Appendix: Details of the Calculations

Coordinates in atomic units to the nearest 0.000 01 bohr were derived from average crystallographic[3] bond parameters for $Rh_2Cl_2(CO)_4$, namely Rh–Cl = 2.36, Rh–C = 1.81, C–O = 1.18 Å, and angle Cl–Rh–Cl = 85°, using the relation 1 bohr = 0.529 177 Å. Schwarz's α_{HF} values[18] were used for the atomic exchange parameters; for the extramolecular and intersphere regions, a weighted average of the atomic α's was employed, the weights being the number of *valence* electrons in the neutral atoms. The outer-sphere center positions were computed using the same sort of average of the atomic positions. Overlapping sphere radii were obtained by our nonempirical procedure;[19] they are given in Table III.

The highest-order spherical harmonic basis functions used were $l = 4$ for the outer region, 2 for Rh, and 1 for Cl, C, and O. Core energy levels were never frozen; in each SCF iteration they were calculated explicitly using only the surrounding-atomic-sphere potential. Iterations were continued until convergence to ±0.0003 hartree or better was attained for all levels. The SCF potentials were used to search for excited-state levels up to −0.05 hartree. The final virial ratio was $-2T/V = 1.0006$ for both molecules.

References and Notes

(1) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 211 (1966).
(2) R. Colton, R. H. Farthing, and J. E. Knapp, *Aust. J. Chem.*, **23**, 1351 (1970).
(3) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).
(4) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).
(5) J. J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat, and R. Poilblanc, *Inorg. Chem.*, **14**, 743 (1975).
(6) J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985 (1970).
(7) K. Klanderman and L. F. Dahl, quoted in *J. Am. Chem. Soc.*, **91**, 7292 (1969).
(8) M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, 1484 (1973).
(9) C. W. Garland and J. R. Wilt, *J. Chem. Phys.*, **36**, 1094 (1962).
(10) J. G. Bullitt and F. A. Cotton, *Inorg. Chim. Acta*, **5**, 637 (1971).
(11) J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).
(12) J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 1032 (1975).
(13) R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, **50**, 53 (1973).
(14) L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).
(15) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, **14**, 3103 (1975).
(16) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organomet. Chem.*, **70**, 413 (1974).
(17) K. H. Johnson, *Annu. Rev. Phys. Chem.*, **26**, 39 (1975).
(18) K. Schwarz, *Phys. Rev. B*, **5**, 2466 (1972); *Theor. Chim. Acta*, **34**, 225 (1974).
(19) J. G. Norman, Jr., *J. Chem. Phys.*, **61**, 4630 (1974); *Mol. Phys.*, **31**, 1191 (1976).

Electron Transfer Processes in Organoplatinum Complexes. Oxidation and Cleavage of Dialkylplatinum(II) with Hexachloroiridate(IV)

J. Y. Chen and J. K. Kochi*

Contribution from the Department of Chemistry, Indiana University,
Bloomington, Indiana 47401.

Received August 9, 1976

Abstract: Dialkyl(bisphosphine)platinum(II) complexes are readily oxidized by hexachloroiridate(IV) to afford two principal types of products depending on the structure of the alkyl group and the coordinated phosphine. Thus, $Me_2Pt^{II}(PMe_2Ph)_2$ undergoes oxidation to dimethylplatinum(IV) species, whereas the diethyl analogue $Et_2Pt^{II}(PMe_2Ph)_2$ affords EtCl and monoethylplatinum(II) species by oxidative cleavage of one Et–Pt bond. The cleavage of the Me–Pt bond can be induced by replacement of the phosphine to $Me_2Pt^{II}(PPh_3)_2$, which competitively undergoes oxidation to dimethylplatinum(IV) species as well as oxidative cleavage to MeCl and methylplatinum(II) species. The stoichiometric requirement of 2 equiv of hexachloroiridate(IV) remains invariant for each dialkylplatinum(II), independent of the products of oxidation. The energetics and kinetics as well as the observation of alkyl radicals by spin trapping and oxygen scavenging support a mechanism involving the rate-limiting electron transfer from dialkylplatinum(II) to hexachloroiridate(IV). The selectivity in product formation leading to cleavage and/or further oxidation is associated directly with the paramagnetic intermediate $R_2PtL_2^+$ (formally a Pt(III) species), the stability of which is discussed in relationship to the strengths of the alkyl-platinum bonds and the phosphine ligands. These processes are compared to the reactions of related radical ions derived by electron transfer from alkylmercury(II), lead(IV), and cobalt(III) complexes.

Previous studies of the oxidation of organoplatinum(II) complexes have been concerned mainly with the synthesis of organoplatinum(IV) complexes by oxidative addition using halogens and alkyl halides.[1-3] The mechanism of these reactions has generally been considered to proceed through an S_N2 transition state such as that postulated for the reaction of alkyl halides with the more extensively studied Vaska-type complexes *trans*-$IrX(CO)L_2$.[4] Recently, there have been reports[5] suggesting the participation of free radical processes in the reaction of *trans*-$IrX(CO)L_2$ with alkyl halides, in addition to S_N2 processes.

We examined the oxidation of dialkylplatinum(II) complexes by the one-electron oxidant hexachloroiridate(IV)[6] in order to delineate free radical processes in organoplatinum intermediates in comparison with their nontransition metal counterparts, dialkylmercury and tetraalkyllead and -tin compounds, described earlier.[7] Retention as well as cleavage of the alkyl-platinum bonds are observed during the oxidation of dialkyl(bisphosphine)platinum(II) complexes, the extent of each depending on the structures of the alkyl group and the coordinated phosphine. The fate of the alkyl groups and the identity of the inorganic products, including platinum(II) and -(IV) complexes as well as reduced iridium(III), strongly implicate a paramagnetic dialkylplatinum(III) species as a prime intermediate following electron transfer. Factors involved in (a) the cleavage of this intermediate to alkyl radicals and alkylplatinum(II) or (b) the further oxidation to dialkylplatinum(IV) are important considerations in this study.

Table I. The Stoichiometry of Oxidation of *cis*-R_2PtL_2 by Hexachloroiridate(IV)[a]

R_2PtL_2, mmol	$IrCl_6{}^{2-}$, mmol	$IrCl_6{}^{2-}$ [b] consumed, mmol	RCl,[c] mmol	RH,[c] mmol	R(-H),[c] mmol	$IrCl_6{}^{2-}/R_2PtL_2$	$\sum R_{ox}/R_2PtL_2$
L = PMe_2Ph; R = Me (0.053)	0.133	0.108	0.0009	<0.0001		2.0	0.02
R = Me (0.029)	0.013	0.013	0.0001	0.0001			0.03[d]
R = Et (0.018)	0.036	0.036	0.016	0.0005	0.0005		0.95
R = Et (0.040)	0.142	0.123	0.042	0.001	0.001	3.1[e]	1.10
L = PPh_3; R = Me (0.034)	0.090	0.065	0.014	0.002		1.9	0.47
R = Me (0.033)	0.087	0.063	0.013	0.002		1.9	0.45
R = Et (0.033)	0.102	0.070	0.035	0.0003	0.0003	2.1	1.08
R = Et (0.038)	0.063	0.063	0.034	0.0003	0.0003		1.10[d]

[a] In CH_3CN at 25 °C. [b] Calculated from unreacted $IrCl_6{}^{2-}$, determined by visible spectrum of the product solution. [c] Determined by gas-liquid chromatography. [d] Assuming a stoichiometry of $IrCl_6{}^{2-}/R_2PtL_2$ = 2.0. [e] Organic products were generated during additions of the first 2 equiv of $IrCl_6{}^{2-}$ only.

Results and Discussion

We examined two series of *cis*-dialkyl(bisphosphine)platinum complexes R_2PtL_2 comprising R = methyl or ethyl groups in which L = triphenylphosphine or dimethylphenylphosphine. All the compounds reacted rapidly on mixing solutions of acetonitrile with hexachloroiridate(IV) at room temperature.

Products and Stoichiometry. The stoichiometry of the oxidation was determined by spectrophotometric titration of $Ir^{IV}Cl_6{}^{2-}$. The reduced iridium(III) products were analyzed by thin layer chromatography as $IrCl_6{}^{3-}$ and $IrCl_5(CH_3CN)^{2-}$. Two classes of platinum products were characterized largely on the basis of their proton (60 and 220 MHz) NMR spectra as dialkylplatinum(IV) and alkylplatinum(II) species. The cleaved alkyl group formed concomitantly with the latter was found mainly as alkyl chloride, accompanied by small amounts of alkane and alkene (from ethyl). Since the nature of the products and the stoichiometry are highly dependent on the alkyl group and the phosphine, the oxidation of each dialkylplatinum(II) complex will be described separately.

***cis*-$Me_2Pt(PMe_2Ph)_2$** reacted with 2 equiv of $IrCl_6{}^{2-}$ to afford essentially no methyl chloride or methane as shown in Table I. The reduced iridium(III) products consisted of an equimolar mixture of $IrCl_6{}^{3-}$ and $IrCl_5(CH_3CN)^{2-}$. Significantly, both methyl groups remained intact on the oxidized platinum(IV) product, which consisted of a mixture of two *cis*-dimethylplatinum(IV) species formed in 60 and 40% yields as described in the Experimental Section.

$$Me_2Pt^{II}(PMe_2Ph)_2 + 2\,IrCl_6{}^{2-} \xrightarrow[CH_3CN]{} Me_2Pt^{IV}(PMe_2Ph)_2X_2 + IrCl_6{}^{3-} + IrCl_5{}^{2-} \quad (1)$$

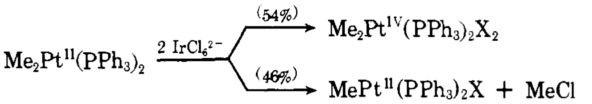
where X = Cl, $Ir^{III}Cl_5(CH_3CN)$ or CH_3CN

***cis*-$Et_2Pt(PMe_2Ph)_2$** and ***cis*-$Et_2Pt(PPh_3)_2$** also reduced 2 equiv of $IrCl_6{}^{2-}$ to afford an equimolar mixture of $IrCl_6{}^{3-}$ and $IrCl_5(CH_3CN)^{2-}$. However, one ethyl group was liberated as ethyl chloride from both complexes during the oxidation (Table I). Small amounts of ethane and ethylene were also observed. The rate of oxidation of the triphenylphosphine complex was noticeably slower than that of the dimethylphenylphosphine complex.

$$cis\text{-}Et_2Pt^{II}L_2 + 2IrCl_6{}^{2-} \xrightarrow[CH_3CN]{} trans\text{-}EtPt^{II}L_2(CH_3CN)^+ + EtCl + IrCl_6{}^{3-} + IrCl_5(CH_3CN)^{2-} \quad (2)$$

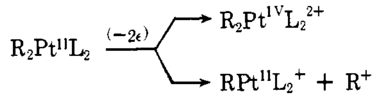
where L = PMe_2Ph, PPh_3. The monoethylplatinum(II) product in eq 2 (L = PMe_2Ph) was subject to further slow oxidation by an additional equivalent of $Ir^{IV}Cl_6{}^{2-}$, but no more ethyl chloride was formed in this subsequent oxidation.

***cis*-$Me_2Pt(PPh_3)_2$** consumed 2 equiv of $Ir^{IV}Cl_6{}^{2-}$. Several reactions were competing in this system, however, since 0.46 mol of methyl groups was cleaved from each mole of *cis*-$Me_2Pt(PPh_3)_2$ during oxidation to afford methyl chloride (87%) and methane (13%). Integration of the NMR spectrum of the products indicated that the remainder (1.54 mol) of the methyl groups remained attached to the platinum products, which are tentatively identified as a mixture of $Me_2PtL_2X_2$ and $MePtL_2X$ species (see Experimental Section).


(3)
(4)

$$Me_2Pt^{II}(PPh_3)_2 \xrightarrow{2\,IrCl_6{}^{2-}} \begin{cases} \xrightarrow{(54\%)} Me_2Pt^{IV}(PPh_3)_2X_2 & (3) \\ \xrightarrow{(46\%)} MePt^{II}(PPh_3)_2X + MeCl & (4) \end{cases}$$

Multiple Pathways in the Oxidation of Dialkylplatinum(II) with Hexachloroiridate(IV). Despite the different products obtained from the oxidation of methyl and ethyl derivatives of dialkyl(bisphosphine)platinum, the stoichiometric requirement for the consumption of hexachloroiridate(IV) always remains invariant at 2 equiv for each mole of reactant. Such an overall two-electron oxidation of organoplatinum(II) can be centered either (a) on the metal by the conversion of Pt(II) to Pt(IV) or (b) on the ligand by the oxidative cleavage of one alkyl-platinum bond to Pt(II) and alkyl chloride as represented *formally* by the half-reactions in eq 5 and 6, respectively. The organic and inorganic products indicate that both types of oxidation are taking place. Thus, $Me_2Pt(PMe_2Ph)_2$ is oxidized to dimethylplatinum(IV) species with both CH_3-Pt bonds intact. On the other hand, the diethyl analogue reacts exclusively by oxidative cleavage of a single CH_3CH_2-Pt bond to afford ethyl chloride and monoethylplatinum(II) species. This dichotomy is influenced by the phosphine ligands, since the oxidative cleavage of the CH_3-Pt bond is promoted simply by replacing the coordinated dimethylphenylphosphine by triphenylphosphine. Any mechanistic formulation of the oxidation of dialkylplatinum(II) complexes by hexachloroiridate(IV) must account for these divergent pathways.


(5)
(6)

$$R_2Pt^{II}L_2 \xrightarrow{(-2e)} \begin{cases} \longrightarrow R_2Pt^{IV}L_2{}^{2+} & (5) \\ \longrightarrow RPt^{II}L_2{}^+ + R^+ & (6) \end{cases}$$

Kinetics. The rates of reactions of dialkylplatinum(II) complexes with hexachloroiridate(IV) in acetonitrile were followed spectrophotometrically by the disappearance of hexachloroiridate(IV). The reactions obeyed second-order kinetics, being first order in each reactant according to the equation

$$-d[IrCl_6^{-2}]/dt = 2k[IrCl_6^{2-}][R_2PtL_2] \tag{7}$$

The kinetic experiments were generally carried out with $IrCl_6^{2-}$ in the concentration range 1-3 × 10^{-5} M and with R_2PtL_2 in tenfold excess in order to approximate pseudo-first-order conditions as described in the Experimental Section.

The second-order rate constants for the oxidation of R_2PtL_2 depend in an interesting manner on the nature of the alkyl group as well as the phosphine ligand as shown in Table II. The greater reactivity of ethyl derivatives compared to the methyl analogues in the two series of R_2PtL_2 is in accord with their ability to act as donor ligands in electron transfer reactions. Similarly, the difference between the phosphine ligands, PMe_2Ph and PPh_3, can be attributed to their varying donor properties. It is unlikely that steric factors are dominant (or even important), since the difference in ethyl/methyl reactivity *increases* tenfold from 3.6 to 38 when the ligand is changed from PMe_2Ph to the more bulky PPh_3. We think the latter reflects a saturation of electronic effects, which is also seen in the change in the reactivity of the methyl derivative by a factor of 22 000 when PMe_2Ph is replaced by PPh_3 compared to a corresponding change of only 2100 observed with the ethyl derivatives.

Electron Transfer Processes with Organoplatinum. In order to investigate the ability of dialkylplatinum(II) complexes to act as electron donors, it is desirable to measure the energetics of electron detachment.

$$R_2PtL_2 \rightarrow R_2PtL_2^+ + \epsilon \tag{8}$$

Direct measurement of the ionization potentials of these organometals by photoelectron spectroscopy is difficult to perform due to their low volatility and thermal instability. Earlier studies have shown, however that alternative methods such as electrochemical oxidation and charge transfer spectra can afford comparable information about the energetics of electron detachment from organometals.[7]

1. Electrochemical Oxidation. Anodic oxidation of *cis*-$Me_2Pt(PMe_2Ph)_2$ and *cis*-$Et_2Pt(PMe_2Ph)_2$ at Pt electrodes in acetonitrile solutions indicated only single peak potentials at 0.72 and 0.40 V (vs. Ag/0.1 M $AgNO_3$), respectively. Cyclic voltammetry showed no reduction wave even at sweep rates as high as 10 V/s, the upper useful limit for Pt electrodes. The apparent irreversibility of the process unfortunately discouraged further coulometric studies. Earlier, we found that among alkylmetals, ethyl derivatives are oxidized[7] more readily than the methyl analogues in processes such as that represented in eq 8, consistent with the 0.32-V difference found above.

2. Charge Transfer Complexes of Dialkylplatinum(II) with Tetracyanoethylene. On the addition of tetracyanoethylene (TCNE) to *cis*-$Me_2Pt(PPh_3)_2$ in 1,2-dichloropropane at −60 °C, the solution turned pale yellow immediately. A broad featureless absorption band ($\Delta\lambda_{1/2}$ = 100 nm) was observed at λ_{max} 440 ± 10 nm, which disappeared, with a half-life of approximately 30 min. A new split band (λ_{max} 400 and 415 nm) due to pentacyanopropenide[7] formed simultaneously. Only the latter was observed when the reaction was carried out at room temperature, the charge transfer band being too transient.

Similarly, on the addition of TCNE to *cis*-$Et_2Pt(PPh_3)_2$ in 1,2-dichloropropane at −77 °C, the solution turned pale yellow immediately. The charge transfer band at 450 nm (showing vibrational fine structure) increased rapidly then disappeared, with a half-life of about 15 min, accompanied by the appearance of the spectrum of pentacyanopropenide.

With *cis*-$Me_2Pt(PMe_2Ph)_2$, the solution turned pale yellow on addition of TCNE (−77 °C), but the charge transfer spectrum was too transient to observe.

Table II. Rate Constants for the Oxidation of R_2PtL_2 by Hexachloroiridate(IV)[a]

R_2PtL_2	k, (L mol^{-1} s^{-1})	k_{rel}[b]
$Me_2Pt(PMe_2Ph)_2$	4.4 × 10^2	2.2 × 10^4
$Et_2Pt(PMe_2Ph)_2$	16 × 10^2	8 × 10^4
$Me_2Pt(PPh_3)_2$	0.02	1.0
$Et_2Pt(PPh_3)_2$	0.76	38

[a] In acetonitrile solutions at 25 °C and constant ionic strength (0.01 M $NaClO_4$). [b] Relative reactivity based on $k[Me_2Pt(PPh_3)_2]$ = 1.0.

The charge transfer bands between R_2PtL_2 and TCNE are characteristic of other weak donor-acceptor complexes previously observed with various organometals.[8]

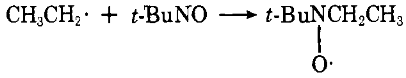
$$R_2PtL_2 + TCNE \rightleftharpoons [R_2PtL_2\ TCNE] \tag{9}$$

The transient nature of such complexes has been shown to arise from subsequent thermal reactions following electron transfer,

$$[R_2PtL_2\ TCNE] \rightarrow [R_2PtL_2{\cdot}^+\ TCNE{\cdot}^-]\ \text{etc.} \tag{10}$$

and to be highly dependent on the ionization potential of the organometal and the stability of the attendant cation radical.[8] [A study of the products arising from R_2PtL_2 and TCNE will be reported later.]

Paramagnetic Species as Intermediates. 1. Spin Trapping of Radicals. Electron spin resonance (ESR) studies were carried out to probe for paramagnetic intermediates in these reactions. With nitroso-*tert*-butane (NB) as spin trap, ethyl radical was successfully detected in acetic acid during the reaction of hexachloroiridate(IV) and *cis*-$Et_2Pt(PMe_2Ph)_2$ in excess (eq 11). The ESR spectrum of the adduct consisted of



$$CH_3CH_2\cdot + t\text{-BuNO} \longrightarrow t\text{-Bu}\underset{\substack{|\\ O\cdot}}{N}CH_2CH_3 \tag{11}$$

the pronounced 1:1:1 nitrogen triplet (a_N = 16.5 G), together with further hyperfine splittings by the protons on the ethyl group ($a_{H\beta}$ = 10.6 and $a_{H\gamma}$ = 0.42 G).[7] The experiment was carried out in the dark. However, on exposure of the solution to room light for approximatley 30 s, the major triplets increased in intensity by a factor of at least 20. The final spectrum consisted of only a simple 1:1:1 triplet (a_N = 16.4 G), which is identical with that of di-*tert*-butyl nitroxide. When the same reaction was carried out in acetonitrile, only the spectrum of di-*tert*-butyl nitroxide was observed.

Subsequent experiments indicated that the same spectrum of di-*tert*-butyl nitroxide was observed when nitroso-*tert*-butane was added to a solution of *cis*-$Et_2Pt(PMe_2Ph)_2$ in the absence of hexachloroiridate(IV). It was again found that the intensity of the signal increased on exposure of the solution to light. The possibility that the products of the reaction between *cis*-$Et_2Pt(PMe_2Ph)_2$ and $IrCl_6^{2-}$ induced the formation of di-*tert*-butyl nitroxide was examined by adding NB to the product solution. No ESR signal was detected in the dark and after exposure to light. It appears, therefore, that di-*tert*-butyl nitroxide is formed by the reaction of *cis*-$Et_2Pt(PMe_2Ph)_2$ with nitroso-*tert*-butane. A similar decomposition of NB to form di-*tert*-butyl nitroxide in the presence of other alkylplatinum(II) and alkylpalladium(II) derivatives has been reported.[9,10]

It is noteworthy that similar reactions carried out with *cis*-$Et_2Pt(PPh_3)_2$ did not afford the ESR spectrum of *t*-Bu(Et)NO· nor that of di-*tert*-butyl nitroxide. However, owing to the low solubility of *cis*-$Et_2Pt(PPh_3)_2$ in acetic acid and in acetonitrile, the reaction with hexachloroiridate(IV) was carried out under heterogeneous conditions, which necessitated

Table III. The Stoichiometry of the Reaction between *cis*-Et_2PtL_2 and Hexachloroiridate(IV) in the Presence of Molecular Oxygen[a]

L	Et_2PtL_2	$IrCl_6^{2-}$	EtCl	CH_3CHO	EtOH	C_2H_4	C_2H_6	$\sum Et$[b]
PPh_3	0.030	0.041[c]	0.0022	0.022	0.0063	0.0007	0.0008	0.032
	0.030	0.036[d]	0.0010	0.021	0.0043	0.0007	0.0009	0.028
PMe_2Ph	0.041	0.041	0.0030	0.034	0.0069	0.0017	0.0018	0.047
	0.044	0.044	0.0035	0.036	0.0078	0.0020	0.0021	0.051

[a] All quantities in millimoles. In acetonitrile solutions under one atmosphere of oxygen at 25 °C. [b] Includes all products derived from cleaved ethyl group. [c] Unreacted amount is 0.0114 mmol. [d] Unreacted amount is 0.0066 mmol (see ref 12).

rather long shaking (~10 min) before the reaction was completed. It is likely that any spin adduct of ethyl radical and NB formed in the reaction was destroyed by prolonged exposure to hexachloroiridate(IV). No ESR spectrum was detected when *cis*-$Et_2Pt(PPh_3)_2$ was mixed with NB alone. In these experiments we could find no evidence of paramagnetic platinum containing species by their ESR spectra. Similarly, no ESR spectrum was observed when a benzene or tetrahydrofuran solution of *cis*-$Me_2Pt(PMe_2Ph)_2$ was irradiated at 2537 nm in the cavity of the spectrometer.

2. Scavenging of Alkyl Radicals by Molecular Oxygen and Hexachloroiridate(IV). The formation of ethyl chloride and minor amounts of ethane and ethylene during the oxidation of diethylplatinum(II) complexes with hexachloroiridate(IV) most likely arises from ethyl radicals. Scavenging experiments with ethyl radicals generated from an independent source have shown that chlorine transfer in eq 12 is extremely rapid.[7]

$$CH_3CH_2\cdot + Ir^{IV}Cl_6^{2-} \xrightarrow[CH_3CN]{} CH_3CH_2Cl + Ir^{III}Cl_5(CH_3CN)^{2-} \quad (12)$$

Alkyl radicals are also known to react with molecular oxygen at diffusion-controlled rates to produce a mixture of alcohols, ketones, and peroxides, depending on their structure.[11] When the reaction of *cis*-Et_2PtL_2 (where L = PPh_3 and PMe_2Ph) and hexachloroiridate(IV) was carried out in the presence of molecular oxygen; ethyl chloride, which is the only organic product formed in a nitrogen atmosphere, was largely eliminated as shown in Table III. In the place of ethyl chloride, high yields of ethyl alcohol and acetaldehyde were found. These products are expected from the self-reaction of ethylperoxy radical.

$$CH_3CH_2\cdot + O_2 \rightarrow CH_3CH_2OO\cdot \quad (13)$$

$$2CH_3CH_2OO\cdot \rightarrow CH_3CHO + CH_3CH_2OH + O_2 \quad (14)$$

The higher yields of acetaldehyde relative to ethyl alcohol observed (in comparison to those expected from the stoichiometry in eq 14) can be attributed to further oxidation of the latter by oxygen under the homolytic conditions extant in the reaction. The results in Table III also indicate that 1.0 and 1.2 mol of ethyl groups were cleaved from *cis*-$Et_2Pt(PPh_3)_2$ and *cis*-$Et_2Pt(PMe_2Ph)_2$, respectively, for each mole of hexachloroiridate(IV) consumed.[12] This observation suggests that homolytic substitution of ethylperoxy radical on *cis*-Et_2PtL_2 is not important under these conditions,

$$EtO_2\cdot + Et_2PtL_2 \rightarrow EtOOPtL_2Et + Et\cdot \quad (15)$$

$$Et\cdot + O_2 \rightarrow EtO_2\cdot \quad (13)$$

$$EtOOPtL_2Et \rightarrow CH_3CHO,\ CH_3CH_2OH,\ \text{etc.} \quad (16)$$

since we expect that chain reactions propagated via eq 13 and 15 would result in increased yields of cleavage products.

In these studies the highly efficient interception of the alkyl group by molecular oxygen supports other studies that ethyl radical is an important intermediate during the oxidative cleavage. Direct autoxidation of Et_2PtL_2 does not occur under these conditions in the absence of hexachloroiridate(IV).

In order to test whether the alkyl-platinum bond is undergoing cleavage to afford alkyl cationoid intermediates, the reaction of *cis*-$Me_2Pt(PMe_2Ph)_2$ with hexachlororidate(IV) was carried out in the presence of a 40-fold excess of bromide (as the tetra-*n*-butylammonium salt) in acetonitrile. Methyl bromide, the product expected from bromide displacement,[13] was absent.

Mechanism of the Oxidation of Dialkylplatinum by Hexachloroiridate(IV). The oxidation of dialkylplatinum(II) complexes by $IrCl_6^{2-}$ is dependent on the nature of both the alkyl group bonded to Pt as well as the coordinated phosphine, the relative rates of oxidation decreasing in the order: $Et_2Pt(PMe_2Ph)_2 > Me_2Pt(PMe_2Ph)_2 > Et_2Pt(PPh_3)_2 > Me_2Pt(PPh_3)_2$. This trend is counter to expectations based on steric hindrance and suggests that the rate-limiting step does not involve bond cleavages to any significant degree. We propose that electron transfer is the rate-limiting process which is common for all dialkylplatinum(II) complexes as presented in Scheme I.[14] This formulation is in general accord with the well-established property of hexachloroiridate(IV) to function as an electron acceptor.[6] According to Scheme I, the activation process is represented by the electron transfer step 17, which is rapidly followed by two competing reactions, in which the intermediate dialkylplatinum cation I either undergoes fragmentation (eq 18a) or reacts further with $IrCl_6^{2-}$ (eq 19[15]). Scheme I accords with all the observations we have made in this system, including (a) the energetics and kinetics of the electron transfer step, (b) the observation of ethyl radicals during oxidative cleavage, and (c) the selectivity between cleavage and further oxidation in methyl and ethyl derivatives as described in the following discussion.

Scheme I

$$R_2PtL_2 + IrCl_6^{2-} \xrightarrow{k} \underset{\text{I}}{R_2PtL_2^+} + IrCl_6^{3-} \quad (17)$$

$$\text{I} \underset{(a)}{\xrightarrow{\text{fast}}} \underset{\text{II}}{RPtL_2^+} + R\cdot \underset{(b)}{\xrightarrow{IrCl_6^{2-}}} RCl + IrCl_5^{2-} \quad (18)$$

$$\text{I} + IrCl_6^{2-} \xrightarrow{\text{fast}} \underset{\text{III}}{R_2PtL_2Cl^+} + IrCl_5^{2-} \quad (19)$$

The second-order kinetics for cleavage indicate that dialkylplatinum(II) and only one $IrCl_6^{2-}$ are involved in the rate-limiting transition state. The other $IrCl_6^{2-}$ required by the stoichiometry must be involved in a fast subsequent step. For an electron transfer process, the second-order rate constant k in eq 17 should increase with increasing ease of electron detachment from R_2PtL_2, a measure of which is obtained from the frequencies ν_{CT} of the charge transfer bands in the $[R_2PtL_2 \cdot TCNE]$ complexes.[7] Indeed there is some correlation between log k for oxidation and ν_{CT}. It is noteworthy that the correlation is not dependent on whether oxidative cleavage or further oxidation of R_2PtL_2 obtains.

Table IV. NMR Spectra of Alkylplatinum(II) and Dialkylplatinum(IV) Products from the Oxidation of R_2PtL_2[a]

Reactant	$Pt-CH_3$ or $Pt-CH_2CH_3$	PMe_2Ph	
R_2PtL_2	δ $(J_{PH})(J_{PtH})$	δ $(J_{PH})(J_{PtH})$	Assignment[b]
cis-$Me_2Pt(PMe_2Ph)_2$	0.79 t (5.5) (67)	2.22 t (4.0) (17)	$Me_2Pt(PMe_2Ph)_2X_2$
	1.20 t (6.0) (65) 1.25 t (6.0) (64)	1.89 t (4.0) (19) 1.90 t (4.0) (20)	$Me_2Pt(PMe_2Ph)_2XY$
			others: δ 1.96 s, CH_3CN-Pt δ 2.30 s, $IrCl_5(CH_3CN)^{2-}$
cis-$Et_2Pt(PMe_2Ph)_2$	0.45–2.22 m	2.22 t (4.5) (–)	*trans*-$EtPt(PMe_2Ph)_2(CH_3CN)^+$
			others: δ 1.98 s, CH_3CN-Pt δ 2.35 s, $IrCl_5(CH_3CN)^{2-}$
cis-$Me_2Pt(PPh_3)_2$	0.57 t (7.0) (70) 0.95 t (5.0) (66)		*trans*-$MePt(PPh_3)_2X$ and $Me_2Pt(PPh_3)_2X_2$
	1.38 d (2.5) (65)		$Me_2Pt(PPh_3)_2X_2$
			others: δ 1.98 s, CH_3CN-Pt δ 2.31 s, $IrCl_5(CH_3CN)^{2-}$
cis-$Et_2Pt(PPh_3)_2$	0.43 t (7.0) (55) 1.1–1.5 m		*trans*-$EtPt(PPh_3)_2(CH_3CN)^+$
			others: δ 1.97 s, CH_3CN-Pt δ 2.31 s, $IrCl_5(CH_3CN)^{2-}$

[a] The reaction was carried out in CH_3CN and the NMR spectra were recorded with product residue in pyridine. Chemical shift in parts per million relative to internal Me_4Si. Coupling constants in hertz; d = doublet, t = triplet, m = multiplet. [b] For discussion of assignments and X or Y see Experimental Section.

Our inability to observe the ESR spectrum of the paramagnetic intermediate $R_2PtL_2^+$ indicates that the lifetime of I is short, consistent with the irreversibility observed in the cyclic voltammetry of R_2PtL_2. Intermediate I as a 17-electron system is expected to be unstable. Other evidence for the formation of transient Pt(III) species has been advanced in the photolysis[6b] of $PtCl_4^{2-}$ and the pulse radiolysis[6c] of $PtCl_4^{2-}$ and $PtCl_6^{2-}$. There is also kinetic evidence for the existence of metastable Pt(III) species in the oxidation of $PtCl_4^{2-}$ by hexachloroiridate(IV).[6a]

According to Scheme I, the paramagnetic intermediate I suffers at least two principal fates: cleavage of an alkyl radical or further oxidation to dialkylplatinum(IV) by unimolecular and bimolecular routes, respectively. The competition between these pathways depends not only on the concentration of $IrCl_6^{2-}$, but more importantly on the stability of I as reflected in the strength of the alkyl-platinum bond. All else being the same, ethyl cleavage is more facile than methyl cleavage, in general accord with the trend in bond strengths.[7,16] The tendency for methyl cleavage to occur more readily in the presence of coordinated dimethylphenylphosphine compared to triphenylphosphine (vide supra) may be attributed to greater electron release by the former. Differences in steric bulk (e.g., cone angles) of the phosphines may also be a factor.[17]

The fragmentation of the alkyl group from I as a free radical in eq 18a during oxidative cleavage of Et_2PtL_2 and $Me_2Pt(PPh_3)_2$ is supported by spin trapping and oxygen scavenging, as well as the ability of $IrCl_6^{2-}$ to convert alkyl radicals to alkyl chlorides efficiently.[18] The latter leads concomitantly to the reduction of hexachloroiridate(IV) to pentachloroiridate(III) as $IrCl_5(CH_3CN)^{2-}$ according to eq 12 and 18b. Indeed, analysis of the reduced iridium products shows the presence of equimolar amounts of $Ir^{III}Cl_5(CH_3CN)^{2-}$ and $Ir^{III}Cl_6^{3-}$, the latter arising from the rate-limiting electron transfer step according to Scheme I.[19]

The instability of I coupled with its rapid rate of oxidation by hexachloroiridate(IV) largely precludes a kinetic study of the competition described in eq 18 and 19.[20] In this connection, the stability of I can be compared to that of other paramagnetic cations formed by electron transfer from organometals such as dialkylmercury(II), tetraalkyllead(IV), tetraalkyltin(IV), and alkylcobalt(III) complexes.[7,13] With the nontransition metal alkyls, we found that fragmentation of alkyl radicals is the exclusive fate of the paramagnetic hypervalent intermediate.[7]

$$R—m^+ \rightarrow R\cdot + m^+ \qquad (20)$$

$$m = HgR, PbR_3, SnR_3$$

On the other hand, electron transfer from the methyl and ethyl derivatives of alkylbis(dimethylglyoximato)cobalt(III), $R(DH)_2Co$, affords rather stable paramagnetic organocobalt(IV) species which undergo further reaction by the formal loss of an alkyl cation, e.g.,[13]

$$[R(DH)_2Co^{IV}]^+ \begin{cases} \xrightarrow{H_2O} ROH + (DH)_2Co^{II} + H^+ & (21) \\ \xrightarrow{Br^-} RBr + (DH)_2Co^{II} & (22) \end{cases}$$

The divergent pathways followed by each of these paramagnetic organometal intermediates is no doubt highly dependent on the accessibility of the various oxidation states of the metals. In a broader sense, the ease with which alkyl cleavage can be induced by electron transfer processes underscores the duality of mechanisms possible (including 1-equiv oxidation centered largely on a metal orbital[7,8,21] as well as 2-equiv oxidation of the alkyl ligand[16,22]) during electrophilic scission of the carbon-metal bond in organometals.[23] Further studies will hopefully delineate these problems in greater detail.

Experimental Section

Materials. The series of *cis*-dialkyl(bisphosphine)platinum(II) compounds used in this study was synthesized by the procedures developed by Chatt and Shaw.[3] Sodium hexachloroiridate(IV), $Na_2IrCl_6 \cdot 6H_2O$, was obtained from Varlacoid Co. and used without purification, since the visible absorption spectrum (e.g., ϵ_{487} 4060 M^{-1} cm^{-1} in 1 M $HClO_4$) of the sample agreed with that in the literature.[26] Acetonitrile (Mallinkrodt, analytical reagent) was stirred with calcium hydride overnight, filtered, and then distilled from P_2O_5 under a nitrogen atmosphere.

Gas Chromatography Analyses. Hydrocarbons and alkyl halides were analyzed on a column consisting of 15-ft 20% apiezon L plus 15-ft 20% FFAP at 100 °C. Methane, ethane, and ethylene were also analyzed with a 2-ft Porapak Q column at room temperature.

NMR Spectra. The proton NMR spectra were recorded either on a Varian EM 360 or 220 MHz spectrometer. The spectra of the dialkyl(bisphosphine)platinum(IV) and alkyl(bisphosphine)platinum(II) complexes are listed in Table IV. The structures of the latter were assigned primarily on the basis of their proton NMR spectra using the correlations described by Ruddick and Shaw.[2] Complete structural assignments were limited by the ambiguities relating to coordination by the solvent and chloroiridium(III) species as described below for each system. Nonetheless, the principal features relating to the alkyl-platinum bonds in the products can be assigned.

Reaction of *cis*-$Me_2Pt(PMe_2Ph)_2$ with $IrCl_6{}^{2-}$. A 25-mL flask containing the desired amount of *cis*-$Me_2Pt(PMe_2Ph)_2$ and a magnetic stirring bar was sealed with a gas-tight rubber serum cap. The flask was then deoxygenated by purging with N_2, and 4 mL of deoxygenated acetonitrile was added. A concentrated solution of $Na_2IrCl_6{\cdot}6H_2O$ in acetonitrile (0.5–1.0 mL) was introduced into the stirred solution by means of a hypodermic syringe. The reaction was complete on the addition of Na_2IrCl_6. Samples of gas were analyzed for methane, ethane, and methyl chloride by gas chromatography. Samples of liquid were spectrally analyzed for the unreacted $IrCl_6{}^{2-}$.

After the analyses were completed, the product solution was pumped to dryness in vacuo, and pyridine was added to digest the residue. The undissolved Na_3IrCl_6 was removed by filtration and the filtrate was again pumped to dryness. The residue was then transferred to an NMR tube with 0.6 mL of pyridine and the spectrum recorded. The proton NMR spectrum can be assigned to two Pt(IV) complexes, both of which have *trans*-phosphines and *cis*-methyl groups. For complex 1, formed in 60% yield, the proton NMR spectrum consists of δ 2.22 t ($J_{PH} = 4.0$, $J_{PtH} = 17$ Hz) for PMe_2Ph and 0.79 t ($J_{PH} = 5.5$, $J_{PtH} = 67$ Hz) for Pt–Me, for which we assign the structure $Me_2Pt(PMe_2Ph)_2IrCl_5(CH_3CN)$, with two chlorides of $IrCl_5(CH_3CN)^{2-}$ occupying two cis coordination sites on platinum. The equivalence of the two methyl groups on the same phosphorus indicates that the two ligands trans to the methyl groups are identical, and all the coupling constants are quite similar to those of $Me_2Pt(PMe_2Ph)_2Cl_2$ with the same configuration [in CD_3Cl, δ 2.10 t ($J_{PH} = 4.1$, $J_{PtH} = 17.6$ Hz), 0.52 t ($J_{PH} = 5.6$, $J_{PtH} = 68$ Hz)].[2] The remaining four triplets in the NMR spectrum can be assigned to the complex 2, $Me_2Pt(PMe_2Ph)_2XY$, formed in 40% yield [δ 1.89 t ($J_{PH} = 4$, $J_{PtH} = 19$ Hz) and 1.90 t ($J_{PH} = 4$, $J_{PtH} = 20$ Hz) for PMe_2Ph, 1.20 t ($J_{PH} = 6$, $J_{PtH} = 65$ Hz) and 1.25 t ($J_{PH} = 6$, $J_{PtH} = 64$ Hz) for PtMe]. The two triplets at δ 1.89 and 1.90 overlap; however the coupling constants are resolved in a 220-MHz NMR spectrum. The nonequivalence of the two Pt methyls and of the two methyl groups on the phosphine indicates that X and Y are different. Since the amount of the complex 2 increased on aging the solution, we infer that one of the two ligands is pyridine, and the other is either Cl^- or $IrCl_5(CH_3CN)^{2-}$. The characteristic singlet for $IrCl_5(CH_3CN)^{2-}$ (δ 2.31)[7] was also present in the spectrum. In addition, there is a minor singlet for coordinated Pt–CH_3CN at δ 1.96, and another singlet for free CH_3CN at δ 1.92. Apparently, most of the CH_3CN originally present in the Pt^{IV} complexes formed during the reaction was replaced by $IrCl_5(CH_3CN)^{2-}$ or by pyridine during the workup. A triplet at δ 1.58 which gradually increased in intensity on aging the solution might be assigned to $Me_2Pt(PMe_2Ph)_2py_2{}^{2+}$ of the same configuration (this complex only accounts for 5% of the platinum compounds after 3 weeks).

A similar reaction was carried out in perdeuterated acetonitrile. The proton NMR spectrum of the product residue dissolved in pyridine contained all the resonances described above, except for the three singlets attributed to $IrCl_5(CH_3CN)^{2-}$, Pt^{IV}–CH_3CN, and free CH_3CN.

Reaction of *cis*-$Et_2Pt(PMe_2Ph)_2$ with $IrCl_6{}^{2-}$. A 25-mL flask containing the desired amount of *cis*-$Et_2Pt(PMe_2Ph)_2$ and a magnetic stirring bar was sealed with a gas-tight rubber serum cap. The flask was deoxygenated by purging with N_2, and 4 mL of deoxygenated acetonitrile was added. Aliquots of a solution of $IrCl_6{}^{2-}$ were added dropwise and gas samples analyzed for ethyl chloride and hydrocarbons after each addition of $IrCl_6{}^{2-}$. [This procedure was followed since spectrophotometric titration of $IrCl_6{}^{2-}$ with *cis*-$Et_2Pt(PMe_2Ph)_2$ indicated a stoichiometry of 3 to 1.] The product solution was then worked up as described for the reaction of *cis*-$Me_2Pt(PMe_2Ph)_2$. The proton NMR spectrum is consistent with the presence of an equimolar solution of *trans*-$EtPt(PMe_2Ph)_2(CH_3CN)^+$ and $IrCl_5(CH_3CN)^{2-}$ [δ 2.22 t ($J_{PH} = 4.5$ Hz) PMe_2Ph, 0.45–2.22 m Pt–Et, 1.98 s (Pt–(CH_3CN)), 2.35 s ($IrCl_5(CH_3CN)^{2-}$)].

The reaction of *cis*-$Et_2Pt(PMe_2Ph)_2$ with 3 equiv of $IrCl_6{}^{2-}$ is noteworthy. The results indicate that *cis*-$Et_2Pt(PMe_2Ph)_2$ reacts readily with the first 2 equiv to give 1 mol of EtCl, and *trans*-$EtPt(PMe_2Ph)_2(CH_3CN)^+$. *trans*-$EtPt(PMe_2Ph)_2(CH_3CN)^+$ then reacts with an additional mole of $IrCl_6{}^{2-}$ in a subsequent slow step to afford another Pt(III) species, which disproportionates to a mixed valence dinuclear (or polynuclear) complex. Alternatively, one-half of the *trans*-$EtPt(PMe_2Ph)_2(CH_3CN)^+$ may be oxidized to a Pt(IV) species, which then combines with *trans*-$EtPt(PMe_2Ph)_2(CH_3CN)^+$ to form a mixed valence complex. Polynuclear complexes consisting of alternating units of $PtCl_4{}^{2-}$ and $PtCl_6{}^{2-}$ are known.[27]

Reaction of *cis*-$Et_2Pt(PPh_3)_2$ with $IrCl_6{}^{2-}$. A 25-mL flask containing the desired amount of *cis*-$Et_2Pt(PPh_3)_2$ and Na_2IrCl_6, and a magnetic stirring bar was sealed with a rubber serum cap. The contents were deoxygenated by passing N_2 through the solution for 20 min. Deoxygenated acetonitrile (4.0 mL) was then added to initiate the reaction. The solution was stirred [*cis*-$Et_2Pt(PPh_3)_2$ was not completely dissolved] and samples of gas were periodically removed from the flask to monitor the formation of ethyl chloride and the hydrocarbons. Samples of liquid were analyzed for the unreacted $IrCl_6{}^{2-}$ by the examination of its visible spectrum after the reaction was complete in 30 min.

The product solution was worked up as described in the reaction of *cis*-$Me_2Pt(PMe_2Ph)_2$. The proton NMR spectrum was consistent with the presence of an equimolar solution of *trans*-$EtPt(PPh_3)_2(CH_3CN)^+$ [δ 0.43 t ($J_{HH} = 7.0$, $J_{PtH} = 55$ Hz, 3 H) for CH_3, 1.1–1.6 m (2 H) for CH_2, 1.97 s (3 H) for Pt–CH_3CN] and $IrCl_5(CH_3CN)^{2-}$ [δ 2.31 s (3 H)].

Reaction of *cis*-$Me_2Pt(PPh_3)_2$ with $IrCl_6{}^{2-}$. Experimental procedures similar to the reaction of *cis*-$Et_2Pt(PPh_3)_2$ were followed. The proton NMR spectra of the product residue in pyridine showed the following resonances: δ 0.57 t ($J_{PH} = 7.0$, $J_{PtH} = 70$ Hz), 0.95 t ($J_{PH} = 5.0$, $J_{PtH} = 66$ Hz), 1.38 d ($J_{PH} = 2.5$, $J_{PtH} = 65$ Hz), 1.98 s, 2.31 s. The ratios of the area of these resonances were: 1:0.6:0.8:1:1. The last two resonances can be assigned to Pt–CH_3CN (δ 1.98) and $IrCl_5(CH_3CN)^{2-}$ (δ 2.31). Gas chromatography analyses indicated that 0.46 mol of methyl group was cleaved from each mole of *cis*-$Me_2Pt(PPh_3)_2$, and spectral analysis indicated that 2 equiv of $IrCl_6{}^{2-}$ were consumed. We deduce that approximately one-half of the platinum products was in the form $MePt(PPh_3)_2S^+$ and the remainder as $Me_2Pt(PPh_3)_2S_2{}^{2+}$, where S is either chloride, $IrCl_5(CH_3CN)^{2-}$, CH_3CN, or pyridine. The doublet at δ 1.38 is assigned to $Me_2Pt(PPh_3)_2S_2{}^{2+}$ in which the two methyl groups are trans to the two phosphines. The two triplets were assigned to $Me_2Pt(PPh_3)_2S_2{}^{2+}$ with *trans*-phosphines, *cis*-methyl groups, and *trans*-$MePt(PPh_3)_2S^+$, where S is derived from the solvent.

Spectrophotometric Analyses of the Iridium(III) Products. A preliminary thin layer chromatographic investigation indicated that $IrCl_6{}^{3-}$ and $IrCl_5(CH_3CN)^{2-}$ were the only Ir(III) products formed in these reactions.[7] Instead of following the usual procedure (i.e., separating the products by thin layer chromatography, followed by spectral determination of each product), the product solution was directly oxidized with chlorine immediately after the reaction was complete, and the spectrum of the oxidized solution (after proper dilution) was recorded. Comparison of this spectrum with that of a synthetic solution consisting of equimolar amounts of $IrCl_6{}^{3-}$ and $IrCl_5(CH_3CN)^{2-}$ indicated that the Ir(III) products consisted equally of $IrCl_6{}^{3-}$ and $IrCl_5(CH_3CN)^{2-}$.

Spectrophotometric Titration of $IrCl_6{}^{2-}$ with *cis*-$Me_2Pt(PMe_2Ph)_2$ and *cis*-$Et_2Pt(PMe_2Ph)_2$. A UV cell sealed with a rubber serum cap was deaerated by purging with N_2, and 2.0 mL of 4.2×10^{-4} M Na_2IrCl_6 ($\approx 8.4 \times 10^{-4}$ mmol) added. The solution was titrated with *cis*-$Me_2Pt(PMe_2Ph)_2$ solution (5 μL $\approx 8.5 \times 10^{-5}$ mmol). The absorbance of the solution (followed at λ 489 nm) decreased by 20% after each addition, and the color of $IrCl_6{}^{2-}$ disappeared completely after 25 μL of the solution was added.

The titration of $IrCl_6{}^{2-}$ with *cis*-$Et_2Pt(PMe_2Ph)_2$ was carried out using the same procedures. It afforded a stoichiometry of 3:1 consumption of $IrCl_6{}^{2-}$. An inverse titration was carried out by the successive addition of 2.7×10^{-4} mmol (in 10-μL solution) of Na_2IrCl_6 to a cell containing 2.7×10^{-4} mmol of *cis*-$Et_2Pt(PMe_2Ph)_2$. The first two aliquots were consumed with a half-life of less than 2 min and the third aliquot was consumed with a half-life of 10 min. $IrCl_6{}^{2-}$ was not consumed on further addition.

Electrochemical Oxidation of *cis*-$Me_2Pt(PMe_2Ph)_2$ and *cis*-$Et_2Pt(PMe_2Ph)_2$. The anodic oxidation of *cis*-$Me_2Pt(PMe_2Ph)_2$ and *cis*-$Et_2Pt(PMe_2Ph)_2$ was carried out in a saturated solution of $NaBF_4$ in acetonitrile under a nitrogen atmosphere. The cell was equipped with a gas bubbler, in addition to the platinum cathode and anode. Ag/0.1 M $AgNO_3$ in acetonitrile was employed as the reference electrode using a cracked-glass tip.[28] A solution (100 mL) containing 20 mg of the platinum complex was introduced into the cell and the solution was purged with N_2 for 15 min. The nitrogen flow was interrupted before the measurements were taken. Only a single peak potential was observed in the anodic sweep (at 5 mV/s) for both *cis*-

Table V. Kinetics of the Reaction of *cis*-R_2PtL_2 with Hexachloroiridate(IV) in Acetonitrile at 25 °C[a]

R_2PtL_2	$10^5[IrCl_6^{2-}]$, M	$10^5[R_2PtL_2]$, M	k_{obsd}, s^{-1}	k, $M^{-1} s^{-1}$
$Et_2Pt(PMe_2Ph)_2$	1.6	1.6	5.0×10^{-2} [b]	1.6×10^3
	1.6	3.3	1.08×10^{-1}	1.6×10^3
	1.6	3.3	1.31×10^{-1}	2.0×10^3
	1.6	5.3	1.54×10^{-1}	1.5×10^3
	1.6	5.3	1.48×10^{-1}	1.4×10^3
				Av $(1.6 \pm 2) \times 10^3$
$Me_2Pt(PMe_2Ph)_2$	1.6	9.0	7.9×10^{-2}	4.4×10^2
	1.6	9.0	8.3×10^{-2}	4.6×10^2
	1.6	6.8	6.3×10^{-2}	4.6×10^2
	1.6	6.8	6.3×10^{-2}	4.6×10^2
	1.6	2.7	2.1×10^{-2} [b]	3.9×10^2
	0.8	9.0	7.3×10^{-2}	4.1×10^2
	0.8	9.0	7.3×10^{-2}	4.1×10^2
	2.4	9.0	8.2×10^{-2}	4.6×10^2
				Av $(4.4 \pm 0.2) \times 10^2$
$Et_2Pt(PPh_3)_2$	1.6	19.0	3.1×10^{-3}	0.82
	1.6	19.0	2.8×10^{-3}	0.74
	1.6	14.0	1.8×10^{-3}	0.64
	1.6	9.0	1.3×10^{-3}	0.72
	0.8	19.0	3.0×10^{-3}	0.79
	2.4	19.0	3.1×10^{-3}	0.82
				Av (0.76 ± 0.6)
$Me_2Pt(PPh_3)_2$	1.6	18	7×10^{-4} [b]	0.02

[a] 1.0×10^{-2} M $NaClO_4$. [b] Values of k_{obsd} are calculated from the initial rates.

$Me_2Pt(PMe_2Ph)_2$ (0.72 V) and *cis*-$Et_2Pt(PMe_2Ph)_2$ (0.40 V).

Cyclic voltammetry was carried out in the same cell used in the anodic oxidation. The voltage was first swept from zero to beyond the anodic peak potential, and then reversed. No reduction wave was observed in the reverse scan even at sweep rates as fast as 10 V/s. No measurements were made beyond this upper limit for the platinum electrode, since the charging current increases steadily at higher sweep rates.

Kinetics. All the reactions were followed spectrophotometrically using a Cary 14 spectrophotometer and carried out under a nitrogen atmosphere, at constant temperature regulated at 25.0 ± 0.2 °C.

The reactions were followed by the disappearance of the absorption band due to hexachloroiridate(IV) at λ_{max} 489 nm. In general, R_2PtL_2 was present in tenfold excess or more to ensure that the concentration remained essentially constant throughout the reaction. The pseudo-first-order plots were linear for more than 3 half-lives and were used to evaluate the rate constants. However, because of the high rates of reaction of *cis*-$R_2Pt(PMe_2Ph)_2$ and the low solubilities of *cis*-$R_2Pt(PPh_3)_2$, it was not always possible to maintain a tenfold excess of the Pt complexes, even at a $IrCl_6^{2-}$ concentration of 10^{-5} M. Under these conditions, the initial rates of the reaction were used to evaluate the rate constants, since the pseudo-first-order plots were not linear. At lower concentrations of $IrCl_6^{2-}$, the absorbance change was too small to measure reliably.

In a typical experiment for the reaction of *cis*-$R_2Pt(PMe_2Ph)_2$, a cell containing 1.6×10^{-5} M $IrCl_6^{2-}$ and 1.0×10^{-2} M $NaClO_4$ in 2.5 mL of acetonitrile was thermostated for 15 min, and a concentrated solution of *cis*-$R_2Pt(PMe_2Ph)_2$ in the amount of 20-100 μL was added with a microsyringe to initiate the reaction (see data, Table V). For the reactions of *cis*-$R_2Pt(PPh_3)_2$, a cell containing 1.0×10^{-2} M $NaClO_4$ and the desired amount of $R_2Pt(PPh_3)_2$ was thermostated for 15 min and a concentrated solution of $IrCl_6^{2-}$ was added in the amount of 10-30 μL to initiate the reaction. The reverse order of addition of the reagents was necessary due to the low solubilities of *cis*-$R_2Pt(PPh_3)_2$ in acetonitrile ($\sim 2 \times 10^{-4}$ M in a saturated solution). Owing to the slow rate of reaction of *cis*-$Me_2Pt(PPh_3)_2$ with $IrCl_6^{2-}$ and the instability of $IrCl_6^{2-}$ in CH_3CN at the low concentrations, it was not possible to measure the rate of this reaction accurately.

Charge Transfer Spectra. The charge transfer complexes of *cis*-R_2PtL_2 with TCNE are unstable and could not be determined at room temperature. The spectra of the complexes of *cis*-$Et_2Pt(PPh_3)_2$ and *cis*-$Me_2Pt(PPh_3)_2$ were recorded at −77 and −60 °C, respectively.

The solutions for the determination of the charge transfer spectra were prepared in a nitrogen atmosphere as described previously.[7] A solution containing 1.0×10^{-3} M R_2PtL_2 in 2.0 mL of 1,2-dichloropropane was allowed to reach thermal equilibrium for 15 min in the cell, and a 0.2-0.6-mL solution of 2.0×10^{-1} M TCNE was then added. The solution was quickly shaken and the cell transferred to the spectrophotometer.

Reaction of *cis*-Et_2PtL_2 with Hexachloroiridate(IV) in the Presence of Oxygen. In a typical experiment, a 25-mL flask containing 0.030 mmol of *cis*-Et_2PtL_2 was sealed with a gas-tight rubber septum cap and purged with oxygen for 15 min. Oxygen-saturated acetonitrile (4.0 mL) was added and the solution stirred magnetically. A solution of hexachloroiridate(IV) consisting of 0.041 mmol in 1.0 mL of acetonitrile was then added dropwise to the vigorously stirred solution. The precipitate was allowed to settle and samples of the liquid removed in order to analyze it for ethyl chloride, acetaldehyde, and ethanol. Samples of the gas phase were also removed for the analysis of ethane and ethylene.

Ethyl chloride was identified by gas liquid chromatography (GLC) on a 30-ft FFAP column at 110 °C. Acetaldehyde and ethanol were identified on two columns of different polarity (30-ft FFAP and 4-ft Porapak Q). Ethane and ethylene were analyzed on a Porapak Q column at 115 °C.

Spin Trapping of Ethyl Radicals in the Reaction of *cis*-Et_2PtL_2 and Hexachloroiridate(IV). 1. *cis*-$Et_2Pt(PPh_3)_2$. In a typical procedure, 3.1×10^{-2} mmol of *cis*-$Et_2Pt(PPh_3)_2$, 2.2×10^{-2} mmol of sodium hexachloroiridate(IV) hexahydrate, and 2.5×10^{-1} mmol of nitroso-*tert*-butane were weighed into an NMR tube. The mixture was deaerated by nitrogen entrainment and 0.5 mL of acetic acid was added to initiate the reaction. No ESR signal was detected. A similar experiment carried out in acetonitrile gave no ESR signal. All of these experiments were carried out in the dark.

2. *cis*-$Et_2Pt(PMe_2Ph)_2$. Nitroso-*tert*-butane (0.11 mmol) and $Na_2IrCl_6 \cdot 6H_2O$ (0.030 mmol) were weighted into an ESR tube, deoxygenated, and 0.3 mL of acetic acid was added in the dark. No ESR spectrum was observed. A solution of *cis*-$Et_2Pt(PMe_2Ph)_2$ consisting of 0.038 mmol in 1.2 mL of acetic acid was then added. The resulting solution showed an ESR spectrum that could be clearly identified as that of the ethyl adduct to nitroso-*tert*-butane. Exposure of this solution to light resulted in a marked increase in intensity of the 1:1:1 triplets due to the spectrum of di-*tert*-butyl nitroxide, which has almost the same nitrogen hyperfine splittings as that of the ethyl adduct.

Reaction of *cis*-$Me_2Pt(PMe_2Ph)_2$ with Hexachloroiridate(IV) in

the Presence of Bromide. Both *cis*-$Me_2Pt(PMe_2Ph)_2$ (17.1 mg, 3.4 × 10^{-2} mmol) and tetra-*n*-butylammonium bromide (1.3 mmol) were weighed into a 25-mL flask, which was sealed with a gas-tight septum and the contents deaerated with a stream of nitrogen. Acetonitrile (2.0 mL) was added and the solution stirred, while a solution of sodium hexachloroiridate(IV) containing 6.6 × 10^{-2} mmol in 1.0 mL of acetonitrile was added. Gas liquid chromatography of the reaction after completion [noted by the rapid decoloration of iridium(IV)] showed a trace of methyl chloride, but no methyl bromide. We infer from the absence of methyl cleavage that the oxidation of $Me_2Pt(PMe_2Ph)_2$ followed the usual course to the platinum(IV) species.

Acknowledgment. We wish to thank the National Science Foundation for financial support and Dr. Dennis Peters and Mr. Gary McNamee for assistance with the electrochemical studies.

References and Notes

(1) U. Belluco, "Organometallic and Coordination Chemistry of Platinum", Academic Press, New York, N.Y., 1974; F. R. Hartley, "The Chemistry of Platinum and Palladium", Halsted Press, New York, N.Y., 1973.

(2) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(4) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

(5) (a) J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Am. Chem. Soc.*, **95**, 7908 (1973); (b) K. S. Lau, R. W. Fries, and J. K. Stille, *ibid.*, **96**, 4983 (1974); (c) Cf. also V. I. Sokolov, *Inorg. Chim. Acta*, **18**, L9 (1976).

(6) (a) J. Halpern and M. Pribanic, *J. Am. Chem. Soc.*, **90**, 5942 (1968); (b) R. C. Wright and G. S. Laurence, *J. Chem. Soc., Chem. Commun.*, 132 (1972); (c) G. F. Adams, R. B. Broszkiewicz, and B. D. Michael, *Trans. Faraday. Soc.*, **64**, 1256 (1968).

(7) (a) H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 1855 (1975); (b) J. Y. Chen, H. C. Gardner, and J. K. Kochi, *ibid.*, **98**, 6150 (1976).

(8) H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 2460 (1976).

(9) D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 350 (1973).

(10) P. K. Wong, K. S. Lau, and J. K. Stille, *J. Am. Chem. Soc.*, **96**, 5956 (1974).

(11) J. A. Howard, *Adv. Free Radical Chem.*, **4**, 49 (1972).

(12) If all the alkyl radicals liberated during oxidation react with oxygen according to eq 13 and 14, the stoichiometric consumption of hexachloroiridate(IV) would decrease from 2 to 1 equiv for each mole of dialkylplatinum(II) undergoing oxidative cleavage. Thus, depending on the efficiency of the trapping of the alkyl radicals and the subsequent reactions of the oxygen-centered radicals, the stoichiometry in the presence of oxygen would vary between 2:1 (no trapping) and 1:1 (complete trapping).

(13) J. Halpern, M. S. Chan, J. Hanson, T. S. Roche, and J. A. Topich, *J. Am. Chem. Soc.*, **97**, 1607 (1975); S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972).

(14) Solvent (CH_3CN) of coordination is implied, but not specifically included.

(15) From the observation that $IrCl_6^{3-}$ and $IrCl_5(CH_3CN)^{2-}$ are formed in more or less equimolar amounts irrespective of the stoichiometry of oxidation (compare eq 5 and 6), we infer that further reaction of I with hexachloroiridate(IV) in eq 19 proceeds by chlorine atom transfer.

(16) N. Clinton and J. K. Kochi, *J. Organomet. Chem.*, **56**, 243 (1973); **42**, 241 (1972).

(17) Cf. C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

(18) It is interesting to note that the methane formed in minor but significant amounts from $Me_2Pt(PPh_3)_2$ is relatively more important than ethane from $Et_2Pt(PPh_3)_2$. The difference could be due to a slower rate of reaction of methyl radicals (compared to ethyl) with hexachloroiridate(IV) in competition with hydrogen transfer from solvent. A more intriguing possibility, however, is an intramolecular hydrogen transfer from the intermediate I directly leading to methane and a carbene complex. [Cf. E. L. Muetterties and P. L. Watson, *J. Am. Chem. Soc.*, **98**, 4667 (1976).] In a preliminary study of the facile reaction of $(CD_3)_2Pt(PMe_2Ph)_2$ with carbon tetrachloride, only 10% of the methane formed consisted of CD_4.

(19) According to Scheme I, the rate of disappearance of hexachloroiridate(IV) should be reduced by a factor of 2, if all the ethyl radicals formed during the oxidative cleavage of Et_2PtL_2 were scavenged by oxygen, as recently found in a related example with dialkylmercury.[7b]

(20) The competition described in eq 18 and 19 is dependent on the concentration of hexachloroiridate(IV). However, depending on the relative rate constants for these processes, the product ratios may be difficult to relate quantitatively to Scheme I.

(21) (a) W. A. Nugent, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 4945 (1974); (b) D. G. Morrell and J. K. Kochi, *ibid.*, **97**, 7262 (1975).

(22) (a) N. A. Clinton, H. C. Gardner, and J. K. Kochi, J. Organomet. Chem., **56**, 227 (1973); (b) W. A. Nugent and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 5979 (1976).

(23) (a) J. K. Kochi, *Acc. Chem. Res.*, **7**, 351 (1974); (b) R. A. Budnick and J. K. Kochi, *J. Organomet. Chem.*, **116**, C3 (1976). (c) For example, alkylplatinum(II) complexes studied by Shaw and co-workers[2,3] could be involved with molecular chlorine[24] and alkyl halides[25] behaving either as electron acceptors in 1-equiv processes, or in their more commonly formulated capacity as (2-equiv) electrophiles.

(24) J. K. Kochi, *Tetrahedron Lett.*, 4305 (1974).

(25) (a) Cf. M. F. Lappert and P. W. Lednor, *Adv. Organomet. Chem.*, **14**, 387 (1976); (b) I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, **84**, C7 (1975).

(26) A. G. Sykes and R. F. Thornley, *J. Chem. Soc. A*, 232 (1970).

(27) B. M. Craven and D. Hall, *Acta Crystallogr.*, **14**, 475 (1971).

(28) J. J. Lingane, *J. Electroanal. Chem.*, **1**, 379 (1960).

Electronic Substituent Effects upon the Selectivity of Synthetic Ionophores

K. H. Pannell,*[1a] Wayne Yee,[1a] G. S. Lewandos,*[1b] and D. C. Hambrick[1b]

Contribution from the Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968, and the Department of Chemistry, Sul Ross State University, Alpine, Texas 79830. Received July 26, 1976

Abstract: Substituted dibenzo-18-crown-6 ethers, *cis*- and *trans*-dinitro, *cis*- and *trans*-diamino, tetrabromo, octachloro, and mono- and bis(tricarbonylchromium), have been synthesized and characterized. Investigations on the ability of these crown ethers to extract sodium and potassium salts from water into methylene chloride have been performed. A very pronounced substituent effect has been observed that results in a reversal of the normal selectivity for this process of $K^+ > Na^+$.

There has been considerable recent interest in the chemical and physical properties of the synthetic ionophores commonly named crown ethers.[2] Since Pedersen first established these compounds as very efficient coordinating agents for the alkali metal cations,[3] many studies have demonstrated the general concept that the size of the crown cavity plays a large role in determining the thermodynamic stability of the resulting complexes.[4,5] Certain gross substituent effects upon their properties have been observed. For example, there are differences in complexing abilities of the various 18-crown-6 ethers: dibenzo-18-crown-6, dicyclohexyl-18-crown-6, and 18-crown-6.[6] However, such variations with substituent may spring in part, if not mostly, from structural changes that restrict important conformational distortions of the crown upon complexing the metal cation.[7] It has also been established that the solvent environment can cause variations from one ether to another often causing changes in cation selectivity.[8] Apart from these results the overriding factor thought to control the formation of cation–crown complexes is the relative cation–oxygen cavity size. Thus, while 14-crown-4 ethers complex