Ruthenium in Isomeric S_4P_2 Co-ordination: Metal Redox and Geometrical Reorganisation

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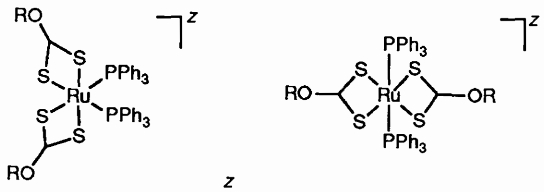
The redox behaviour of dithiocarbonato complexes *cis*-$[Ru^{II}(ROCS_2)_2(PPh_3)_2]$ (**1**) has been electrochemically examined. One-electron oxidation affords *cis*-$[Ru^{III}(ROCS_2)_2(PPh_3)_2]^+$, ($\mathbf{1}^+$), which rapidly isomerises to the *trans* form, ($\mathbf{2}^+$). Electroreduction of ($\mathbf{2}^+$) furnishes *trans*-$[Ru(ROCS_2)_2(PPh_3)_2]$, (**2**), which isomerises at a measurable rate to (**1**) probably by a twist mechanism ($\Delta S^\ddagger \approx -110$ J K^{-1} mol^{-1}). The formal potentials of the couples ($\mathbf{1}^+$)—(**1**) and ($\mathbf{2}^+$)—(**2**) are respectively ≈ 0.7 and ≈ 0.3 V *vs.* saturated calomel electrode. The equilibrium constants for the reactions $(\mathbf{1}^+) \rightleftharpoons (\mathbf{2}^+)$, $(\mathbf{2}) \rightleftharpoons (\mathbf{1})$, and $(\mathbf{1}^+) + (\mathbf{2}) \rightleftharpoons (\mathbf{2}^+) + (\mathbf{1})$ are respectively $>10^2$, $>10^2$, and $\approx 10^6$. The *cis* and *trans* S_4P_2 co-ordination spheres are thus specific for bi- and tri-valent ruthenium respectively. The species ($\mathbf{2}^+$) (low-spin d^5) display rhombic e.s.r. spectra in frozen solution (77 K). The rhombic crystal-field component ($\approx 2\,000$ cm^{-1}) is relatively small compared to the axial component ($\approx 8\,000$ cm^{-1}). An optical transition within Kramers doublets is observed at $\approx 6\,000$ cm^{-1}. One ($\mathbf{2}^+$) complex (R = $PhCH_2$) has been isolated in the pure state as its PF_6^- salt.

This work stems from our interest[1] in the redox properties of chelated ruthenium and deals with the metal in S_4P_2 co-ordination. Such co-ordination is documented in ruthenium(II) dithiocarbonate (xanthate) complexes of the type $[Ru(ROCS_2)_2(PPh_3)_2]$[2,3] which have *cis* configuration,[3b,c] but nothing is known about complexes in other oxidation states. Herein we report an electrochemical examination of $[Ru(ROCS_2)_2(PPh_3)_2]$. Oxidation to $[Ru^{III}(ROCS_2)_2(PPh_3)_2]^+$ is facile. The two oxidation states recognise and strongly differentiate the isomeric (*cis* and *trans*) S_4P_2 environments, spontaneous isomerisation occurring following metal redox.



	z	
(**1**)	0	(**2**)
($\mathbf{1}^+$)	+1	($\mathbf{2}^+$)

Results and Discussion

Variable-temperature Voltammetry.—The *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]$ species, (**1**), examined in the present work are listed in Table 1. These were synthesised by reported methods.[2a,b] The R = Pr, Pr^i, Bu, Bu^i, or $PhCH_2$ complexes are new. In this article we shall also be concerned with ($\mathbf{1}^+$), the ruthenium(III) congener of (**1**), as well as with (**2**) and ($\mathbf{2}^+$) the *trans* analogues of (**1**) and ($\mathbf{1}^+$).

Complexes of type (**1**) were electrochemically examined in the temperature range 258—298 K in dichloromethane solution at a platinum working electrode. Cyclic voltammetric results illustrated for one case in Figure 1 are representative of the entire group. At 298 K a one-electron (see below) anodic peak (A_1) is observed; on scan reversal a cathodic peak (C_2) appears but it is separated from A_1 by ≈ 400 mV. The same voltammogram is observed in subsequent cycles. At lower temperatures the first cycle voltammogram is the same (A_1, C_2) as above, but an anodic peak A_2 separated from C_2 by 70—100 mV appears in the second and subsequent cycles (Figure 1). No cathodic peak corresponding to A_1 could however be observed even at low temperatures and high scan rates (1 V s^{-1}).

On coulometric oxidation of *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]$ at potentials more positive to A_1 the colour of the solution changes from yellow to green and the coulomb count after exhaustive electrolysis corresponds to the transfer of one electron (Table 1). The nature of the oxidised solution is independent of the temperature at which oxidation is performed. This oxidised species can be quantitatively reduced back to *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]$ by one-electron transfer but only at potentials below C_2. Above C_2 no reduction occurs. The cation $[Ru(ROCS_2)_2(PPh_3)_2]^+$ can be isolated from the oxidised solution (see below). The cyclic voltammogram of the oxidised solution at 258 K comprises a single couple with peak potentials C_2 and A_2 (Figure 2). Upon raising the temperature the A_1 response begins to grow at the expense of A_2. Eventually at 298 K the voltammogram displays only A_1 and C_2 (Figure 2) as with the parent complex *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]$.

Redox Couples with Isomerisation Reactions.—The electrochemical observations taken collectively with e.s.r. results (see below) can be rationalised as follows. The parent complex *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]$ undergoes stereoretentive one-electron oxidation, equation (1), affording the corresponding *cis*-

$$cis\text{-}[Ru(ROCS_2)_2(PPh_3)_2]^+ + e \rightleftharpoons cis\text{-}[Ru(ROCS_2)_2(PPh_3)_2] \quad (1)$$

ruthenium(III) complex. The latter is thermodynamically unstable and undergoes rapid isomerisation to the *trans* form, equation (2). The rate of isomerisation is too fast on the electrochemical time-scale for direct detection of *cis*-$[Ru(ROCS_2)_2$-

$$cis\text{-}[Ru(ROCS_2)_2(PPh_3)_2]^+ \xrightarrow{\text{fast}} trans\text{-}[Ru(ROCS_2)_2(PPh_3)_2]^+ \quad (2)$$

Table 1. Analytical and electrochemical data

Compound	Elemental analysis (%)[a] C	Elemental analysis (%)[a] H	Ru^{III}–Ru^{II} couples,[b] $E_{258}°$/V *cis*[c]	Ru^{III}–Ru^{II} couples,[b] $E_{258}°$/V *trans*	n[d]	10^{-6} K^{cr}[e]
$[Ru(MeOCS_2)_2(PPh_3)_2]$	57.55 (57.20)	4.45 (4.30)	0.62	0.35	0.98	0.7
$[Ru(EtOCS_2)_2(PPh_3)_2]$	58.05 (58.10)	4.80 (4.60)	0.68	0.32	1.02	2.8
$[Ru(PrOCS_2)_2(PPh_3)_2]$	58.90 (59.00)	4.95 (4.90)	0.74	0.35	1.03	4.4
$[Ru(Pr^iOCS_2)_2(PPh_3)_2]$	59.10 (59.00)	4.85 (4.90)	0.63	0.31	0.97	0.7
$[Ru(BuOCS_2)_2(PPh_3)_2]$	59.85 (59.80)	5.15 (5.20)	0.72	0.33	0.98	4.4
$[Ru(Bu^iOCS_2)_2(PPh_3)_2]$	59.90 (59.80)	5.25 (5.20)	0.70	0.29	1.03	6.9
$[Ru(PhCH_2OCS_2)_2(PPh_3)_2]$	62.90 (62.95)	4.40 (4.45)	0.69	0.34	0.99	1.7

[a] Calculated values are in parentheses. [b] Conditions: solvent, dichloromethane; supporting electrolyte, $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}); working electrode, platinum; reference electrode, s.c.e.; solute concentration, $\approx 10^{-3}$ mol dm^{-3}. Cyclic voltammetric data: $E_{258}° = 0.5(E_{p_a} + E_{p_c})$, where E_{p_a} and E_{p_c} are anodic and cathodic peak potentials respectively at 258 K; scan rate, 50 mV s^{-1}. [c] For the *cis* isomer E_{p_c} is not observed; $E_{258}°$ is calculated by assuming that the peak-to-peak separation is 80 mV which is the observed average separation of E_{p_a} and E_{p_c} for the *trans* isomers. [d] $n = Q/Q'$ where Q' is the calculated coulomb count for transfer of one electron and Q is the coulomb count found after exhaustive electrolysis; oxidation was performed at 0.9 V *vs.* s.c.e. in dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$). [e] From equation (8).

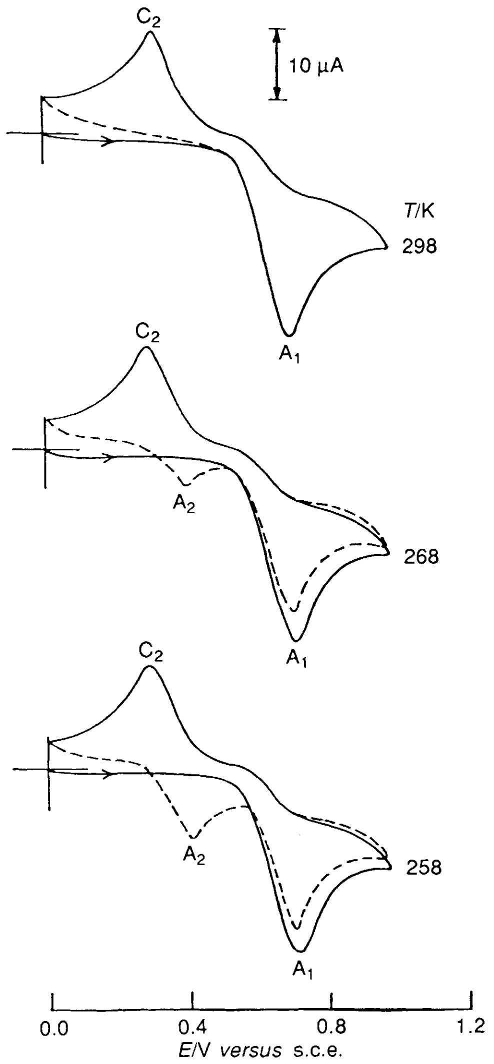


Figure 1. Variable-temperature cyclic voltammograms of $[Ru(MeOCS_2)_2(PPh_3)_2]$ ($\approx 10^{-3}$ mol dm^{-3}) in dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at a platinum electrode [first cycle (——), second cycle (- - - -)]

$(PPh_3)_2]^+$. Consequently the cathodic peak corresponding to A_1 is not observed (Figure 1).

The *trans*-ruthenium(III) complex gives rise to the couple, equation (3), comprising peaks A_2 and C_2 (Figure 2). The *trans*

$$trans\text{-}[Ru(ROCS_2)_2(PPh_3)_2]^+ + e \rightleftharpoons trans\text{-}[Ru(ROCS_2)_2(PPh_3)_2] \quad (3)$$

isomer of $[Ru^{II}(ROCS_2)_2(PPh_3)_2]$ is unstable and isomerises back to the *cis* form, equation (4). Here isomerisation is

$$trans\text{-}[Ru(ROCS_2)_2(PPh_3)_2] \xrightarrow{k} cis\text{-}[Ru(ROCS_2)_2(PPh_3)_2] \quad (4)$$

relatively slow and the rate is tractable electrochemically at temperatures below 285 K (see below).

The formal potentials ($E_{258}°$) of couples (1) and (3) at 258 K are listed in Table 1. The *cis* potentials are systematically higher than the *trans* potentials. For low-spin d^5–d^6 redox couples in systems of type MA_4B_2 (where B is a stronger π acceptor than A) the inequality $E°(cis) > E°(trans)$ is expected due to better stabilisation of the redox orbital in the reduced (d^6) *cis* isomer.[4] In the present complexes, π acceptance by the phosphine ligands in the ruthenium(II) complex (low-spin d^6) may be a reason for the observed trend.

E.S.R. and Near-I.R. Spectra of $[Ru(ROCS_2)_2(PPh_3)_2]^+$.—Solutions of $[Ru(ROCS_2)_2(PPh_3)_2]^+$ produced coulometrically display rhombic e.s.r. spectra in frozen dichloromethane–toluene solution (77 K) (Table 2, Figure 3). The spectra were analysed by g-tensor theory of low-spin d^5 ions, affording values for axial distortion (Δ) which splits the t_2 shell into $e + b$ and the superimposed rhombic distortion (V) which splits e further into two non-degenerate components.[1a–d,5,6] Two optical transitions (ΔE_1 and ΔE_2) among the three Kramers doublets are predicted (Table 2) to lie at $\approx$7 000 and $\approx$9 500 cm^{-1} [taking λ the spin–orbit coupling constant for ruthenium(III) as 1 000 cm^{-1} (refs. 5*d* and 7)]. A relatively weak transition ($\varepsilon \approx 40$ dm^3 mol^{-1} cm^{-1}) is indeed observed at $\approx$6 000 cm^{-1} (Table 2, Figure 4) which is assigned to ΔE_1. The ΔE_2 transition is not observable probably due to the rapid rise in absorption pertaining to allowed transitions occurring in nearby regions (Table 3).

The relatively small rhombic distortion reflected in the closeness of g_x and g_y signals (split components of $g_{\parallel}$) is compatible with the *trans* geometry of $[Ru(ROCS_2)_2(PPh_3)_2]^+$. An idealised *trans*-$RuS_4P_2$ co-ordination sphere can have tetragonal symmetry. However the chelate rings and phosphine

Table 2. E.s.r. g values,[a] distortion parameters, and near-i.r. transitions

Compound[b]	g_x	g_y	g_z	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$	$\Delta E_1/\lambda$ Obs.[c]
$[Ru(MeOCS_2)_2(PPh_3)_2]^+$	2.412	2.314	1.939	8.034	−2.024	7.024	9.245	5.880
$[Ru(EtOCS_2)_2(PPh_3)_2]^+$	2.417	2.315	1.943	8.392	−2.201	7.296	9.581	6.060
$[Ru(PrOCS_2)_2(PPh_3)_2]^+$	2.421	2.314	1.944	8.504	−2.336	7.344	9.854	6.060
$[RuPr^iOCS_2)_2(PPh_3)_2]^+$	2.433	2.313	1.939	8.143	−2.455	6.934	9.552	5.880
$[Ru(BuOCS_2)_2(PPh_3)_2]^+$	2.421	2.311	1.939	8.082	−2.269	6.959	9.405	6.250
$[Ru(Bu^iOCS_2)_2(PPh_3)_2]^+$	2.420	2.314	1.939	8.075	−2.180	6.993	9.356	6.250
$[Ru(PhCH_2OCS_2)_2(PPh_3)_2]^{+d}$	2.417	2.315	1.940	8.139	−2.123	7.081	9.394	6.060

[a] In frozen glass (77 K); symbols have the same meaning as in the text. Signs of g values are negative, negative and positive for g_x, g_y, and g_z respectively. [b] Produced by exhaustive electrolysis at 0.9 V *vs.* s.c.e. in dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$). [c] Observed frequency converted into $\Delta E_1/\lambda$ by setting λ = 1 000 cm^{-1}. [d] The e.s.r. spectrum of the isolated species $[Ru(PhCH_2OCS_2)_2(PPh_3)_2]PF_6$ in dichloromethane is identical.

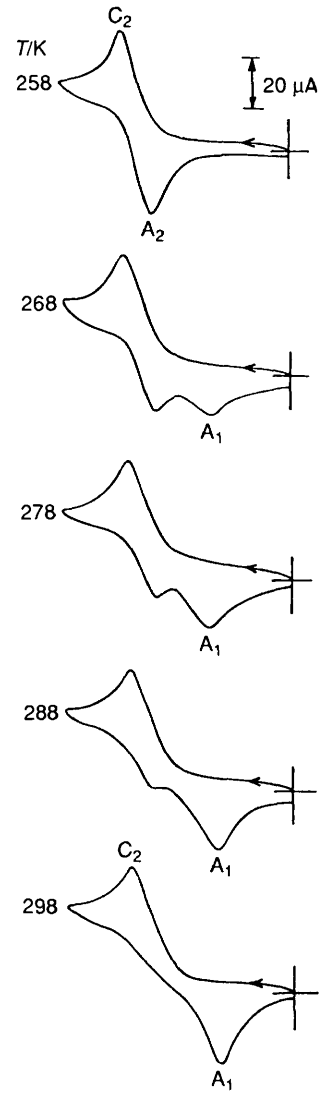


Figure 2. Variable-temperature cyclic voltammograms of coulometrically produced $[Ru(MeOCS_2)_2(PPh_3)_2]^+$ ($\approx 10^{-3}$ mol dm^{-3}) in dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at a platinum electrode

phenyls are expected to provide a small rhombic perturbation as is actually observed.

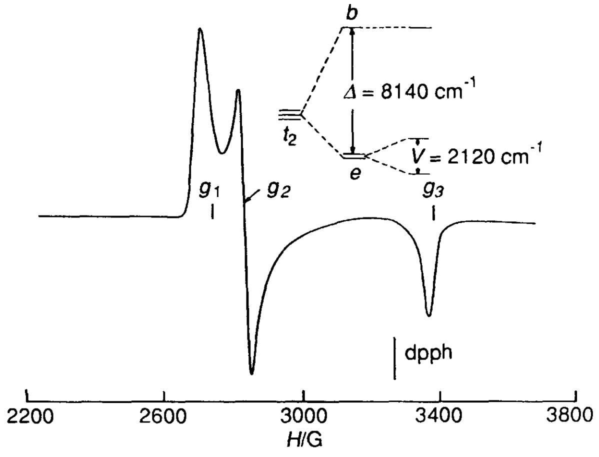


Figure 3. X-Band e.s.r. spectrum and t_2 splittings of $[Ru(PhCH_2OCS_2)_2(PPh_3)_2]^+$ in a dichloromethane–toluene (1:1) glass (77 K)

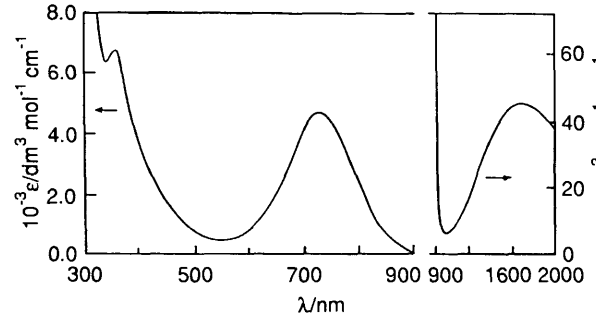


Figure 4. Electronic spectra of $[Ru(PrOCS_2)_2(PPh_3)_2]^+$ in dichloromethane at 298 K

Isolation of trans-$[Ru(PhCH_2OCS_2)_2(PPh_3)_2]^+$ *Species.*—The complex $[Ru(PhCH_2OCS_2)_2(PPh_3)_2]^+$ has been electrosynthesised and isolated in the pure state as its PF_6^- salt. The magnetic moment of the solid is 1.95 μ_B at 298 K corresponding to one unpaired electron (t_2^5) and its e.s.r. spectrum in frozen solution (Table 2) and solution electronic spectrum (Table 3) are very similar to those of other $[Ru(ROCS_2)_2(PPh_3)_2]^+$ species produced coulometrically in solution.

Isomerisation Rate of $[Ru(ROCS_2)_2(PPh_3)_2]$.—Cyclic voltammetric (Figure 2) current-height data of coulometrically produced solutions of $[Ru(ROCS_2)_2(PPh_3)_2]^+$ have afforded[8] the rate (k) of *trans* $\longrightarrow$ *cis* isomerisation of $[Ru(ROCS_2)_2(PPh_3)_2]$, equation (4). Measurements were made in the temperature range 268—283 K. Results for two representative complexes are given in Table 4. The large and negative entropy of activation is suggestive of a twist mechanism.[9,10]

Table 3. Electronic spectral data[a] of $[Ru(ROCS_2)_2(PPh_3)_2]^+$ species

Compound[b]	$\lambda_{max.}$/nm(ε/dm^3 mol^{-1} cm^{-1})
$[Ru(MeOCS_2)_2(PPh_3)_2]^+$	1 700 (40), 725 (3 500), 370 (4 800), 290 (29 300)
$[Ru(EtOCS_2)_2(PPh_3)_2]^+$	1 650 (40), 725 (3 700), 370 (5 300), 290 (31 300)
$[Ru(PrOCS_2)_2(PPh_3)_2]^+$	1 650 (45), 725 (4 700), 360 (6 700), 290 (37 500)
$[Ru(Pr^iOCS_2)_2(PPh_3)_2]^+$	1 700 (40), 725 (3 600), 370 (6 400), 290 (30 800)
$[Ru(BuOCS_2)_2(PPh_3)_2]^+$	1 600 (40), 725 (3 500), 370 (5 400), 290 (29 400)
$[Ru(Bu^iOCS_2)_2(PPh_3)_2]^+$	1 600 (35), 730 (3 900), 375 (5 800), 310 (32 500)
$[Ru(PhCH_2OCS_2)_2(PPh_3)_2]^{+c}$	1 650 (40), 730 (4 100), 370 (5 600), 290 (28 400)

[a] In dichloromethane at 298 K. [b] Produced by exhaustive electrolysis at 0.9 V *vs.* s.c.e. in dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$). [c] The electronic spectrum of the isolated species $[Ru(PhCH_2OCS_2)_2(PPh_3)_2]PF_6$ in dichloromethane is identical.

Table 4. Rate constants and activation parameters in dichloromethane

Compound	T/K	k/s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
$[Ru(MeOCS_2)_2(PPh_3)_2]$	268	3.0×10^{-2}	46.6	−96.6
	273	7.0×10^{-2}		
	278	12.0×10^{-2}		
	283	15.0×10^{-2}		
$[Ru(Pr^iOCS_2)_2(PPh_3)_2]$	268	3.4×10^{-2}	40.7	−122.6
	273	4.7×10^{-2}		
	278	6.0×10^{-2}		
	283	9.5×10^{-2}		

The Cross-reaction.—In principle the isomerisation reactions (2) and (4) are equilibria with constants defined by equations (5) and (6). However voltammetric responses due to *cis*-

$$K^+ = [trans\text{-}Ru(ROCS_2)_2(PPh_3)_2{}^+]/[cis\text{-}Ru(ROCS_2)_2(PPh_3)_2{}^+] \quad (5)$$

$$K = [cis\text{-}Ru(ROCS_2)_2(PPh_3)_2]/[trans\text{-}Ru(ROCS_2)_2(PPh_3)_2] \quad (6)$$

$[Ru(ROCS_2)_2(PPh_3)_2]^+$ and *trans*-$[Ru(ROCS_2)_2(PPh_3)_2]$ are *not* observable in the respective equilibrated solutions. Their concentrations are thus small and it is estimated that both K^+ and K are $>10^2$ and consequently $KK^+ > 10^4$. Though K^+ and K could not be individually determined it is possible to compute the value of the product KK^+ which is equal to the equilibrium constant K^{cr} of the cross-reaction (7). This constant

$$trans\text{-}[Ru^{II}(ROCS_2)_2(PPh_3)_2] + cis\text{-}[Ru^{III}(ROCS_2)_2(PPh_3)_2]^+ \rightleftharpoons cis\text{-}[Ru^{II}(ROCS_2)_2(PPh_3)_2] + trans\text{-}[Ru^{III}(ROCS_2)_2(PPh_3)_2]^+ \quad (7)$$

is related to formal potentials (258 K) as in equation (8).[11] The

$$K^{cr} = \exp\{44.96[E^\circ(cis) - E^\circ(trans)]\} \quad (8)$$

K^{cr} values ($\approx 10^6$) calculated in this manner (Table 1) are consistent with the requirement $KK^+ > 10^4$. The large K^{cr} values reflect the superior stability of *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]$ and *trans*-$[Ru(ROCS_2)_2(PPh_3)_2]^+$ compared to *trans*-$[Ru(ROCS_2)_2(PPh_3)_2]$ and *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]^+$. A theoretical study of $[Mo(CO)_2(PPh_3)_4]^z$ has shown that due to π bonding and interligand interactions the 18e($z = 0$) and 17e($z = +1$) systems prefer *cis* and *trans* geometries respectively.[12] We note that the $[Ru(ROCS_2)_2(PPh_3)_2]^z$ species also represent an 18e($z = 0$)–17e($z = +1$) pair.

There has been some discussion about the occurrence of *trans*-$[Ru(ROCS_2)_2(PPh_3)_2]$.[3b,c] The present results demonstrate that under certain conditions this isomer is an observable species in solution. It is however unstable with respect to the *cis* form and its equilibrium concentration is small.

Conclusion

The bi- and tri-valent states of ruthenium have entirely different affinities for isomeric S_4P_2 environments assembled from dithiocarbonates and triphenylphosphines. They display specificity for *cis* and *trans* geometries respectively. Mismatched combinations of *cis*-$[Ru(ROCS_2)_2(PPh_3)_2]^+$ and *trans*-$[Ru(ROCS_2)_2(PPh_3)_2]$ can be created by electrochemical metal redox, but they are unstable and undergo spontaneously isomerisation affording the matched combinations. Redox-driven isomerisation reactions have been documented among substituted metal carbonyls.[13] Examples among non-carbonyl species are sparse[14] evidently due to a lack of research. Just one other example is known in ruthenium chemistry.[15] Attempts to grow *X*-ray quality single crystals of $[Ru(ROCS_2)_2(PPh_3)_2]$ have not succeeded; badly twinned crystals were invariably obtained. Single crystals of $[Ru(ROCS_2)_2(PPh_3)_2]^+$ salts could not be obtained either. The gross geometrical structures of the species are not in doubt but the details of bonding parameters remain elusive.

Experimental

Materials.—Commercial ruthenium trichloride (Arora Matthey, Calcutta, India) was purified by repeated evaporation to dryness with concentrated hydrochloric acid.[16] The compound $[Ru(PPh_3)_3Cl_2]$ was prepared according to the reported procedure.[17] Preparation of $K(S_2COR)$ salts and purification of alcohols were as reported.[18] The purification of dichloromethane and acetonitrile and the preparation of tetraethylammonium perchlorate for electrochemical/spectroscopic work were done as before.[6] All other chemicals and solvents were of reagent grade and used without further purification.

Physical Measurements.—U.v.–visible–near-i.r. spectra were recorded on a Hitachi 330 spectrophotometer, i.r. (4 000—300 cm^{-1}) spectra on a Perkin-Elmer 783 spectrophotometer. The magnetic susceptibility was measured on a PAR 155 vibratingsample magnetometer. Electrochemical measurements were done by using the PAR model 370-4 electrochemistry system. The three-electrode measurements were carried out with the use of a planar Beckman model 39273 platinum-inlay working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (s.c.e.). A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were done under dinitrogen atmospheres, and the reported potentials are uncorrected for junction contribution. Low-temperature electrochemical measurements were done with the help of a Haake model F3-K digital cryostat and circulator connected with jacketed cell bottoms. E.s.r. measurements were made with a Varian model 109C E-line *X*-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All spectra were calibrated with the help of diphenylpicrylhydrazyl (dpph) ($g = 2.0037$). Microanalytical data (C,H,N) were obtained with the use of a Perkin-Elmer model 240C elemental analyzer.

Preparation of Complexes.—The complexes $[Ru(ROCS_2)_2(PPh_3)_2]$ were prepared by the modification of a reported method[2a,b] involving the use of ethanol in place of acetone as solvent. This reduces the reaction time considerably. Specific details are given for one complex.

Bis(O-*methyldithiocarbonato*)*bis*(*triphenylphosphine*)*ruthenium*(II), $[Ru(MeOCS_2)_2(PPh_3)_2]$. To a warm solution of $[Ru(PPh_3)_3Cl_2]$ (100 mg, 0.104 mmol) in ethanol (35 cm^3) was added $K(S_2COMe)$ (35 mg, 0.24 mmol). The mixture was refluxed for 0.5 h. Upon cooling a yellow microcrystalline solid separated which was collected by filtration, washed thoroughly with water and ethanol, and dried *in vacuo* over P_4O_{10}. Yield 90%.

Bis(O-*benzyl dithiocarbonato*)*bis*(*triphenylphosphine*)*ruthenium*(III) *hexafluorophosphate*, $[Ru(PhCH_2OCS_2)_2(PPh_3)_2]PF_6$. The complex $[Ru(PhCH_2OCS_2)_2(PPh_3)_2]$ (100 mg, 0.11 mmol) was oxidised coulometrically in acetonitrile (0.1 mol dm^{-3} in NH_4PF_6) at 0.9 V. After the oxidation was over (coulomb count corresponding to one electron) the green solution was evaporated to dryness under reduced pressure. The solid mass thus obtained was washed thoroughly with cold water to remove NH_4PF_6 and dried *in vacuo* over P_4O_{10}. The yield was quantitative (Found: C, 55.10; H, 3.80. Calc.: C, 54.90; H, 3.85%).

Treatment of E.S.R. Data.—The essentials of our treatment and the methods used for assigning the observed signals to g_x, g_y, and g_z have been given in recent publications.[1d,6d] The sign of the parameter V changes when g_x and g_y are interchanged. We note that a second solution having very small distortions and ΔE_1 and ΔE_2 values ($\approx 1\,500$ cm^{-1}) also exists, but the near-i.r. data make this solution unacceptable.

Kinetic Measurements.—The rate of *trans* $\longrightarrow$ *cis* isomerisation of $[Ru(ROCS_2)_2(PPh_3)_2]$ was computed from the cyclic voltammetric current height of coulometrically produced $[Ru(ROCS_2)_2(PPh_3)_2]^+$ species using the method described by Nicholson and Shain.[8] A working curve of i_{pa}/i_{pc} as a function of $k\tau$ was used, where τ is the time in s from $E_{\frac{1}{2}}$ to the switching potential and k is the rate constant. The rate constants (k) at different temperatures were measured from experimental i_{pa}/i_{pc} and τ values by using the working curve. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from an Eyring plot.

Acknowledgements

We thank the Department of Science and Technology, the Council of Scientific and Industrial Research, and the University Grants Commission, New Delhi, India, for financial support. We are thankful to Dr. Samaresh Bhattacharya for preliminary experiments.

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Received 22nd September 1989; *Paper* 9/04068J