967. *Mechanisms of Substitution Reactions of Octahedral Bis(ditertiary arsine) Complexes. Part II.*[1] *Reduction of Dichlorobis-(*o*-phenylenebisdimethylarsine)platinum(*IV*) Salts by Thiocyanate Ions*

By G. Dolcetti, A. Peloso, and M. L. Tobe

Thiocyanate ions reduce $[\mathrm{Pt\,diars_2\,Cl_2}]^{2+}$ (diars = *o*-phenylenebisdimethylarsine) in methanol to the platinum(II) complex, $[\mathrm{Pt\,diars_2}]^{2+}$, in equilibrium with its thiocyanate adduct, $[\mathrm{Pt\,diars_2\,SCN}]^{+}$. One thiocyanate ion is consumed for each complex ion that is reduced and the rate has the form

$$-\mathrm{d}[\mathrm{Pt^{IV}}]/\mathrm{d}t = k_1[\mathrm{Pt^{IV}}] + k_2[\mathrm{Pt^{IV}}][\mathrm{SCN^-}]$$

at high thiocyanate concentration, with the k_1 term having only a marginal effect upon the rate. This apparent first-order term is spurious because, at low concentrations of thiocyanate, the second-order rate law is retained and the rate constant is only a little greater than k_2 mentioned above. The activation energy, measured at an ionic strength of $1{\cdot}96 \times 10^{-2}$M, is 16·7 kcal./mole and the dependence of rate upon ionic strength is consistent with a reaction between a dipositive cation and a uninegative anion. The equilibrium between $[\mathrm{Pt\,diars_2}]^{2+}$ and $\mathrm{SCN^-}$ has been studied spectrophotometrically as a function of temperature and ionic strength. The process is exothermic with $\Delta H = -3 \pm 1$ kcal./mole and the dependence upon ionic strength is normal for an equilibrium involving the combination of a dipositive and a uninegative species.

The mechanism of the reaction is a bimolecular attack of thiocyanate upon the platinum(IV) complex, the reaction taking place at the chlorine and not the metal, and the process of reduction being the transfer of a chlorine from platinum to thiocyanate.

In Part I of this Series [1] we discussed some reactions of the *cis*-dichlorobis-(*o*-phenylenebisdimethylarsine)cobalt(III) cation and showed that, once extraneous catalytic effects were removed, the substitution reactions were clearly unimolecular. In extending this work to the complexes of other metals we have started to examine the analogous complexes of platinum(IV). Although at one time it was thought that the higher formal charge on the metal might promote a bimolecular mechanism,[2] subsequent work has shown that the normal mode of reaction of a platinum(IV) ammine complex is a *redox*-catalysed bridge

---

[1] Part I, A. Peloso and M. L. Tobe, *J.*, 1964, 5063.

[2] F. Basolo, *Record Chem. Progress*, 1957, **18**, 1.

transfer process involving platinum(II) as catalyst.[3] The observation of a direct substitution process is rare [4] and there is, as yet, no indication that any process is bimolecular.

Complexes of the type [Pt diars$_2$ X$_2$]$^{2+}$, where X = Cl, Br, and I, were reported by Harris, Nyholm, and Phillips.[5] In each case the complex was prepared by oxidation of the appropriate platinum(II) species, [Pt diars X]X, and there was no information about the interconversion of these complexes by means of substitution reactions of the octahedral platinum(IV) species. It was reported, however, that the di-iodo-complex was unstable and, in the presence of iodide ions in aqueous solution, underwent rapid *redox* conversion into the platinum(II) complex. We have studied the reactions of [Pt diars$_2$ Cl$_2$]$^{2+}$ (presumably *trans*) with the reagents SCN$^-$, Br$^-$, and NO$_2^-$ in anhydrous methanol. The reaction with thiocyanate is readily reproducible and preliminary studies indicated that the rate of the reaction was unaffected by the addition of small quantities of the platinum(II) diarsine complexes. The reactions with bromide and nitrite are more complicated both from the point of view of reproducibility and catalysis and are still being studied. The reaction with thiocyanate is reported in this Paper.

(i) *General Chemistry*.—A study of the changing spectrum of a methanol solution of [Pt diars$_2$ Cl$_2$]$^{2+}$ containing excess of sodium thiocyanate indicated that, in any one experiment, there were two isosbestic points in the region 290—330 mμ, indicating that no light-absorbing intermediate was produced in significant quantity. However, the spectrum at the end of the reaction was a function of the concentration of added thiocyanate, as were the wavelengths and extinction coefficients of the isosbestic points, and, at low enough concentrations of thiocyanate, isosbestic points were not observed since the initial and final spectra did not cross. The final spectrum became independent of the concentration of thiocyanate when this was greater than 5 × 10^{-2}M. The spectrum of the product, and its dependence upon thiocyanate concentration was identical in every respect to that of the platinum(II) complex, [Pt diars$_2$]$^{2+}$, previously reported by Harris, Nyholm, and Phillips,[5] the spectral changes being due to the equilibrium

$$[\text{Pt diars}_2]^{2+} + n\text{SCN}^- \overset{K}{\rightleftharpoons} [\text{Pt diars}_2(\text{SCN})_n]^{(2-n)+},$$

so that $$[\text{Pt diars}_2(\text{SCN})_n{}^{(2-n)+}]/[\text{Pt diars}_2{}^{2+}][\text{SCN}^-]^n = K$$

The value of " n " was determined by plotting the function, $\log_{10}[(D_x - D_0)/(D_\infty - D_x)]$ against $\log_{10}[\text{SCN}^-]$, D_0, D_x, and D_∞ being the optical densities, at 310 mμ, of solutions of [Pt diars$_2$](NO$_3$)$_2$ containing no sodium thiocyanate, xM-sodium thiocyanate and [NaSCN] > 5 × 10^{-2}M, respectively. This function is equal to $\log_{10}\{[\text{Pt diars}_2(\text{SCN})_n{}^{(2-n)+}]/[\text{Pt diars}_2{}^{2+}]\}$ which, in turn, is equal to $\log_{10}K + n\log_{10}[\text{SCN}^-]$ and so the resultant plot should be a straight line with slope = n. The linear behaviour was observed and the slope of 1·002 confirms the suggestion of Nyholm [5] that only one anion is added to the square planar species to form a five-co-ordinated product. The equilibrium constant, K, was calculated for each point by using the above expression with $n = 1$, and the values obtained are tabulated as a function of temperature and ionic strength in Table 1.

TABLE 1

Equilibrium constants for the association of [Pt diars$_2$]$^{2+}$ with thiocyanate ions in anhydrous methanol

Ionic strength (M)	0·00287	0·00859	0·0429	0·00282	0·00859	0·0429
Temp. (°)	20·0	20·0	20·0	30·0	30·0	30·0
K (mole^{-1} l.)	1390	797	254	1226	670	188

---

[3] (*a*) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Pearson, and R. G. Wilkins, *J. Inorg. Nuclear Chem.*, 1958, **8**, 203; *ibid.*, 1958, **6**, 161; (*b*) F. Basolo, M. L. Morris, and R. G. Pearson, *Discuss. Faraday Soc.*, 1960, **29**, 80.

[4] F. Basolo and R. Johnson, *J. Inorg. Nuclear Chem.*, 1960, **13**, 36.

[5] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J.*, 1960, 4379.

The very close agreement between the final spectrum of the reaction between $[\mathrm{Pt\ diars_2\,Cl_2}]^{2+}$ and thiocyanate and the spectrum of a mixture of $[\mathrm{Pt\ diars_2}](\mathrm{NO_3})_2$ and NaSCN of the same molar composition showed that the platinum(IV) complex was quantitatively reduced to platinum(II) in the following way:

$$[\mathrm{Pt\ diars_2\,Cl_2}]^{2+} + a\mathrm{SCN}^- \longrightarrow [\mathrm{Pt\ diars_2}]^{2+} + 2\mathrm{Cl}^- + \text{oxidation products of SCN}^-$$
$$[\mathrm{Pt\ diars_2}]^{2+} + \mathrm{SCN}^- \rightleftharpoons [\mathrm{Pt\ diars_2\ SCN}]^+$$

It was not possible to determine " *a* " directly by analysis for thiocyanate at the beginning and at the end of the reaction because the low solubility of the complexes in methanol prevented studies at concentrations much greater than 10^{-4}M. However, " *a* " could be determined from the kinetics and is reported in the next section.

(2) *Kinetics*.—The progress of the reaction was followed spectrophotometrically at 310 mμ. Most of the data were collected under pseudo first-order conditions where $[\mathrm{SCN}^-] \gg [\text{complex}]$. The pseudo first-order rate constants were determined from the slope of the plot of $\log_{10}(D_\infty - D_t)$ against time, where D_t and D_∞ are the optical densities of the reaction mixture at time t and after ten half-lives, respectively. Repeating this treatment at other wavelengths where there was sufficient change in absorption gave the same rate constants, thereby confirming the conclusion that no intermediate was formed in observable amounts. These rate constants are readily reproducible and are unaffected by the addition of small amounts of the platinum(II) complex. For two experiments carried out at 20·0° with $[\mathrm{Pt\ diars_2\,Cl_2}^{2+}] = 2{\cdot}2 \times 10^{-5}$M and $[\mathrm{NaSCN}] = 4{\cdot}13 \times 10^{-3}$M, the observed first-order rate constants in the absence of, and in the presence of $2{\cdot}8 \times 10^{-5}$M $[\mathrm{Pt\ diars_2}](\mathrm{NO_3})_2$ were $4{\cdot}70 \times 10^{-3}$ and $4{\cdot}73 \times 10^{-3}$ sec.$^{-1}$, respectively. The pseudo first-order rate constants are plotted against $[\mathrm{SCN}^-]$ in Figure 2 for a series of different ionic strengths and it will be seen that, at constant ionic strength, the rate is linearly proportional to the concentration of added sodium thiocyanate. There is a small finite intercept at $[\mathrm{SCN}^-] = 0$, indicating the possibility of a thiocyanate-independent reaction path, but it is not possible, within the limits of experimental error, to say whether or not

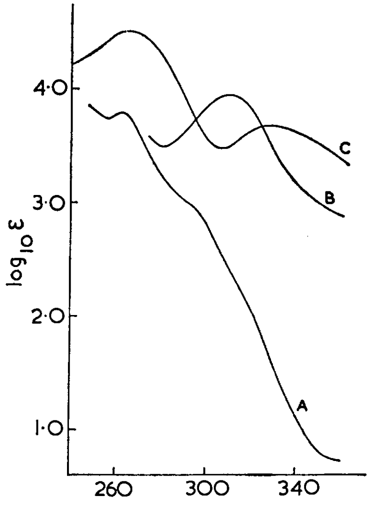


FIGURE 1. Ultraviolet absorption spectra in methanol of
A, $[\mathrm{Pt\ diars_2}](\mathrm{NO_3})_2$.
B, $[\mathrm{Pt\ diars_2\ SCN}]\mathrm{SCN}$.
C, $[\mathrm{Pt\ diars_2\ Cl_2}]\mathrm{Cl_2}$.

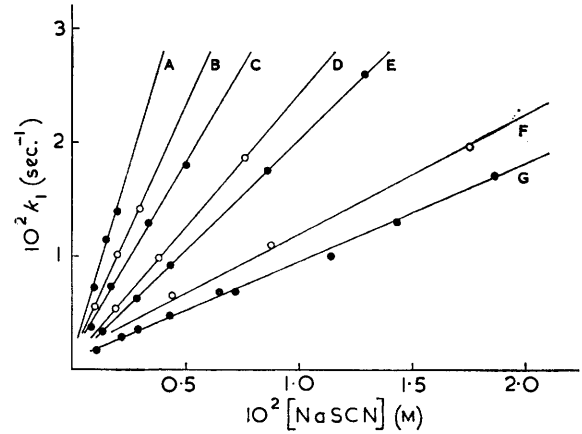


FIGURE 2. Pseudo first-order rate constants for the reaction between $[\mathrm{Pt\ diars_2\ Cl_2}]^{2+}$ and excess of thiocyanate plotted as a function of sodium thiocyanate concentration in methanol at 30·0° at the following ionic strengths: A, 0·002; B, 0·003; C, 0·005; D, 0·0114; E, 0·0129; F, 0·026; G, 0·043M

this is significant. The second-order rate constants are plotted as a function of [ionic strength]$^{\frac{1}{2}}$ in Figure 3 and the dependence of rate constant, measured at constant ionic strength, upon temperature, is given in Table 2.

TABLE 2

Second-order rate constants for the reduction of [Pt diars$_2$ Cl$_2$]$^{2+}$ by thiocyanate ions in methanol at constant ionic strength: ($\mu = 1{\cdot}96 \times 10^{-2}$M)

Temp. (°)	20·5	24·9	30·0	35·0	40·0
k_2 (sec.$^{-1}$ mole^{-1} l.)	0·83	1·18	1·96	3·12	5·27

The curvature of the $\log_{10}k_2$ versus $\mu^{\frac{1}{2}}$ in Figure 3 makes any extrapolation to zero ionic strength inaccurate and so it was not possible to obtain Arrhenius parameters related to pure methanol as standard state. At an ionic strength of $1{\cdot}96 \times 10^{-2}$M, the second-order rate constants obey the temperature dependence, $k_2 = 10^{12 \cdot 31} \exp(-16{,}700/\boldsymbol{R}T)$. The stoicheometry of the reaction with respect to thiocyanate ions was determined by studying the kinetics under conditions where the concentration of thiocyanate was similar to that of complex. Two experiments were carried out, the first with $[\mathrm{Pt^{IV}}]_{\mathrm{init.}} = [\mathrm{NaSCN}]_{\mathrm{init.}} = 5{\cdot}5 \times 10^{-5}$M and the second with $[\mathrm{Pt^{IV}}]_{\mathrm{init.}} = 5{\cdot}5 \times 10^{-5}$M and $[\mathrm{NaSCN}]_{\mathrm{init.}} = 12{\cdot}0 \times 10^{-5}$M. (All in methanol at 30·0° with $\mu = 1{\cdot}14 \times 10^{-2}$M.) In both cases the reaction went to completion and the data were used to test and distinguish between the following rate equations:

$$(1)\ -\mathrm{d}(a - x)/\mathrm{d}t = k_2(a - x)(b - x) \text{ and } (2)\ -\mathrm{d}(a - x)/\mathrm{d}t = k_2(a - x)(b - 2x)$$

corresponding, respectively, to the consumption of one or two thiocyanate ions per platinum(IV) reduced [a = initial concentration of complex, b = initial concentration of sodium thiocyanate and x = concentration of platinum(III) species at time t]. "x" was determined spectrophotometrically by using the relationship, $x = a(D_0 - D_t)/(D_0 - D_\infty)$ where D_0, D_t, and D_∞ are the optical densities of the reaction mixture at the start of the reaction, at time t, and at the end of the reaction respectively. Under these conditions of low thiocyanate concentration, D_∞ is very small compared with D_0 and can almost be approximated to zero. In Figure 4, $1/(a - x)$ is plotted against time for both experiments. When the initial concentrations of the reagents are equal, the relationship is linear, whereas, in the second experiment, the plot is very curved. The linear relationship is consistent with the consumption of one thiocyanate ion per complex ion reduced and the maintenance of the second-order kinetic form even at these low thiocyanate concentrations. k_2 computed from the slope of this line, =2·9 l. mole^{-1} sec.$^{-1}$. The data from the second experiment, plotted in the form, $\log_{10}[(b - x)/(a - x)]$ against time, gave a straight line, from the slope of which a second-order rate constant of 2·7 l. mole^{-1} sec.$^{-1}$ can be calculated. These two constants are to be compared with the value of 2·2 l. mole^{-1} sec.$^{-1}$ determined at much higher thiocyanate concentration but at the same ionic strength and temperature. A further experiment showed that the addition of chloride ions ($2{\cdot}85 \times 10^{-3}$M), had no effect upon the rate of the reaction.

Discussion.—The spectrophotometric studies of the equilibrium confirm the suggestion by Nyholm *et al.*[5] that the five-co-ordinate [Pt diars$_2$SCN]$^+$ is partially dissociated in solution. It is not possible, by using the data obtained at two temperatures only, to obtain a precise value for the enthalpy changes involved in the addition of a fifth ligand, but the data in Table 1 indicate that the reaction, $[\mathrm{Pt\,diars_2}]^{2+} + \mathrm{SCN}^- \longrightarrow [\mathrm{Pt\,diars_2SCN}]^+$ is exothermic with $\Delta H = -3 \pm 1$ kcal./mole at an ionic strength of $8{\cdot}6 \times 10^{-3}$M in methanol. The value, extrapolated to pure methanol as solvent should be some 0·5 kcal./mole less negative.

The kinetics indicate a bimolecular reaction between the platinum(IV) complex and the thiocyanate ion. The kinetic form observed at high thiocyanate concentrations,

$$\text{Rate} = k_1[\mathrm{Pt^{IV}}] + k_2[\mathrm{Pt^{IV}}][\mathrm{SCN^-}],$$

would indicate a first-order contribution to the rate process but this is certainly not a solvolytic contribution of the type found in the substitution reactions of square planar complexes.[6] The studies carried out at very low thiocyanate concentrations indicate that the reaction retains its second-order kinetic form but has a second-order rate constant some 50% greater than k_2 measured in the presence of a large excess of thiocyanate. This circumstance would lead to a decrease in the slope of Rate/[$\mathrm{Pt^{IV}}$] plotted against [$\mathrm{SCN^-}$] as the anion concentration increased and, if the effect was only important in the region of low thiocyanate concentration, the above plot, which at higher thiocyanate concentrations is completely equivalent to plotting pseudo first-order rate constants against thiocyanate concentration, would have the appearance of these reported in Figure 2. This change in slope can be explained by assuming that there is some interaction between the complex platinum(IV) cation and thiocyanate ions that reaches saturation when [$\mathrm{SCN^-}$] $> 5 \times 10^4$M. This should produce an environmental effect upon the rate constant, adequate to explain the 50% difference. The primary salt effects, however, indicate that this interaction is neither strong enough, nor specific enough for the complex to be behaving as a unipositive species, such as the intimate ion-pair, $[\mathrm{Pt\ diars_2\ Cl_2}]^{2+} \cdots \mathrm{SCN^-}$ (which would require only one half of the observed limiting slope of the $\log_{10} k_2$ against $\mu^{\frac{1}{2}}$ plot shown in Figure 3).

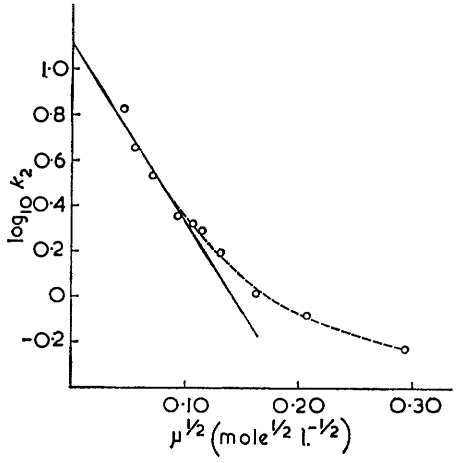


FIGURE 3

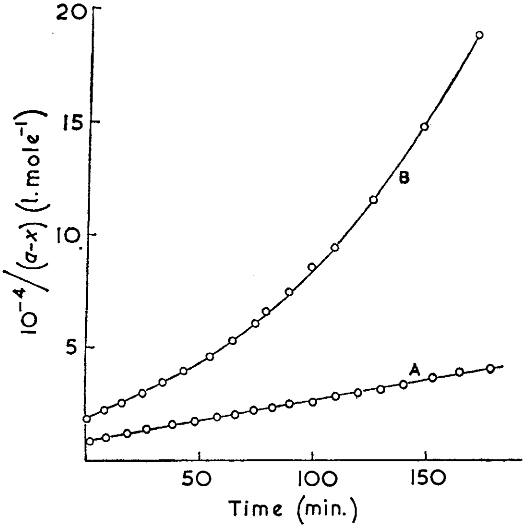


FIGURE 4

FIGURE 3. Primary salt effects on the second-order rate constant for the reaction between $[\mathrm{Pt\ diars_2\ Cl_2}]^{2+}$ and thiocyanate in methanol at 30·0°. The straight line represents the limiting slope expected for the Bronsted relationship, $\log_{10} k = \log_{10} k_0 + 2z_A z_B A\sqrt{\mu}$, $z_A = 2$, $z_B = -1$, $A = 2{\cdot}01$ (using a value of 30·9 for the dielectric constant of methanol at 30·0°)

FIGURE 4. Kinetic determination of the stoicheiometry of the reduction of $[\mathrm{Pt\ diars_2\ Cl_2}]^{2+}$ by thiocyanate. $1/(a - x)$ plotted against time for the reaction mixture initially containing, A, $5{\cdot}5 \times 10^{-5}$M-$[\mathrm{Ptdiars_2Cl_2}]^{2+}$ + $5{\cdot}5 \times 10^{-5}$M-NaSCN; B, $5{\cdot}5 \times 10^{-5}$M-$[\mathrm{Ptdiars_2Cl_2}]^{2+}$ + $12{\cdot}0 \times 10^{-5}$M-NaSCN. Ionic strength = 0·0114M. Temperature = 30·0°

The bimolecular reaction of the complex can be one of at least three possible types:

(*a*) Bimolecular substitution at platinum, whereby a chlorine is replaced by thiocyanate

---

[6] H. B. Gray, *J. Amer. Chem. Soc.*, 1962, **84**, 1548; H. B. Gray and R. J. Olcott, *Inorg. Chem.*, 1962, **1**, 481; U. Belluco, L. Cattalini, and A. Turco, *J. Amer. Chem. Soc.*, 1964, **86**, 226, 3257.

to form a chloroisothiocyanatobis(ditertiaryarsine)platinum(IV) complex which immediately undergoes an internal *redox* process, *i.e.*,

$$[\mathrm{Pt\ diars_2\ Cl_2}]^{2+} + \mathrm{SCN}^- \xrightarrow{k_2} [\mathrm{Pt\ diars_2\ Cl\ NCS}]^{2+} + \mathrm{Cl}^-$$

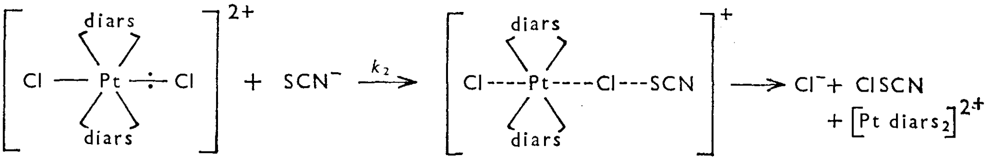
$$[\mathrm{Pt\ diars_2\ Cl\ NCS}]^{2+} \xrightarrow{\text{fast}} [\mathrm{Pt\ diars_2\ Cl}]^{+} + [\mathrm{SCN}^- - 2e^-]$$

$$\uparrow\downarrow$$

$$[\mathrm{Pt\ diars_2}]^{2+} + \mathrm{Cl}^-$$

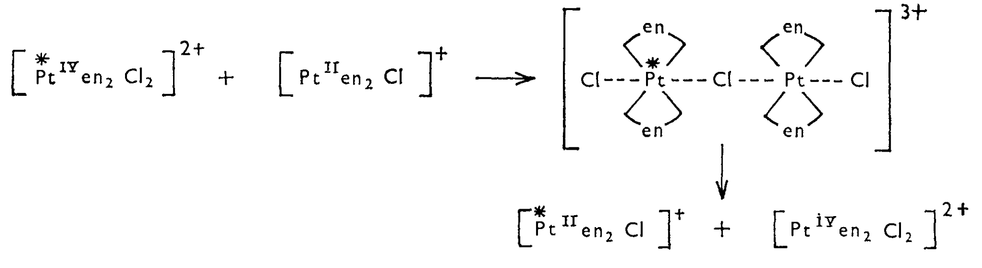
(*b*) Outer-sphere electron transfer from thiocyanate to the platinum which could be a two-electron transfer process or else two one electron transfers (only the first necessarily from the thiocyanate) thereby involving a platinum(III) intermediate.

(*c*) An atom-transfer *redox* process in which the chlorine atom is transferred from platinum to thiocyanate, leaving an electron pair on the platinum.



At present there is no clear cut evidence directly pertinent to this system to allow us to make an unequivocal choice. The first mechanism cannot be completely ruled out until thiocyanate containing diarsine complexes of platinum(IV) have been synthesised and studied. We have not been able to prepare such complexes, but, in view of the existence of $[\mathrm{Pt\ diars_2\ I_2}](\mathrm{NO_3})_2$, (and perchlorate),[5] we believe that, since iodide is normally a better reducing agent than thiocyanate, such thiocyanato-complexes could be obtainable given the right technique. It can be inferred from reference 5 that the $[\mathrm{Pt\ diars_2\ I_2}]^{2+}$ cation is relatively inert to *redox* decomposition in solution but, when iodide ions are present, there is a fairly rapid reaction forming $[\mathrm{Pt\ diars_2\ I}]^+$ and $\mathrm{I_2}$. This indicates that the *redox* decomposition is external rather than internal. If a similar reaction was responsible for the thiocyanate reduction reaction, *i.e.*, if the fast stage of reaction (*a*) is the attack of a thiocyanate ion on the slowly formed thiocyanato-complex, it would require two thiocyanates oxidised per platinum reduced instead of the 1 : 1 stoicheiometry observed. For these reasons we believe that mechanism (*a*) is unlikely and we are not observing the consequences of bimolecular attack at the platinum.

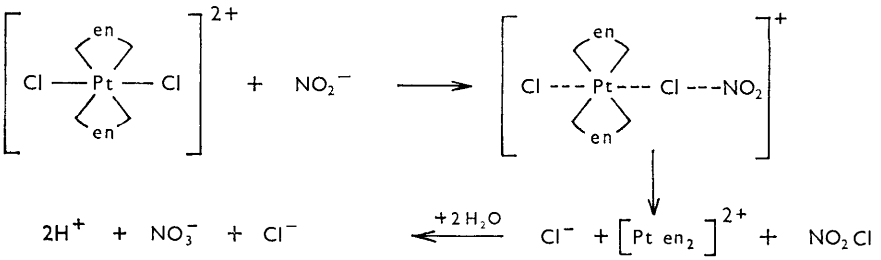
The choice between mechanisms (*b*) and (*c*) is even more difficult to make with any certainty. However, the known ability of platinum(IV) complexes to undergo two electron reductions with bridge transfer [3] of the type,



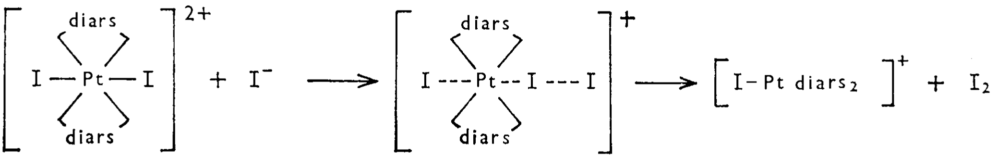
makes us prefer mechanism (*c*) to (*b*). We were unable to detect thiocyanogen chloride, ClSCN, in the reaction product, but, in view of its low concentration ($<10^{-4}$M) and high reactivity,[7] this is not surprising.

[7] A. B. Angus and R. G. R. Bacon, *J.*, 1958, 774; R. G. R. Bacon and R. G. Guy, *J.*, 1960, 318.

The idea of a bridge transfer from the metal to the anionic reducing agent can also be applied to the reduction of *trans*-[Pt en$_2$ Cl$_2$]$^{2+}$ by nitrite ions.[8] *



and the reaction of [Pt diars$_2$ I$_2$]$^{2+}$ with iodide ions:



The absence of any platinum(II) catalysis of thiocyanate substitution is perhaps somewhat surprising since there is a chlorine bridge available and the five-co-ordinate platinum(II) species is present in adequate concentration. The lack of catalysis cannot be ascribed to steric reasons as in the reactions of [Pt (tetrameen)$_2$ Cl$_2$]$^{2+}$ with chloride [3b] or hydroxide [4] even though models indicate that the methyl groups on the arsenics will prevent the two platinum atoms approaching too closely, since the reactions between [Pt diars$_2$ Cl$_2$]$^{2+}$ and bromide is most certainly catalysed. In this case, the most probable reason is that [Pt diars$_2$ SCN]$^+$ is not a strong enough reducing agent to act as catalyst.

EXPERIMENTAL

Dichlorobis-(*o*-phenylenebisdimethylarsine)platinum(IV) perchlorate was prepared by Nyholm's method.[5]

Dichlorobis-(*o*-phenylenebisdimethylarsine)platinum(IV) chloride was prepared from the perchlorate by passing a solution of the latter salt in dimethylformamide down a column of Dowex 1X anion exchange resin in the chloride form. Diethyl ether was added to the effluent and the [Pt diars$_2$ Cl$_2$]Cl$_2$ was precipitated as a pale yellow powder. The compound was recrystallised, filtered off, and washed with methanol and then suspended in boiling methanol to remove any soluble [Pt diars$_2$Cl]Cl. The *solid* was dried in vacuum (Found: C, 25·7; H, 3·7; Cl, 15·2. $C_{20}H_{32}As_4Cl_4Pt$ requires C, 26·4; H, 3·5; Cl, 15·6%). Every operation was carried out as much as possible in the absence of light. The absorption spectrum was identical to that of the perchlorate.

Chlorobis-(*o*-phenylenebisdimethylarsine)platinum(II) chloride was prepared by Nyholm's method [5] (Found: C, 27·8; H, 3·9; Cl, 8·0. $C_{20}H_{32}As_4Cl_2Pt$ requires C, 28·7; H, 3·9; Cl, 8·5%). The chloro-chloride was converted to the dinitrate by Nyholm's method.[5]

All other materials, *e.g.*, sodium thiocyanate, sodium nitrate, and methanol were of AnalaR grade and was recrystallised or otherwise purified by standard methods. Care was taken to ensure that the materials were dried as much as possible and stored and handled in the absence of moisture.

Spectrophotometric studies were made by using a Beckman DK 2A ratio recording spectrophotometer. The reactions were studied *in situ*, the silica cells being used as reaction vessels and a constant temperature being maintained by circulating water from a thermostat through

---

* This reaction is kinetically similar to ours, *i.e.*, first-order with respect to complex and to nitrite in the initiation step, but the reaction is complicated by a bridge-transfer *redox* process in which the [Pt en$_2$]$^{2+}$ cation acts as catalyst for the reaction that forms the stable [Pt en$_2$ NO$_2$ Cl]$^{2+}$. (Further indications that these *redox* processes do not involve direct attack on the metal.)

[8] H. R. Ellison, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1961, **83**, 3943.

the cell holder. The spectrum of the reacting solution was scanned as rapidly as possible over the range 260—360 mμ at appropriate times. In general, the rate of the reaction was slow enough for the time of scanning to be negligible compared to the reaction time but, in the fastest reaction, the time noted was that when the optical density at 310 mμ was recorded or else the wavelength was held constant at 310 mμ.

Stock solutions of the reagents were prepared by weight and appropriate volumes of the solutions, previously brought to the reaction temperature, were mixed in the spectrophotometer cell at the start of the reaction. The ionic strength was adjusted by adding the appropriate amount of sodium nitrate solution.

We are grateful for financial support from N.A.T.O.

William Ramsay and Ralph Forster Laboratories,
University College, Gower Street, London W.C.1.
Istituto di Chimica Generale, Università di Padova,
Padova, Italy.

[*Received, November 24th,* 1964.]