and hence that the complex anion is present to any extent only in concentrated sulfuric acid solutions.

The electromigration experiments are in accord with the above conclusions. In 1.5 *f* sulfuric acid the tin migrates readily to the cathode, but in 6.0 *f* acid little migration is observed and that is toward the anode. At 3 *f* sulfuric acid some migration (as a streak rather than a spot) to the cathode is observed, which might indicate a very slow rate for reaction 3.

It is believed that all these equilibria are slow, since the spectra of freshly prepared samples were about the same as in the perchlorate solutions and slowly changed to the recorded values. Equilibrium was reached in about 24 hours. Hence all solutions were aged for one to two days before spectrophotometric examinations were undertaken.

An alternative description which would also agree with the spectrophotometric data is suggested as

$$\mathrm{SnO^{+2} + SO_4^{=} \rightleftarrows SnOSO_4} \quad k_1 \qquad (5)$$

$$\mathrm{SnOSO_4 + H_2SO_4 \rightleftarrows H_2SnO(SO_4)_2^{=}} \quad k_2 \qquad (6)$$

which are combined to give

$$\mathrm{SnO^{+2} + 2HSO_4^- \leftrightarrows H_2SnO(SO_4)_2} \quad K_1 \qquad (7)$$

And in concentrated sulfuric acid we would have

$$\mathrm{H_2SnO(SO_4)_2 + H_2SO_4 \leftrightarrows H_2Sn(SO_4)_3 + H_2O} \quad K_2 \qquad (8)$$

In view of the strong tendency toward hydrolysis exhibited by tin(IV), this explanation seems more reasonable than the previous interpretation. However, if we remember that the spectrum changes very little in perchloric acid of from 1.5 to 9 *f*, this second description loses some force.

Unless *k* for the following

$$\mathrm{SnO^{++} + 2H_3O^+ \rightleftarrows Sn^{+4} + 2H_2O} \qquad (9)$$

is small indeed, we should detect this reaction spectrophotometrically. Since we see no hydronium ion dependence in the spectrum, even in strongly acid solution, it seems more reasonable to assume the hydrated stannic ion is in fact the predominant species at hydronium ion concentrations above 1.5 *f*.

Acknowledgment.—This work is part of a program supported by the Atomic Energy Commission at Michigan State College.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Reaction between Platinum Chlorides and Carbon Monoxide. The Preparation and Configuration of Dichlorodicarbonylplatinum(II)[1]

BY J. M. LUTTON AND R. W. PARRY

RECEIVED APRIL 13, 1954

Pure dichlorodicarbonylplatinum(II) can be synthesized in good yield by the reaction between $\mathrm{PtCl_3}$ and high pressure carbon monoxide at 125°. On the other hand, very poor yields of $\mathrm{PtCl_2(CO_2)}$ are obtained at all temperatures and pressures if $\mathrm{PtCl_2}$ is the starting material. Pure $\mathrm{PtCl_2(CO)_2}$ loses CO irreversibly in vacuum or under nitrogen, but is stable under a CO pressure of one atmosphere. The relationship of these facts to the equilibria involved is considered. A value of 4.85 ± 0.05 Debye for the dipole moment of dichlorodicarbonylplatinum(II) in benzene solution confirms an earlier approximate value and eliminates the *trans* structure as one of the principal forms. Kurnakov's thiourea test also implies a *cis* structure for the compound, but results of the chemical test are not unequivocal. A preparation of $\mathrm{PtCl_2}$ from commercial $\mathrm{PtO_2}$ is described.

The unusual chlorocarbonyls of platinum were first prepared by Schutzenberger[2] using the reaction between platinum sponge at 250° and a rapidly flowing gaseous mixture of chlorine and carbon monoxide. The reaction, which has been studied in this and other laboratories, proceeds rapidly to give a mixture of the three known chlorocarbonyls in good yield provided active platinum sponge, such as is obtained from the thermal decomposition of ammonium chloroplatinate, is used.

A number of modifications of this procedure have been described. Phosgene gas has been used in place of chlorine and carbon monoxide with relatively poor results.[3] In a second modification platinous chloride has been treated with CO. Literature reports on this procedure are not consistent; an excellent modern reference book[4] reports that $\mathrm{PtCl_2}$ takes up CO more readily than does platinum sponge, yet preparative procedures involving the use of $\mathrm{PtCl_2}$ have been relatively ineffective.[5] In view of these observations the reactions between carbon monoxide and the chlorides of platinum have been reinvestigated in some detail with results as described below.

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[1] Abstracted in part from a dissertation submitted by J. M. Lutton to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] P. Schutzenberger, *Ann. Chem. Phys.*, **15**, 100 (1868); *ibid.*, **21**, 350 (1870).

[3] F. Mylius and F. Foerster, *Ber.*, **24**, 2424 (1891).

[4] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford University Press, New York, N. Y., 1950, p. 1627.

[5] (a) W. O. Walker, Thesis, University of Chicago (1930); (b) this investigation.

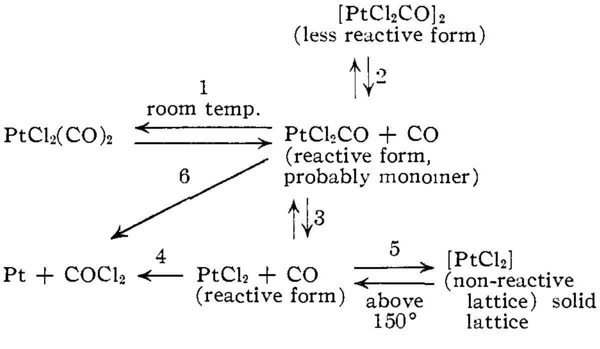
At low temperatures (100–125°) and all pressures $PtCl_2$ is inert to CO. When the temperature is raised (150–225°) and reaction begins, the principal product at all pressures is metallic platinum containing adsorbed carbon monoxide. Only small amounts of the dichlorodicarbonylplatinum(II) were ever obtained using olive-drab $PtCl_2$ as a starting material. In contrast, the black powder of empirical composition $PtCl_3$ gave 50 to 75% yields of crystalline $[PtCl_2(CO)_2]$ when treated with CO at 40 atmospheres pressure and 125°. No lower carbonyls were present. Variations in starting material, temperature and carbon monoxide pressure produced the effects summarized in Table I.

TABLE I

Platinum chloride	Temp., °C.	CO pressure, atm.	Result
$PtCl_2$ and $PtCl_3$	100–125	1	No reaction
	150–200	1	About 2 to 3% $PtCl_2(CO)_2$ Largely Pt metal
	Above 200	1	Pt metal
$PtCl_2$	100	40 to 150	No reaction
	125	40 to 150	3–5% $PtCl_2(CO)_2$ Some Pt metal
	150	40 to 150	Pt metal
$PtCl_3$	100	120	No reaction
	125	40 to 120	50–75% yield $PtCl_2(CO)_2$
	150	40 to 120	Pt metal with trace $PtCl_2(CO)_2$

In view of the fact that both platinum(II) chloride and $[PtCl_2CO]_2$ are inert to carbon monoxide at one atmosphere pressure and room temperature, it was rather surprising to find that an atmosphere of CO represses the dissociation of pure $[PtCl_2(CO)_2]$. The dissociation proceeds irreversibly in a nitrogen atmosphere or high vacuum. The above facts suggested that a consideration of the reaction possibilities in the system carbon monoxide–platinum carbonyl halides–platinum halides might be interesting.

The Dissociation Process.—The experimental observations can be interpreted in terms of the following equations



From equation 1 it can be seen that CO will repress the decomposition of the dicarbonyl at room temperature; but since the dimeric crystalline solid $[PtCl_2CO]_2$ is not reactive at room temperature (equation 2), the CO will not convert crystalline $[PtCl_2CO]_2$ to $PtCl_2(CO)_2$. At somewhat higher temperatures (125°) the conversion proceeds rapidly, the extent depending upon the fugacity of the carbon monoxide. In the high pressure synthesis the dichlorodicarbonylplatinum(II) is the sole product; in the low pressure synthesis a mixture of lower carbonyls is obtained. Besides the dimerization reaction, active $PtCl_2CO$ can undergo irreversible internal reduction to give Pt and $COCl_2$ (equation 6)[6] or it can lose its last CO to give active $PtCl_2$ (equation 3). The active $PtCl_2$ may condense to give the non-reactive polymer (equation 5) or it may be rapidly reduced by CO to give Pt and $COCl_2$ (equation 4). In the presence of CO above 130° the reduction is a rapid process. No significant amounts of $PtCl_2$ have ever been isolated from the decomposition products of $PtCl_2(CO)_2$, but the reverse process—the formation of coördination compounds from $PtCl_2$—proceeds rapidly above 200° to give essentially quantitative yields of $PtCl_2(PF_3)_2$ when the non-reducing PF_3[7] is used in place of the reducing CO.

The reactivity of $PtCl_3$ at high CO pressure and the inert character of $PtCl_2$ must be due to lattice factors. $PtCl_2$ is a surprisingly inert material, presumably due to its chain-like structure. Reactivity of the system is enhanced by breaking up this structure as in $PtCl_3$. The formation of the mixed carbonyls from active platinum, carbon monoxide and chlorine is also reasonable since in this case the non-reactive variety of $PtCl_2$ does not form; instead the active monomer reacts rapidly with CO at one atmosphere to give the observed mixture of carbonyls. These are swept out of the heated region before decomposition. The known[8] role of spongy platinum as a catalyst for the high temperature combination of CO and Cl_2 to give $COCl_2$ is also suggested by the foregoing relationships ($Pt + Cl_2 \rightarrow PtCl_2$ and equation 5).

The Configuration of Dichlorodicarbonylplatinum(II) and its Reaction with Thiourea.—Chatt and Williams[9] reported a value of 4.65 ± 0.5 as the dipole moment of $PtCl_2(CO)_2$ in benzene solution. The result was interpreted in terms of a predominantly *cis* structure. An independent and more precise measurement, completed in this Laboratory concurrent with publication of the data of Chatt and Williams, gave 4.85 ± 0.05 debye. A molecular weight measurement on the benzene solution confirmed the monomeric formula for $PtCl_2(CO)_2$. The *cis* configuration is indicated.

Chemical tests for configuration are also of interest. Kurnakov[10] noted that *cis*-dichlorodiammineplatinum(II) reacts with aqueous thiourea to give the tetrathioureaplatinum(II) chloride as yellow needles while the *trans* isomer reacts to give a colorless solution from which snow white needles of dithioureadiammineplatinum(II) can be recovered on cooling. This test has been suggested as a means of differentiating *cis* and *trans* isomers of platinum(II) complexes. As pointed out by Quagliano and Schu-

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[6] The conversion of $[PtCl_2CO]$ to Pt and $COCl_2$ is assumed to be irreversible or an equilibrium which lies well toward the Pt since earlier observations[3] indicate that Pt and $COCl_2$ do not react easily over a wide temperature range to give platinum chlorocarbonyls.

[7] (a) J. Chatt, *Nature*, **165**, 637 (1950); (b) confirmed in this Laboratory.

[8] J. N. Friend, "Textbook of Inorganic Chemistry," Vol. 5, 1921, p. 98.

[9] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

[10] S. Kurnakov, *J. prakt. Chem.*, [2] **50**, 483 (1948).

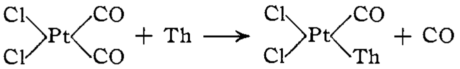
bert[11] no general check on the applicability of the test using substances of known configuration has been recorded.

Rapid mixing of a dry benzene solution of the carbonyl and a saturated aqueous solution of thiourea results in rapid formation of the yellow needles of $Pt(Th)_4Cl_2$. No reduction or formation of other platinum compounds could be detected.

The tempting conclusion to be drawn from the result described is that the presence of the *cis* isomer is established by chemical as well as physical means, but closer analysis suggests that the chemical test may not be reliable under certain conditions.

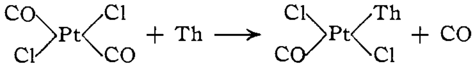
If one accepts the usual assumption that the CO group has a strong *trans* effect, comparable to or greater than Cl^-, either CO or Cl^- could be eliminated as the first step in the reaction, the choice between the two depending upon the relative strength of the metal ligand bond after labilization. Available evidence seems to indicate that the CO is liberated first since the related [Pt CO Py Cl_2] is a known compound.

The initial reaction for the *cis* isomer is then



This would be followed rapidly by replacement of the CO and Cl^-. Since all attached groups are now *trans* labilizing, $Pt(Th)_4Cl_2$ would be expected as a product just as in the case of the *cis* $Pt(NH_3)_2Cl_2$.

For the *trans* isomer, CO might again be liberated as in the initial reaction, since the two CO groups are assumed to be *trans* labilizing. The reaction then becomes



Again, since all groups on the platinum are still *trans* labilizing, just as in the previous case, one would expect the remaining CO and $2Cl^-$ ions to be replaced yielding again $Pt(Th)_4Cl_2$. The chemical thiourea test would probably be inconclusive if all groups attached to the platinum had a *trans* labilizing effect equal to or greater than that of chloride. The test is most effective when two groups of low *trans* effect are attached to the platinum along with two strong *trans* labilizing groups.

Experimental

Materials. Carbon Monoxide.—Tank carbon monoxide (Matheson) was passed through alkaline pyrogallol and dried with soda lime followed by magnesium perchlorate. The procedure did not remove all traces of iron carbonyl.

Chlorides of Platinum.—Platinous chloride was prepared by two methods. In the first procedure, reagent grade chloroplatinic acid was gradually heated in a stream of chlorine until a temperature of 500° was reached. (Heating period was about 8 to 10 hours.) The 500° temperature was then maintained for two hours with the chlorine flowing. The color of the product varied from brown to light yellow, the lighter color being associated with lower chloride content. The average percentage of chloride in the olive drab product was 28.0%; theoretical for $PtCl_2$ is 26.64% Cl^-.

In the second procedure, commercial PtO_2 (Adams catalyst) was chlorinated using Cl_2 at a temperature of 550°. Heating in HCl or mixtures of HCl and Cl_2 brought about reduction to the metal and only partial recombination to the dichloride. The chlorination of PtO_2, not heretofore reported, offers considerable experimental advantage over the first procedure for preparing $PtCl_2$ since the PtO_2 is currently cheaper, not strongly hygroscopic, and does not spatter during initial heating.

The yellow olive-drab $PtCl_2$ obtained in both procedures was surprisingly inert. It showed almost no tendency to dissolve in boiling aqua regia and dissolved only partially on prolonged boiling with concentrated HCl. It dissolved in concentrated HI and in alkaline sodium formate. In the latter reagent the platinum was reduced to the metal and could be weighed for analysis. The chlorine could be titrated after destruction of the excess formate with hydrogen peroxide and destruction of the excess peroxide by boiling in the presence of the finely divided platinum.

When the decomposition of chloroplatinic acid in a stream of chlorine was stopped at 400°, a material of approximate empirical composition $PtCl_3$ could be obtained as a jet black powder, greatly resembling platinum black in appearance. Average chloride content of the black product was 38.0%. Theoretical for $PtCl_3$ is 32.27% chloride. The black solid was readily soluble in HCl.

The Low Pressure Synthesis.—The reaction system consisted of a 25-mm. Pyrex tube into which a cold finger, cooled by running water, projected from one end. The tube was heated by means of an electric furnace. As recommended by Walker[5] the boat containing platinum chloride was placed at the exit end of the furnace and the end of the cold finger extended slightly into the heated region. The system was always dried and outgassed under high vacuum before use; then with the platinum chloride in place and a rapid stream of CO flowing, the temperature was slowly raised. At a temperature of 150° white needles of $PtCl_2(CO)_2$ condensed on the cold finger but the reaction stopped after only a small amount of product had been obtained. At higher temperatures additional small amounts of carbonyl were formed, but the principal reaction product was always metal from reduction of the halide. The platinum chloride starting material did not seem to be an important variable in the low pressure work. When PF_3 was used in a similar system in place of CO, copious amounts of $PtCl_2(PF_3)_2$ were obtained from the $PtCl_2$ at 200 to 250° as described by Chatt.[7]

The High Pressure Synthesis.—The platinum chloride was placed in a small glass bulb; then the neck of the bulb was bent into a small hook and the tip was constricted but not sealed. About an inch of indicating Drierite (6 mesh) was placed in the bottom of a high pressure hydrogenation bomb, a pad of glass wool was inserted, then the sample bulb was placed on top of the pad. The bomb was fastened to the high pressure hydrogenation apparatus and carbon monoxide was admitted at full tank pressure. The system was heated up to the predetermined temperature and maintained for two hours. Longer heating had no effect and it was not considered worthwhile to investigate shorter times since the bomb required 6 to 8 hours to cool to room temperature. Data are summarized in Table I. As noted in Table I, $PtCl_3$ gave $PtCl_2(CO)_2$ as long pure white needles interlaced through a fragile black platinum mat. The black platinum residue contained appreciable amounts of adsorbed CO as was indicated by its initial vigorous reaction with concentrated nitric acid.

The small orifice of the sample container was immediately closed with a drop of black wax as it was removed from the bomb. The product was thus maintained under a CO atmosphere and was stable until worked up. The pure dichlorodicarbonylplatinum(II) was separated from the reduced platinum by benzene extraction in the vacuum line. Great care was taken to exclude moisture during the transfer of the crude product into the extractor. The benzene was dried by distilling it from CaH_2 in the vacuum line just before use. Details are given elsewhere.[12]

The product as obtained in the receiving tube consisted of long pure white needles. On standing in vacuum or dry nitrogen, traces of yellow appeared within 24 hours, indicating loss of CO and polymerization to $[PtCl_2(CO)]_2$ and $Pt_2Cl_4(CO)_3$. On longer standing the color deepened to orange and ultimately to black. The white needles were stable in a CO atmosphere.

The Molecular Weight of $PtCl_2(CO)_2$ in Benzene.—The molecular weight of $PtCl_2(CO)_2$, determined by freezing point depression in benzene, was 354 as compared to a

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[11] J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50**, 201 (1952).

[12] J. M. Lutton, Dissertation, University of Michigan, Ann Arbor, 1953.

theoretical value of 322. Slight polymerization during measurement was also indicated by the development of a faint yellow color in the solution.

Attempts to measure the vapor pressure of $PtCl_2(CO)_2$ and $PtCl_2(PF_3)_2$ by static methods resulted in irreversible decomposition before any measurable pressures were obtained.

Dipole Moment Measurements.—From the Clausius-Mossotti equation the experimental quantities required are: (1) the densities and concentrations of solutions and solvent, (2) the dielectric constants of solutions and solvent, and (3) the refractive indices of solutions and solvent. Because of the extreme sensitivity of the dichlorodicarbonylplatinum(II) to moisture and thermal decomposition, special techniques involving rapid vacuum line manipulations were used to obtain the necessary values.

Solutions were made up by weight in a specially calibrated pycnometer, so that both concentration and density were obtained concurrently. The density of benzene at 25°, determined as a check on the measurement, was 0.8729 ± 0.0006 g./cc. which is in good agreement with the "best" value of 0.87332 g./cc. reported by Egloff.[13] For making up solutions the weighed pycnometer was fixed by its ground joint to the extraction apparatus; the carbonyl was extracted into the flask; then the solvent was removed very slowly to avoid spattering. The vacuum system was cracked with dry nitrogen; the flask was removed, rapidly stoppered and weighed; then pure dry benzene was added with a hypodermic syringe and the solution was carefully equilibrated at 25° and brought to volume.

The dielectric constant was measured by the heterodyne beat method using a circuit patterned after that of Hudson and Hobbs.[14] The carrier wave of radio station WHRV, Ann Arbor, was used as the fixed frequency oscillator. The sample condenser, as described by Bender,[15] consisted of a midget variable air condenser from which all but two of the fixed and two of the movable plates had been removed. The sample container was a small 4-cc. cup which just surrounded the plates of the sample condenser and which could be sealed to the support plate of the condenser with Cenco Sealstix Cement to give an air tight system. The sample was admitted by glass syringe through a small side tube sealed into the cup and closed with a ground glass stopper.

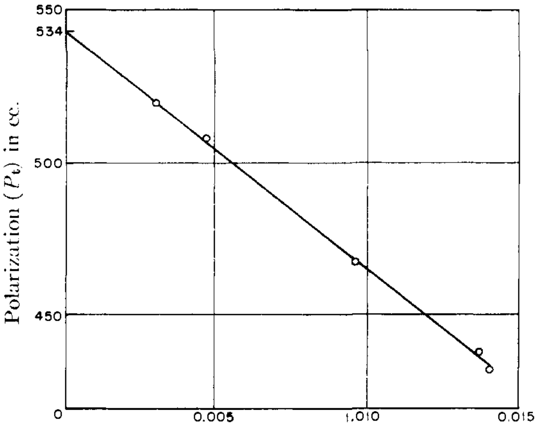

Fig. 1.—Polarization of $PtCl_2(CO)_2$ as a function of concentration in benzene solution at 25°.

A cathode ray oscilloscope was used as a detector for the electrical system as suggested by Smyth.[16a] The measuring condenser in the instrument was a precision type 25 $\mu\mu$f air condenser which could be read to one part in 25,000. The condenser was calibrated as described by Smyth.[16b] All measurements were made at 25 ± 1°.

Measurements on benzene itself gave ϵ = 2.279 ± 0.002 which is in good agreement with the currently accepted value ϵ = 2.2773. Finally, as a check on the system, the total polarization of purified CBr_4 was measured in benzene solutions. A value of 41 cc. was obtained. Since the electronic polarization of CBr_4 calculated from atomic refractions is 37.9 cc. and the atomic polarization is about 4 cc., the orientation polarization of CBr_4 is essentially zero as would be expected.

All measurements on the carbonyl were made using freshly prepared solutions to minimize errors arising from decomposition. The apparent total polarization is shown as a function of solution concentration in Fig. 1. The molar polarization at infinite dilution is 543 cc.

The refractive indexes of solutions were measured with an Abbé refractometer thermostated at 25°. Measurements on benzene gave 1.4979 as compared to 1.49776 given by Egloff.[13] Measurements on carbonyl solutions were complicated by the photosensitivity of the solute. Solutions began to decompose after being placed between the prisms to give indistinct and drifting boundaries. Precise values were obtained only by setting the scale, cleaning the plates, resetting on a new sample, etc., until introduction of a new sample required no adjustment of the instrument. The total electronic polarization thus determined was 42 cc.

If the total molar polarization of 543 cc. is corrected only for the measured electronic polarization, 42 cc., one obtains a dipole moment of 4.91 debyes. If an additional generous correction of 25%[17] of the electronic polarization is made for the atomic polarization the value changes to 4.85 debyes. The main limitation in the accuracy of this value is the instability of the solutions. Although each solution was freshly prepared it began to decompose slowly almost at once. It can be said with some confidence, however, that the value obtained (4.85 ± 0.05) does represent a lower limit and is reasonably accurate.

ANN ARBOR, MICH.

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[13] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946.

[14] B. E. Hudson and M. E. Hobbs, *J. Chem. Educ.*, **17**, 366 (1940).

[15] P. J. Bender, *ibid.*, **23**, 179 (1946).

[16] (a) C. P. Smyth, in Weissberger, "Technique of Organic Chemistry," 2nd Ed., Vol. I, Pt. 2, Interscience Publishers, Inc., New York, N. Y., 1949, p. **1511**; (b) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N.Y., 1931.

[17] K. A. Jensen (*Z. anorg. Chem.*, **229**, 225, 265 (1936)) found that the atomic polarization in the dichloro-bis-trialkylphosphine-platinum(II) complexes is about 20% of the electronic polarization. The 25% used is thus a maximum value; in any event, its effect is relatively small.