(6) L. L. Rines, J. A. Plambeck, and D. J. Francis, "ENLLSQ Reprogrammed," Program Library, Department of Chemistry, University of Alberta, 1970.
(7) (a) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964); (b) A. M. Chmelnick and D. Fiat, *ibid.*, **49**, 2101 (1968).
(8) This correction results because outer-sphere broadening is independent of *n*, but experimental results in a given system usually are divided by P_M which does depend on *n*.
(9) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970). This equation assumes $T_{1e} < \tau_r$ which appears to be the case here from the field dependence of T_{2M}.
(10) B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).
(11) This also presumes that only the contact interaction is important for the CH_3 protons, as seems justified from later calculations.
(12) I. D. Campbell, J. P. Carver, R. A. Dwek, A. J. Nummetin, and R. E. Richards, *Mol. Phys.*, **20**, 913 (1971).
(13) J. W. Neely and R. E. Connick, *J. Amer. Chem. Soc.*, **94**, 3419, 8646 (1972).
(14) A. D. McLachlan, *Proc. Roy. Soc., Ser. A*, **280**, 271 (1961).
(15) Subsequent calculations indicate that this condition is not valid for systems discussed here. But it is likely that the functional form of the frequency-dependent terms in eq 19 is correct in which case the τ_c values derived should be valid.
(16) The d_0 values are of limited significance since the outer-sphere contribution has been estimated empirically as described in the text.
(17) N. S. Angerman and R. B. Jordan, *J. Chem. Phys.*, **43**, 837 (1971).
(18) K. J. Irvin, R. Jamison, and J. J. McGarvey, *J. Amer. Chem. Soc.*, **94**, 1763 (1972), have observed a relaxation time of about 3 × 10^{-7} sec for the diamagnetic → paramagnetic change of $Ni(2,3,2\text{-tet})^{2+}$ in water at 23°, but analogous values for $NiCR^{2+}$ are not known.

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Ligand-Exchange Reactions and Isomerization of an Isoquinoline–Platinum(II) Complex

FREDERICK PESA and MILTON ORCHIN*

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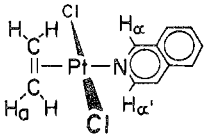
The ^1H nmr spectrum of a freshly prepared $CDCl_3$ solution of *trans*-$[PtCl_2(C_2H_4)(\text{iquin})]$, **1**, shows no $^3J_{\text{Pt-NCH}}$ owing to fast exchange with a small amount of adventitious free isoquinoline (iquin). However, after storage at room temperature in the dark for several days, the spectrum of the solution clearly shows the $^3J_{\text{Pt-NCH}}$. During the elapsed time, the uncomplexed isoquinoline is slowly consumed by reaction with **1** to form *trans*-$[PtCl_2(\text{iquin})_2]$. Irradiation of a $CHCl_3$ solution of **1** with ultraviolet light results in the isomerization of **1** to its cis isomer, probably *via* the bridged dimer $[PtCl_2(\text{iquin})]_2$.

Introduction

We have shown earlier[1] that the ^1H nmr spectrum of a freshly prepared $CDCl_3$ solution of *trans*-$[PtCl_2(C_2H_4)(\text{iquin})]$, **1**, does not exhibit $^3J_{\text{Pt-NCH}}$. However, this coupling appears when the solution is allowed to stand at room temperature for several days. We originally thought this behavior to be a consequence of a slow conformational conversion of the isoquinoline (iquin) moiety to a rigid rotamer. It was assumed that, owing to steric shielding of the empty p orbital on Pt, such a rotamer would be resistant to solvolysis and hence its ^1H nmr spectrum would exhibit the observed $^3J_{\text{Pt-NCH}}$. Subsequently this interpretation was shown to be incorrect.[2] Instead it was suggested that the complex was exchanging with free ligand and the latter gradually disappeared with time. However, it was claimed that the exchange was accompanied by a slow isomerization of the trans complex **1** to its cis isomer. The cis isomer, **2**, was assumed to be responsible for the inhibition of isoquinoline exchange and hence the gradual appearance of coupling. The increase in the concentration of **2** was monitored by the appearance of a new ethylene proton signal.



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We confirm that the initial presence, followed by the gradual disappearance of free isoquinoline, rather than conformational change, accounts for the coupling phenomena in the ^1H nmr spectra. However, we find that the reported[2] trans → cis rearrangement in solution probably is an adventitious photochemical reaction and the presence of the cis isomer is irrelevant to the pertinent coupling behavior. We also clarify the source and the eventual fate of the free ligand.

Results and Discussion

The 90-MHz ^1H nmr spectrum of **1** (Figure 1a) taken promptly in $CDCl_3$ solution at room temperature shows no coupling of ^{195}Pt with either of the α protons of isoquinoline. Although not shown in Figure 1, on cooling to about 0°, coupling with H_α ($J = 41$ Hz) becomes clearly apparent and on further cooling ($\sim$−40°) coupling with the second α proton, $H_{\alpha'}$, also becomes apparent ($J = 30$ Hz). On warming to room temperature and again determining the ^1H nmr spectrum, the original spectrum is reproduced. In order for spin–spin coupling to be observed,[3] the average lifetime of the coordinated complex, PtL, must be larger than $1/J$ and apparently the rate of exchange of L at the intermediate temperature is accidentally such that only coupling with the proton having the higher coupling constant is readily discernible.

Although no $^3J_{\text{PT-NCH}}$ is present in the spectrum of the fresh solution, after about 3 or more days of standing at room temperature in $CDCl_3$ solution, the spectrum of the solution of **1** clearly shows coupling of both H_α and $H_{\alpha'}$ at room temperature. A typical spectrum of an aged solution is shown in Figure 1b. The coupling constants and chemical shifts of H_α and $H_{\alpha'}$ are virtually the same as those observed in the nmr spectrum of the fresh solution of −40°.

When the freshly prepared $CDCl_3$ solution is extracted with either HBF_4 or passed over a cation-exchange resin,[4] free ligand is removed and the solution now exhibits $^3J_{\text{Pt-NCH}}$. The recovery of pure isoquinoline from the extract has been demonstrated.[4] Addition of a small quantity of isoquinoline to the treated solution results in the loss of coupling. The generality of this behavior and its quantitative aspects are under study.

It is clear from the above facts that free ligand is responsible for fast exchange and the absence of coupling in the freshly prepared solution of **1**. However, the fate of the ligand in aged solutions remains to be demonstrated. We believe that the free ligand gradually disappears by irreversible formation of *trans*-$[PtCl_2(\text{iquin})_2]$, **3**. The presence of **3** is difficult to show because it is present in such small amounts. However, if a small quantity of additional isoquinoline is added to the aged $CHCl_3$ solution of **1**, **3** is precipitated. The properties of this precipitate correspond to those of **3** separately prepared in good purity and yield by adding stoichiometric quantities of isoquinoline to a chloroform solution of **1**. We find no evidence for the formation of the cis isomer **2** in the absence of ultraviolet light.

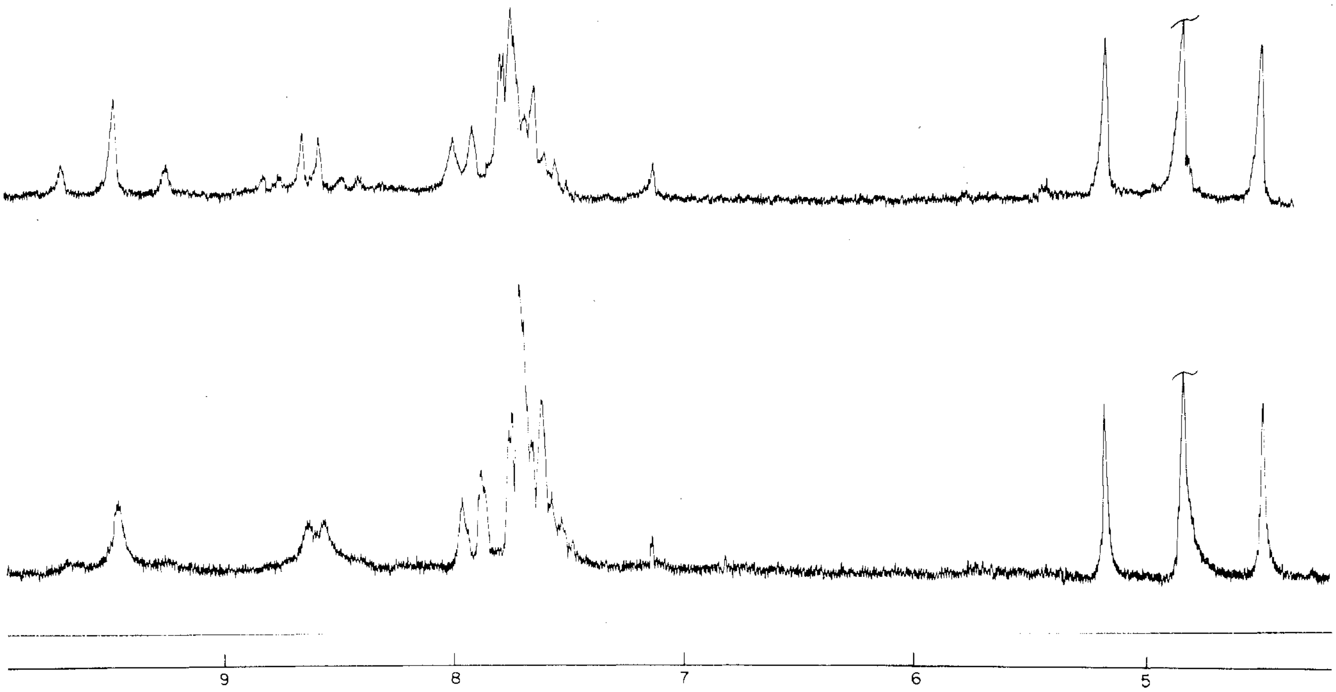
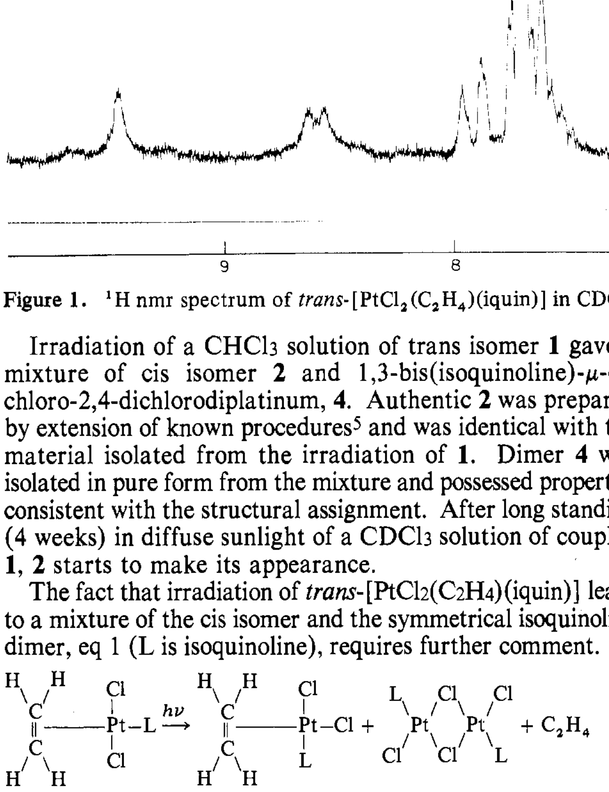


Figure 1. ^{1}H nmr spectrum of *trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)] in CDCl$_3$: (a) bottom–freshly prepared solution; (b) top–aged solution.

Irradiation of a CHCl$_3$ solution of trans isomer **1** gave a mixture of cis isomer **2** and 1,3-bis(isoquinoline)-μ-dichloro-2,4-dichlorodiplatinum, **4**. Authentic **2** was prepared by extension of known procedures[5] and was identical with the material isolated from the irradiation of **1**. Dimer **4** was isolated in pure form from the mixture and possessed properties consistent with the structural assignment. After long standing (4 weeks) in diffuse sunlight of a CDCl$_3$ solution of coupled **1**, **2** starts to make its appearance.

The fact that irradiation of *trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)] leads to a mixture of the cis isomer and the symmetrical isoquinoline dimer, eq 1 (L is isoquinoline), requires further comment. It


(1)

is possible that the irradiation initiates ethylene dissociation and that the dimer is the first stable complex produced. The ethylene which remains in solution may then cleave the bridged dimer to give the cis isomer. Separate treatment of the dimer in the dark in CHCl$_3$ with ethylene at 1 atm readily gave pure cis. If, as seems likely, the dimer is the first product of irradiation in the isomerization of trans to cis, the photochemical isomerization must proceed by a different mechanistic pathway than the thermal isomerization[6] of analogous Pt(II) complexes.

The reactions which occur when **1** is dissolved in CHCl$_3$ are as shown by eq 2–4. Reaction 2 has been demonstrated by

$$\textit{trans}\text{-}[\mathrm{PtCl_2(C_2H_4)(L)}] + \mathrm{L} \rightleftharpoons \textit{trans}\text{-}[\mathrm{PtCl_2(C_2H_4)(L)}] + \mathrm{L}\ (\text{fast}) \qquad (2)$$

$$\textit{trans}\text{-}[\mathrm{PtCl_2(C_2H_4)(L)}] + \mathrm{L} \rightleftharpoons \textit{trans}\text{-}[\mathrm{PtCl_2(L)_2}] + \mathrm{C_2H_4}^*\ (\text{slow}) \qquad (3)$$

$$\textit{trans}\text{-}[\mathrm{PtCl_2(C_2H_4)(L)}] + \mathrm{C_2H_4}^* \rightleftharpoons \textit{trans}\text{-}[\mathrm{PtCl_2(C_2H_4)^*(L)}] + \mathrm{C_2H_4}\ (\text{fast}) \qquad (4)$$

extraction of L and recovery of it in the extract and by the nmr behavior discussed above. Reaction 3 has been demonstrated by the isolation of **3** formed by the addition of small amounts of isoquinoline to solutions of **1**. Reaction 3 can be suppressed by allowing a solution of **1** in CHCl$_3$ (which does not show $^3J_{\text{Pt-NCH}}$) to stand under 1 atm of ethylene at room temperature. Whereas, without ethylene, coupling of the isoquinoline protons would be observed after about 3 days, no such coupling is observed after a similar period when ethylene is present. The broadening of the ethylene signal under an atmosphere of C$_2$H$_4$ demonstrates the well-known reaction 4.[7] Despite the rapid exchange which occurs in reaction 4, coupling between ethylene proton, H$_a$, and ^{195}Pt is always observed probably because of the large $^2J_{\text{Pt-CH}}$ of 62 Hz.

Although the present work is concerned exclusively with complex **1**, our experience indicates that whenever related complexes are prepared, the fresh solutions may contain free ligand and this should be removed before ^{1}H nmr spectra can be properly interpreted.

Experimental Section

Infrared spectra were obtained using a Beckman IR-12 spectrophotometer and Nujol mulls mounted between polyethylene plates. The ^{1}H nmr spectra were obtained on a Varian T-60 or a Brucker HX-90 MHz spectrophotometer and all chemical shifts are reported relative to CHCl$_3$. Differential scanning calorimetry (dsc) and thermal gravimetric analysis were performed on Perkin-Elmer DSC-1b and TGS-1 instruments, respectively. The symbols T_i and T_f in the text refer to the initial and final temperatures (°C) of decomposition. The calculated per cent weight losses correspond to removal of all coordinated groups from the PtCl$_2$. The dsc analysis can frequently disclose whether complexes melt with or without rearrangement or decomposition and the tga data give information on the composition of the complex.

***trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)], 1.** The following preparation is an extension of that reported previously.[4] The use of a water-insoluble base, L, such as isoquinoline requires HCl for its solution. In such cases care must be exercised to free the desired complex from the salt LH$^+$[PtCl$_3$]$^-$, which may contaminate the neutral complex.

To a suspension of 1.52 ml (0.130 mol) of isoquinoline in 20 ml of H$_2$O, 0.1 N HCl was added until the base dissolved. The solution was then added dropwise to 5.0 g (0.130 mol) of K[PtCl$_3$(C$_2$H$_4$)] dissolved in 50 ml of H$_2$O. The yellow solid which precipitated immediately was filtered, washed with water, and dried *in vacuo*. The isoquinoline salt, **5**, which is precipitated along with the neutral complex in a yield of about 5%, can be separated from the more soluble neutral complex by differential solubility in CHCl$_3$. The salt was prepared separately, in quantitative yield by bubbling HCl(g) into a CHCl$_3$ solution of *trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)].

***trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)], 1.** The complex was dissolved in CDCl$_3$ and this solution treated as described elsewhere[4] to free it of uncomplexed isoquinoline. ^{1}H nmr (CDCl$_3$): 4.98 (t, 4, $^2J_{\text{Pt-CH}}$ = 62 Hz. ^{1}H nmr (C$_2$H$_4$): 8.75 (m, 1, 3$J_{\text{Pt-NCH}}$ = 30 Hz), 9.62 (t, 1, $^3J_{\text{Pt-NCH}}$ = 41 Hz). $\nu_{\text{Pt-Cl}}$: 345 cm^{-1}. Dsc: mp 129°; T_{i} = 142°, T_{f} = 310°; % wt loss = 39.9 (obsd), 37.1 (calcd). *Anal.* Calcd for C$_{11}$H$_{11}$NPtCl$_2$: C, 31.19; H, 2.62; Pt, 46.10. Found: C, 31.16; H, 2.87; residue, 45.91.

[C$_9$H$_8$N][PtCl$_3$(C$_2$H$_4$)], 5. ^{1}H nmr (CDCl$_3$): 4.87 (t, 4, $^2J_{\text{Pt-CH}}$ = 62 Hz). $\nu_{\text{Pt-Cl}}$: 338, 309 cm^{-1}. Dsc: mp 120°; T_{i} = 129°, T_{f} = 298°; % wt loss = 41.9 (obsd), 42.1 (calcd). *Anal.* Calcd for C$_{11}$H$_{12}$NPtCl$_3$: C, 28.72; H, 2.63; Pt, 42.45. Found: C, 28.80; H, 2.56; residue, 40.60.

***trans*-[PtCl$_2$(iquin)$_2$], 3.** To 100 mg of *trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)] dissolved in 5 ml of CHCl$_3$ was added an equimolar amount of isoquinoline. A yellow precipitate appeared after 6 hr. The solution was allowed to stand for 36 hr and filtered, and the solid product was washed with hexane and dried. *Anal.* Calcd for C$_{18}$H$_{14}$Cl$_2$N$_2$Pt: C, 41.23; H, 2.69; N, 5.34. Found: C, 39.34; H, 2.72; N, 4.77. $\nu_{\text{Pt-Cl}}$: 338 cm^{-1} and a peak at 294 cm^{-1} which has yet to be unequivocally assigned. Dsc: T_{i} = 298°, T_{f} = 337°, % wt loss = 46.3 (obsd), 49.2 (calcd). This compound has been prepared previously[8] by irradiation of *cis*-[PtCl$_2$(iquin)$_2$] but was not isolated. The analogous pyridine complex has been prepared by a similar method.[9]

1,3-Bis(isoquinoline)-μ-dichloro-2,4-dichlorodiplatinum(II), 4. A solution of 432 mg (1 mmol) of *trans*-[PtCl$_2$(C$_2$H$_4$)(iquin)] in 20 ml of CHCl$_3$ was irradiated (500-W Hg lamp) in a Pyrex vessel for 48 hr. The orange-yellow precipitate was filtered, washed with hexane, and dried. The solid consisted of two compounds, the less soluble **2** (in CHCl$_3$), *cis*-[PtCl$_2$(C$_2$H$_4$)(iquin)], and the more soluble, previously unreported [Pt$_2$Cl$_4$(iquin)$_2$]. *Anal.* Calcd for *cis*-[PtCl$_2$(C$_2$H$_4$)(iquin)], C$_{11}$H$_{11}$NPtCl$_2$: C, 31.19; H, 2.62; N, 3.36. Found: C, 31.18; H, 2.61; N, 3.38. $\nu_{\text{Pt-Cl}}$: 344, 310 cm^{-1}. ^{1}H nmr (CDCl$_3$) (3200 spectra were time-averaged because of the low solubility in CDCl$_3$): 4.83 (t, 4, $^2J_{\text{Pt-CH}}$ = 62 Hz (C$_2$H$_4$)), 8.80 (m, 1, $^3J_{\text{H-H}}$ = 6 Hz, $^3J_{\text{Pt-NCH}}$ = 31 Hz), 9.81 (t, 1, $^3J_{\text{Pt-NCH}}$ = 39 Hz). Dsc: T_{i} = 155°, T_{f} = 338°; % wt loss = 37.9 (obsd), 37.1 (calcd).

1,3-Bis(isoquinoline)-μ-dichloro-2,4-dichlorodiplatinum(II). *Anal.* Calcd for C$_{18}$H$_{14}$N$_2$Pt$_2$Cl$_4$: C, 27.34; H, 1.79; Cl, 17.96. Found: C, 27.19; H, 1.82; Cl, 18.19. $\nu_{\text{Pt-Cl}}$: 351, 324 cm^{-1}.

The corresponding piperidine dimer was isolated[10] from an aged (2 months) petroleum ether solution of *trans*-[PtCl$_2$(C$_2$H$_4$)(piperidine)] but it is not clear whether this was just a slow reaction or was the result of inadvertent irradiation.

***cis*-[PtCl$_2$(iquin)$_2$].** To a solution of 100 mg of *cis*-[PtCl$_2$(C$_2$H$_4$)(iquin)] in 50 ml of CHCl$_3$ was added an equimolar amount of isoquinoline. The solution was allowed to stand for 48 hr and evaporated to dryness. The solid *cis*-[PtCl$_2$(iquin)$_2$] was washed with hexane and dried. This complex was also prepared by cleavage of the isoquinoline dimer with isoquinoline. *Anal.* Calcd for C$_{18}$H$_{14}$N$_2$PtCl$_2$: C, 41.23; H, 2.69; N, 5.24. Found: C, 41.17; H, 2.80; N, 5.09. $\nu_{\text{Pt-Cl}}$: 338, 330 cm^{-1}. Dsc: T_{i} = 229, T_{f} = 302; % wt loss = 46.3 (obsd), 51.7 (calcd). This complex has been previously prepared by treatment of K$_2$PtCl$_4$ with isoquinoline.[8]

Precipitation of *trans*-[PtCl$_2$(iquin)$_2$] from Solution of 1. A freshly prepared 1 *M* CDCl$_3$ solution of **1** (no $^3J_{\text{Pt-NCH}}$) was allowed to stand in the dark for 1 day after which $^3J_{\text{Pt-NCH}}$ was observed. To 1 ml of this solution was added 12 μl (10 mol %) of isoquinoline. After 24 hr a yellow-white precipitate appeared which was separated from the supernatant by centrifugation. The solid precipitate was washed with 5 ml of cold hexane and dried *in vacuo*. The ir spectrum and a dsc analysis showed it to be *trans*-[PtCl$_2$(iquin)$_2$] containing a small amount of **1**. The supernatant solution, after standing in the dark for 1 additional day, showed $^3J_{\text{Pt-NCH}}$.

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References and Notes

(1) L. Spaulding and M. Orchin, *J. Chem. Soc., Chem. Commun.*, 1249 (1972).
(2) J. Powell and D. Cooper, *J. Chem. Soc., Chem. Commun.*, 486 (1973).
(3) J. Emsley, J. Feeney, and L. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N.Y., 1965.
(4) F. Pesa and M. Orchin, *J. Organometal. Chem.*, **78**, C26 (1974).
(5) "Gmelins Handbuch der Anorganischen Chemie," Vol. 68D, Verlag Chemie, Weinheim, Germany, 1957, p 408.
(6) R. Ellis, T. Weil, and M. Orchin, *J. Amer. Chem. Soc.*, **92**, 1078 (1970).
(7) R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).
(8) P. Haake, private communication.
(9) L. Cattalini, *Progr. Inorg. Chem.*, **13** (1969).
(10) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2787 (1955).

Contribution from the School of Chemistry,
The University of Sydney, Sydney 2006, Australia

Cis and Trans Elimination in the Reduction of *cis*-Dichlorobis(propylenediamine)platinum(IV) Ion

JAMES K. BEATTIE* and JON STARINK

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Reduction of *cis*-[Pt(pn)$_2$Cl$_2$]$^{2+}$ by Eu^{2+} in acidic aqueous solution results in the immediate release of two chloride ions with the formation of Pt(pn)$_2$$^{2+}$. Reduction by Cr^{2+} produces no ionic chloride. The products are Cr(H$_2$O)$_5$Cl^{2+}, Cr(H$_2$O)$_6$$^{3+}$, and a chloride-containing platinum(II) complex presumed to be Pt(pn)(pnH)Cl^{2+} with a monodentate propylenediamine ligand. The results are interpreted in terms of an inner-sphere two-electron reduction of Pt(IV) by Cr^{2+} with trans elimination of ligands, in contrast with one-electron reductions by Eu^{2+} with cis elimination.

Introduction

The mechanisms of oxidative addition and reductive elimination reactions are not well understood.[1] In the interconversion of four-coordinate d^8 Pt(II) and six-coordinate d^6 Pt(IV), trans addition and elimination are generally observed, but there have been few examples in which cis addition or elimination is likely. In the present study we have investigated the reduction of *cis*-dichlorobis(propylenediamine)platinum(IV) ion to determine whether cis elimination occurs to give the thermodynamically stable Pt(pn)$_2$$^{2+}$ product (A) or whether trans elimination occurs to give a metastable species with a monodentate propylenediamine ligand (B). Two different reducing agents were used, to examine any differences between the probable one-electron reduction by Eu^{2+} and the possible two-electron reduction by Cr^{2+}.

Experimental Section

Preparation of Complexes. *cis*-Dichlorobis(propylenediamine)-platinum(IV) Chloride. The preparation of *cis*-[Pt(pn)$_2$Cl$_2$]Cl$_2$