Complexes of the Platinum Metals. Part VI.[1] Dithiocarbamato- and *O*-Alkyl Dithiocarbonato-derivatives of Ruthenium, Osmium, and Iridium

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New dithiocarbamato- and *O*-alkyl dithiocarbonato-derivatives, $[M(S-S)_2(PPh_3)_2]$, $[M(S-S)_2(CO)(PPh_3)]$, $[MH(S-S)(CO)(PPh_3)_2]$ (M = Ru or Os; S–S = $R_2NCS_2^-$ or $ROCS_2^-$; R = Me or Et), $[OsCl(S_2CNR_2)(CO)(PPh_3)_2]$, and $[IrH_2(S-S)(PPh_3)_2]$, have been prepared by treating the appropriate chloro- or carboxylato-complexes with sodium salts of the ligand. In several instances, hydride ligands, present in the parent complex, are also replaced by S–S groups. Tetramethylthiuram disulphide reacts with $[IrCl(CO)(PPh_3)_2]$, $[RuH_2(PPh_3)_4]$, and $[RuH_2(CO)(PPh_3)_3]$ or $[RuHCl(CO)(PPh_3)_3]$ to afford the complexes $[Ir(S_2CNMe_2)_2(CO)(PPh_3)]Cl$, $[Ru(S_2CNMe_2)_2(PPh_3)_2]$, and $[Ru(S_2CNMe_2)_2(CO)(PPh_3)]$ respectively. Structural and stereochemical assignments based on n.m.r. and i.r. spectroscopic data for the $R_2NCS_2^-$ and $ROCS_2^-$ complexes confirm the expected substantial barrier to rotation about the S_2C-NR_2 bond in the former, but reveal no evidence of a comparable barrier to rotation about the S_2C-OR bond in the latter.

RELATIVELY few complexes containing hydrido and sulphur-donor ligands bound within the same co-ordination sphere have been reported.[2] In particular, the only examples of dithiocarbamato- and *O*-alkyl dithiocarbonato-complexes containing hydrido-ligands are the iridium species $[IrH_2L(EPh_3)_2]$ (L = S_2CNEt_2 or S_2COEt; E = P or As) recently reported by Araneo and Napoletano.[3] The paucity of data on systems of this type is particularly surprising in view of the extensive

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[1] Part V, A. Dobson, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1975, 370.

[2] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

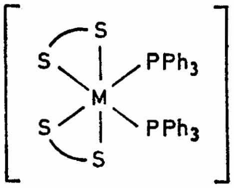
[3] A. A. Araneo and T. Napoletano, *Inorg. Chim. Acta*, 1972, **6**, 363.

interest in platinum-metal hydride complexes and the large number of hydrido-derivatives now known.[2] We have now attempted to prepare a range of hydrido-complexes of the platinum-group metals containing dithiocarbamato- or *O*-alkyl dithiocarbonato-ligands by treating the appropriate metal chlorohydrido- or carboxylatohydrido-complexes with sodium dithiocarbamates or *O*-alkyl dithiocarbonates in organic solvents under reflux. In all instances the expected metathesis of the chloride or carboxylate ligands occurs to yield dithiocarbamato- or *O*-alkyl dithiocarbonato-derivatives. However, in several instances the hydride ligands are also replaced by the sulphur-donor ligands, thus affording hydride-free products. The latter reaction, which has been observed before but passed without comment,[3,4] presumably proceeds by some form of redox reaction possibly involving formation of sodium alkylimidodithiocarbonates, $Na_2[S_2CNR]$. However, attempts to identify by-products and thus elucidate the nature of this process were unsuccessful.

All complexes show i.r. bands consistent with the presence of chelate dithiocarbamate or *O*-alkyl dithiocarbonate ligands [5,6] and all have molecular weights consistent with their formulation as monomers. We have assumed that the temperature-dependent ^{1}H n.m.r. effects noted for the methyl resonances of several dimethyldithiocarbamato-complexes (see below) arise from the well established phenomena of restricted rotation about the S_2C-NR_2 bonds of the dithiocarbamate ligands. Alternative processes involving Bailer twist, Rây–Dutt twist, or ligand-dissociation steps have been examined in recent papers [7] on related ruthenium–sulphur chelates and shown to be improbable. However, the stereochemical assignments in the present paper, which follow from the low-temperature n.m.r. data, are valid irrespective of mechanistic considerations.

RESULTS AND DISCUSSION

Ruthenium and Osmium Complexes.—$[M(S_2CNR_2)_2(PPh_3)_2]$ *and* $[Ru(S_2COR)_2(PPh_3)_2]$ (M = Ru *or* Os). These complexes were obtained by treating the hydrides $[MH(OCOMe)(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$ with sodium dithiocarbamates or *O*-alkyl dithiocarbonates; the ruthenium dimethyldithiocarbamate was also prepared by reacting tetramethylthiuram disulphide $[(Me_2NCS_2)_2]$ with $[RuH_2(PPh_3)_4]$. They form air-stable yellow or orange crystals but show evidence of some decomposition in chlorinated solvents. Ruthenium complexes of stoicheiometry $[Ru(S_2CNR_2)_2(PPh_3)_2]$ [7,8] and $[Ru(S_2COR)_2(PPh_3)_2]$ [8] have previously been reported; however, their osmium analogues have not hitherto been described. The dialkyldithiocarbamato-derivatives showed temperature-dependent n.m.r. spectra similar to those previously reported [7] for the ruthenium complex $[Ru(S_2CNMe_2)_2(PPh_3)_2]$ and are thus assigned *cis* stereochemistry (I). We observed no evidence of formation of less stable *trans* isomers similar to those claimed by Wilkinson,[8] and subsequently found to exist for $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$.[7] We were unable to establish the stereochemistry of the corresponding *O*-alkyl dithiocarbonato-complexes $[Ru(S_2COR)_2(PPh_3)_2]$ by variable-temperature n.m.r. spectroscopy since their decoalescence temperatures are inaccessible (see below). However, it seems reasonable to assume that they adopt *cis* structures analogous to those found for the related ruthenium–sulphur chelates $[Ru(S_2CNR_2)_2(PPh_3)_2]$ and $[Ru(S_2PR_2)_2(PPh_3)_2]$.[7]



(I) M=Ru or Os

$[M(S_2CNR_2)_2(CO)(PPh_3)]$. The yellow air-stable complexes $[M(S_2CNMe_2)_2(CO)(PPh_3)]$ and $[Ru(S_2CNEt_2)_2(CO)(PPh_3)]$ were obtained by vigorous and/or prolonged treatment of $[RuCl(OCOMe)(CO)(PPh_3)_2]$ or $[OsCl(OCOCF_3)(CO)(PPh_3)_3]$ with sodium dimethyl- or diethyldithiocarbamates. The reaction of $[OsCl(OCOCF_3)(CO)(PPh_3)_3]$ with sodium diethyldithiocarbamate afforded only the monosubstituted product $[OsCl(S_2CNEt_2)(CO)(PPh_3)_2]$ (see below). The ruthenium complex $[Ru(S_2CNMe_2)_2(CO)(PPh_3)]$ was also obtained by treating $[(Me_2NCS_2)_2]$ with $[RuH_2(CO)(PPh_3)_3]$ or $[RuH(Cl)(CO)(PPh_3)_3]$ in boiling benzene. Repeated attempts to obtain the corresponding *O*-alkyl dithiocarbonates $[M(S_2COR)_2(CO)(PPh_3)]$ by metathesis were unsuccessful, thus lending some support to the conclusion of Malatesta [9] that such complexes are less stable than their dithiocarbamato-analogues. Complexes of stoicheiometry $[M(S_2CNR_2)_2(CO)(PPh_3)]$ have not previously been prepared; recent attempts to obtain the ruthenium species $[Ru(S_2CNR_2)_2(CO)(PPh_3)]$ by carbonylation of the complexes $[Ru(S_2CNR_2)_2(PPh_3)_2]$ were unsuccessful.[8,10] The products $[M(S_2CNMe_2)_2(CO)(PPh_3)]$ are assigned *cis* stereochemistry (II) on the basis of their ambient-temperature ^{1}H n.m.r. spectra, each of which showed four singlets of equal intensity indicative of four magnetically non-equivalent methyl groups (a)—(d). On raising the temperature these singlets coalesced in pairs to form two singlets of equal intensity; this behaviour is attributed to the onset of rapid rotation about the S_2C-NMe_2 bonds leading to magnetic equivalence of methyl groups on the same dithiocarbamate ligand. The high-field pairs of singlets had τ values and coalescence temperatures very

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[4] A. A. Araneo, F. Bonati, and G. Minghetti, *Inorg. Chim. Acta*, 1970, **4**, 61.

[5] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, p. 256 and refs. therein.

[6] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kem.*, 1956, **B29**, 75; *Nature*, 1956, **177**, 1042.

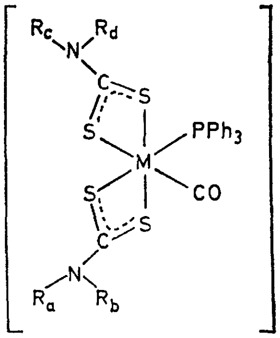
[7] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 739, 754.

[8] C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 84.

[9] L. Malatesta, *Gazzetta*, 1940, **70**, 553.

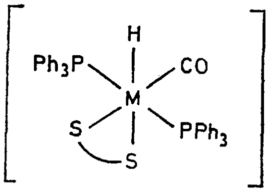
[10] D. J. Cole-Hamilton, P. W. Armit, and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 917.

similar to those recorded[11] for the complexes *cis*-$[M(S_2CNMe_2)_2(PPh_3)_2]$ and are thus assigned to methyl groups, (a) and (b), situated on the dithiocarbamate ligand *trans* to P and S donor atoms. By a process of elimination the low-field resonances are attributed to methyl groups (c) and (d).

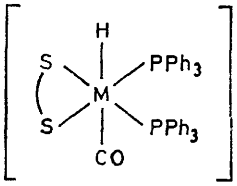


(II) M = Ru or Os
R = Me or Et

$[MH(S_2CNR_2)(CO)(PPh_3)_2]$ *and* $[MH(S_2COR)(CO)(PPh_3)_2]$. These air-stable yellow products were obtained by treating the complexes $[MH(Cl)(CO)(PPh_3)_3]$ with sodium dithiocarbamates or *O*-alkyl dithiocarbonates in boiling acetone (Ru) or 2-methoxyethanol (Os). Their high-field ^1H n.m.r. spectra each contained a triplet pattern τ *ca.* 21—23 [^2J(PH)(*cis*)18—20 Hz] indicative of hydride *cis* to two equivalent ^{31}P nuclei, and are thus consistent with two possible stereochemical arrangements, (IIIa) and (IIIb). However, the ^1H n.m.r. spectra of the dithiocarbamato-complexes showed the presence of non-equivalent alkyl groups at low temperature (*ca.* 250 K) and therefore favour stereochemistry (IIIa); at higher temperatures, rapid rotation about the S_2C-NR_2 bonds renders the alkyl groups R magnetically equivalent. Given the close parallel between the spectroscopic data for the dithiocarbamato-complexes and those of their *O*-alkyl dithiocarbonato-analogues (Table 2) it seems highly probable that these complexes share a common stereochemistry.



(IIIa)

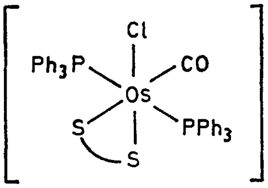


(IIIb)

M = Ru or Os

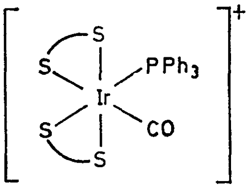
$[OsCl(S_2CNR_2)(CO)(PPh_3)_2]$. These yellow air-stable complexes were isolated by treating $[OsCl(OCOCF_3)(CO)(PPh_3)_3]$ with sodium dithiocarbamates under mild conditions. Their low-temperature ^1H n.m.r. spectra revealed the presence of non-equivalent alkyl groups and thus favour stereochemistry (IV).

Rhodium Complexes.—Attempts to prepare triphenylphosphine-substituted rhodium dithiocarbamato-derivatives by treating the complexes $[RhCl(PPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$, $[Rh(NO)(PPh_3)_3]$, and $[Rh(OCOCF_3)_2(NO)(PPh_3)_2]$ with sodium dimethyldithiocarbamate or tetramethylthiuram disulphide under mild conditions led to formation of $[Rh(S_2CNMe_2)_3]$ in good yield. Similar reactions involving rhodium complexes and sodium *O*-methyl dithiocarbonate gave intractable products.



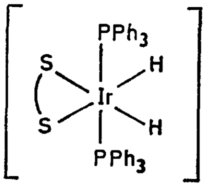
(IV)

Iridium Complexes.—$[Ir(S_2CNMe_2)_2(CO)(PPh_3)]Cl$. This ionic complex, obtained as air-stable yellow crystals by treating $[IrCl(CO)(PPh_3)_2]$ with tetramethylthiuram disulphide in benzene under reflux, had a temperature-dependent ^1H n.m.r. spectrum very similar to that found for $[Ru(S_2CNMe_2)_2(CO)(PPh_3)]$ and the cation is therefore assigned stereochemistry (V). Solubility, conductivity, and ionic-exchange properties are in accord with the proposed ionic formulation.



(V)

$[IrH_2(S_2CNR_2)(PPh_3)_2]$ *and* $[IrH_2(S_2COR)(PPh_3)_2]$. The iridium acetate, $[IrH_2(OCOMe)(PPh_3)_3]$, reacted with sodium dithiocarbamates and *O*-alkyl dithiocarbonates in boiling acetone to yield pale yellow $[IrH_2(S_2CNR_2)(PPh_3)_2]$ and white $[IrH_2(S_2COR)(PPh_3)_2]$, respectively. These complexes (R = Et) and their triphenylarsine analogues have previously been prepared by treating the complexes '$[IrH_3(PPh_3)_2]$' and '$[IrH_3(AsPh_3)_2]$' with sodium salts of the appropriate ligands in boiling acetone.[3] Attempts to induce further reactions between $[IrH_2(S_2CNR_2)(PPh_3)_2]$ and excess of sodium dithiocarbamate under vigorous conditions (2 h reflux in 2-methoxyethanol) were unsuccessful. Our spectroscopic data for these iridium complexes (Table 2) fully confirm the stereochemistry (VI) assigned by previous authors.[3]



(VI)

Variable-temperature N.M.R. Studies on O-*Alkyl Dithiocarbonato-complexes.*—To account for the small but

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[11] Data from Table 2 and ref. 7.

TABLE 1

Analytical, molecular-weight, and m.p. data for some dithiocarbamato- and *O*-alkyl dithiocarbonato-complexes

				Analyses [c]/%		
Complex	R	M.p. (θ_c/°C) [a]	M [b,c]	C	H	N
$[Ru(S_2CNR_2)_2(PPh_3)_2]$	Me	235—236		57·5 (58·25)	5·1 (4·9)	3·0 (3·25)
	Et	218—220		59·6 (59·9)	5·4 (5·45)	2·9 (3·05)
$[Ru(S_2COR)_2(PPh_3)_2]$	Me	170—171		56·9 (57·2)	4·25 (4·4)	
	Et	191—194		58·05 (58·1)	4·7 (4·65)	
$[Os(S_2CNR_2)_2(PPh_3)_2]$	Me	244—246	900 (955)	52·85 (52·8)	4·45 (4·45)	2·6 (2·95)
	Et	220—221		53·75 (54·6)	4·85 (5·0)	2·25 (2·75)
$[Ru(S_2CNR_2)_2(CO)(PPh_3)]$	Me	248—250	657 (632)	47·6 (47·5)	4·45 (4·3)	4·15 (4·45)
	Et	186—188		50·85 (50·6)	5·2 (5·1)	4·1 (4·05)
$[Os(S_2CNR_2)_2(CO)(PPh_3)]$	Me	251—252		41·6 (41·65)	3·85 (3·75)	3·8 (3·9)
$[RuH(S_2CNR_2)(CO)(PPh_3)_2]$	Me	216—217		61·35 (61·9)	4·85 (4·8)	1·7 (1·8)
	Et	169—171	785 (810)	62·7 (62·8)	4·9 (5·15)	1·6 (1·75)
$[RuH(S_2COR)(CO)(PPh_3)_2]$	Me	226—228		61·15 (61·45)	4·55 (4·5)	
	Et	188—189	768 (776)	62·0 (61·9)	4·8 (4·65)	
$[OsH(S_2CNR_2)(CO)(PPh_3)_2]$	Me	266—267	885 (864)	55·6 (55·6)	4·05 (4·3)	1·55 (1·6)
	Et	180—183		56·75 (56·55)	4·45 (4·65)	1·4 (1·55)
$[OsH(S_2COR)(CO)(PPh_3)_2]$	Me	187—189		54·8 (55·0)	4·05 (4·05)	
	Et	187—190	875 (865)	55·5 (55·55)	4·2 (4·2)	
$[OsCl(S_2CNR_2)(CO)(PPh_3)_2]$	Me	136—137		53·3 (53·5)	4·05 (4·05)	1·55 (1·55)
	Et	177—179	932 (927)	54·75 (54·45)	4·45 (4·35)	1·45 (1·5)
$[Ir(S_2CNR_2)_2(CO)(PPh_3)]Cl$	Me	235—240		39·25 (39·6)	3·8 (3·6)	3·7 (3·6)
$[IrH_2(S_2CNR_2)(PPh_3)_2]$	Me	195—196		55·75 (56·0)	4·8 (4·55)	1·85 (1·65)
	Et	237—239	876 (867)	56·9 (56·8)	4·85 (4·6)	1·3 (1·6)
$[IrH_2(S_2COR)(PPh_3)_2]$	Me	190—191	830 (826)	55·15 (55·25)	4·2 (4·25)	
	Et	208—209		56·1 (55·8)	4·55 (4·45)	

[a] Recorded in sealed tubes under nitrogen. [b] Obtained by osmometry at 42 °C in chloroform solution. [c] Calculated figures are given in parentheses.

TABLE 2

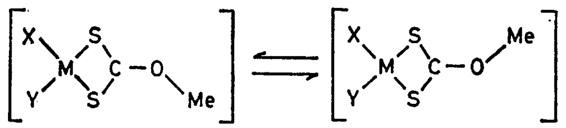
I.r.[a] and n.m.r.[b] data

							Variable temperature n.m.r.	
Complex	R	$\tilde{\nu}$(CO)/ cm^{-1}	$\tilde{\nu}$(MH)/ cm^{-1}	τ(MH)	^2J(PH)/ Hz	^3J(HH)/ Hz	T/K	τ(Me)
$[Ru(S_2CNR_2)_2(PPh_3)_2]$	Me						297	7·05(s), 7·25(s)
	Et					7·0	245	8·95(t), 9·1(t)
$[Ru(S_2COR)_2(PPh_3)_2]$	Me						230—297	6·25(s)
	Et					7·0	245—297	8·77(t)
$[Os(S_2CNR_2)_2(PPh_3)_2]$	Me						297	7·16(s)
	Et						297	8·98(t)
$[Ru(S_2CNR_2)_2(CO)(PPh_3)]$	Me	1 930s					335	6·72(s), 7·15(s)
		1 930s					329	6·70(s), 6·74(s), 7·15(s)
							297	6·70(s), 6·74(s), 7·14(s), 7·16(s)
	Et	1 920s				7·5	335	8·74, 9·07(t)
						7·5	297	8·72(t), 8·76(t), 9·07(t)
$[Os(S_2CNR_2)_2(CO)(PPh_3)]$	Me	1 910s					297	6·75(s), 6·79(s), 7·17(s), 7·19(s)
$[RuH(S_2CNR_2)(CO)(PPh_3)_2]$	Me	1 920s	1 950m	21·1(t)	19·5		297	7·54(s)
	Et	1 915s	1 970w	21·0(t)	20·0	7·0	297	9·30(t), 9·34(t)
$[RuH(S_2COR)(CO)(PPh_3)_2]$	Me	1 950s	1 930(sh)	20·95(t)	19·5		245—297	6·77(s)
	Et	1 950s	1 930(sh)	20·95(t)	19·5	7·0	203—297	9·08(t)
$[OsH(S_2CNR_2)(CO)(PPh_3)_2]$	Me	1 905s	2 040m	23·95(t)	18·0		297	7·65(s)
				23·95(t)	18·0		245	7·64(s), 7·66(s)
	Et	1 895s	2 060w	22·8(t)	16·0	7·0	297	9·30(t), 9·32(t)
$[OsH(S_2COR)(CO)(PPh_3)_2]$	Me	1 930s	2 020m	22·75(t)	18·5		297	6·8(s)
	Et	1 910s	1 950m	22·75(t)	18·5	7·0	297	9·02(t)
$[OsCl(S_2CNR_2)(CO)(PPh_3)_2]$	Me	1 925s					297	6·93(s), 6·95(s)
	Et	1 915s				7·0	297	8·84(t)
$[Ir(S_2CNR_2)_2(CO)(PPh_3)]Cl$	Me	2 050s					335	6·62(s), 7·07(s)
							297	6·60(s), 6·63(s), 7·07(s)
							233	6·60(s), 6·63(s), 7·06(s), 7·08(s)
$[Ir(S_2CNR_2)_2(CO)(PPh_3)][BPh_4]$	Me	2 060s					297	7·12(s), 7·24(s), 7·59(s)
$[IrH_2(S_2CNR_2)(PPh_3)_2]$	Me		2 125m				297	7·48(s)
			2 100m				297	7·48(s)
	Et		2 130m	29·4(t)	16·5	7·0	297	9·20(t)
			2 090m					
$[IrH_2(S_2COR)(PPh_3)_2]$	Me		2 170m	28·95(t)	15·5			6·65(s)
			2 140m					
	Et		2 165m					
			2 130m					8·97(t)

[a] Recorded for Nujol mulls; s = strong, m = medium, w = weak, and sh = shoulder. [b] Recorded for solutions in $CDCl_3$ with reference to internal tetramethylsilane; s = singlet, d = doublet, and t = triplet; coupling constants ±0·2 Hz.

significant differences in the properties of dithiocarbamato-complexes and their *O*-alkyl dithiocarbonato-analogues Chatt *et al.*[6] suggested that whereas the canonical form $R_2\overset{+}{N}{=}CS_2^{2-}$ is important in the former the form $R\overset{+}{O}{=}CS_2^{2-}$ is of minor significance in the latter. More recently several workers have presented i.r.[12] and *X*-ray [13] evidence to support the view that in many metal *O*-alkyl dithiocarbonato-complexes the form $R\overset{+}{O}{=}CS_2^{2-}$ makes a small but significant contribution to the overall structure. Thus on the basis of structural data ($S_2C{-}NR_2$ and $S_2C{-}OR$ bond lengths) Merlino [13] concludes that the $Et_2\overset{+}{N}{=}CS_2^{2-}$ form contributes 42% to the structure of $[Co(S_2CNEt_2)_3]$ whereas the contribution of $Et\overset{+}{O}{=}CS_2^{2-}$ to the corresponding complex $[Co(S_2COEt)_3]$ is *ca.* 13%. We have now attempted to investigate this problem by variable-temperature n.m.r. spectroscopy.

Restricted rotation due to multiple $S_2C{-}OMe$ bond order in asymmetric *O*-methyl dithiocarbonato-complexes of the form $[MX(Y)(S_2COMe)]$ should give rise to rotamers (A) and (B) at low temperatures, which in turn should generate separate methyl resonances similar to those found for the corresponding dimethyldithiocarbamato-derivatives. The absence of any detectable change in the methyl resonances of the complexes $[RuH(S_2COMe)(CO)(PPh_3)_2]$ and $[Ru(S_2COMe)_2(PPh_3)_2]$ * over the temperature range 203—297 K † is therefore taken to indicate either that the rotational barrier in the *O*-methyl dithiocarbonato-complexes is very small or that one rotamer is preferred to the virtual exclusion of the other. Assuming that the latter situation is improbable, and that the chemical-shift difference, $\Delta\nu$, between methyl resonances for pairs of rotamers is similar to that found for pairs of methyl groups in the corresponding dimethyldithiocarbamato-complexes under non-exchange conditions, approximate calculations, based on coalescence temperatures and use of the Eyring equation, indicate that the free energy of activation for rotation in the *O*-alkyl dithiocarbonato-complexes is much lower than that found for their dithiocarbamato-analogues. Thus calculations for the complexes *cis*-$[Ru(S_2CNMe_2)_2(PPh_3)_2]$ and *cis*-$[Ru(S_2COMe)_2(PPh_3)_2]$ give $\Delta G_c^{\ddagger}$ values of *ca.* 70 and *not greater than* 40 kJ mol^{-1}, respectively. The latter value supports previous conclusions that the double-bond character of the $S_2C{-}OR$ linkage is substantially smaller than that of the $S_2C{-}NR_2$ linkage.



(A) (B)

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Bruker HFX 90 spectrometer, i.r. spectra on Perkin-Elmer 457 and 621 spectrometers, and molecular weights were determined using a Hitachi–Perkin-Elmer 115 osmometer. Microanalyses were by the Microanalytical Laboratory, University College.

Bis(dimethyldithiocarbamato)bis(triphenylphosphine)-ruthenium(II).—*Method* (a). A solution of sodium dimethyldithiocarbamate (0·2 g) and acetatohydridotris(triphenylphosphine)ruthenium (0·4 g) in acetone (60 cm^3) was heated under reflux for 1·5 h. The solution was cooled to room temperature, diluted with methanol (40 cm^3), and set aside to crystallise. The required product was filtered off, recrystallised from dichloromethane–methanol, washed with ethanol then hexane, and dried *in vacuo* as mustard yellow *crystals* (1·50 g, 41%). The following were similarly prepared using the appropriate sodium dialkyldithiocarbamate or sodium *O*-alkyl dithiocarbonate: *bis(diethyldithiocarbamato)bis(triphenylphosphine)ruthenium*(II) as large orange crystals (47%); *bis(*O*-methyl dithiocarbonato)bis(triphenylphosphine)ruthenium*(II) as orange crystals (20%); and *bis(*O*-ethyl dithiocarbonato)bis(triphenylphosphine)ruthenium*(II) as yellow microcrystals (77%).

Method (b). A solution of sodium dimethyldithiocarbamate (0·2 g) and dihydridotetrakis(triphenylphosphine)ruthenium (0·4 g) in acetone (60 cm^3) was heated under reflux for 1·5 h. The solution was cooled to room temperature, diluted with methanol (40 cm^3), and set aside to crystallise. The required product was filtered off, recrystallised from dichloromethane–methanol, washed with ethanol then hexane, and dried *in vacuo* as mustard yellow *crystals* (0·15 g, 49%). Similarly prepared was *bis(diethyldithiocarbamato)-bis(triphenylphosphine)ruthenium*(II) as orange crystals (89%).

Method (c). A solution of tetramethylthiuram disulphide (0·2 g) and dihydridotetrakis(triphenylphosphine)ruthenium (0·4 g) in benzene (40 cm^3) was heated under reflux for 30 min, then evaporated to dryness under reduced pressure, and the residue extracted with dichloromethane (20 cm^3). The extract, after filtration, was diluted with methanol (20 cm^3) and set aside to crystallise. The required product was filtered off, washed with ethanol then hexane, and dried *in vacuo* as mustard yellow *crystals* (0·11 g, 48%).

Bis(dimethyldithiocarbamato)bis(triphenylphosphine)-osmium(II).—A solution of sodium dimethyldithiocarbamate (0·2 g) and hydrido(trifluoroacetato)tetrakis(triphenylphosphine)osmium (0·4 g) in 2-methoxyethanol (40 cm^3) was heated under reflux for 1 h. After concentrating to half volume, the solution was cooled to room temperature, diluted with methanol (40 cm^3), and set aside to crystallise. The required product was filtered off, recrystallised from dichloromethane–methanol, and washed with ethanol then hexane, and dried *in vacuo* as mustard yellow *crystals* (0·22 g, 60%). Similarly prepared was *bis(diethyldithiocarbamato)bis(triphenylphosphine)osmium*(II) as a mustard yellow powder (41%).

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* Fine splitting of the methylene quartet signals observed by Wilkinson and his co-workers [8] to occur in the n.m.r. spectra of the complex $[Ru(S_2COEt)_2(PPh_3)_2]$ and its analogue $[Ru(S_2CNEt_2)_2(PPh_3)_2]$ may be attributed to the intrinsic asymmetry of the methylene groups in these species.

† Studies at temperatures below 203 K were prevented by solubility problems.

[12] R. Mattes and G. Pauleickhoff, *Spectrochim. Acta*, 1974, **A30**, 379 and refs. therein.

[13] S. Merlino, *Acta Cryst.*, 1969, **B25**, 2270.

Carbonylbis(dimethyldithiocarbamato)(triphenylphosphine)-ruthenium(II).—*Method* (a). A solution of sodium dimethyldithiocarbamate (0·2 g) and acetatocarbonylchlorobis(triphenylphosphine)ruthenium (0·4 g) in acetone (60 cm^3) was heated under reflux for 2 h, then evaporated to dryness under reduced pressure, and the residue extracted with dichloromethane (20 cm^3). The extract, after filtration, was diluted with hexane (20 cm^3) and set aside to crystallise. The required product was filtered off, washed with cold methanol (2 × 5 cm^3) then hexane, and dried *in vacuo* as yellow *microcrystals* (0·30 g, 88%). Similarly prepared was *carbonylbis(diethyldithiocarbamato)(triphenylphosphine)ruthenium*(II) as yellow microcrystals (45%).

Method (b). A solution of tetramethylthiuram disulphide (0·2 g) and carbonylchlorohydridotris(triphenylphosphine)-ruthenium (0·4 g) in benzene (40 cm^3) was heated under reflux for 30 min, then evaporated to dryness under reduced pressure, and the residue extracted with dichloromethane (20 cm^3). The extract, after filtration, was diluted with hexane (20 cm^3) and set aside to crystallise. The required product was filtered off, washed with cold methanol (2 × 5 cm^3) then hexane, and dried *in vacuo* as yellow *microcrystals* (0·24 g, 90%).

Method (c). As (b), but using carbonyldihydridotris(triphenylphosphine)ruthenium (0·4 g) as precursor, yield 0·16 g (58%).

Carbonylbis(dimethyldithiocarbamato)(triphenylphosphine)-osmium(II).—A solution of sodium dimethyldithiocarbamate (0·2 g) and carbonylchloro(trifluoroacetato)tris(triphenylphosphine)osmium (0·4 g) in 2-methoxyethanol (40 cm^3) was heated under reflux for 1 h. After concentrating to half volume, the solution was cooled to room temperature, diluted with methanol (40 cm^3), and set aside to crystallise. The required product was filtered off, recrystallised from dichloromethane–methanol, washed with ethanol then hexane, and dried *in vacuo* as yellow *microcrystals* (0·30 g, 92%).

Carbonyl(dimethyldithiocarbamato)hydridobis(triphenylphosphine)ruthenium(II).—A solution of sodium dimethyldithiocarbamate (0·2 g) and carbonylchlorohydridotris(triphenylphosphine)ruthenium (0·4 g) in acetone (60 cm^3) was heated under reflux for 40 min, then evaporated to dryness under reduced pressure, and the residue extracted with dichloromethane (20 cm^3). The extract, after filtration, was diluted with methanol (20 cm^3) and set aside to crystallise. The required product was filtered off, washed with ethanol then hexane, and dried *in vacuo* as pale yellow *crystals* (0·27 g, 83%). The following were similarly prepared from the appropriate sodium dialkyldithiocarbamate or *O*-alkyl dithiocarbonate: *carbonyl(diethyldithiocarbamato)hydridobis(triphenylphosphine)ruthenium*(II) as pale yellow crystals (36%); *carbonylhydrido*(O-*methyl dithiocarbonato*)*bis(triphenylphosphine)ruthenium*(II) as orange crystals (62%); and *carbonyl*(O-*ethyl dithiocarbonato*)*hydridobis(triphenylphosphine)ruthenium*(II) as pale yellow microcrystals (42%).

Carbonyl(dimethyldithiocarbamato)hydridobis(triphenylphosphine)osmium(II).—A solution of sodium dimethyldithiocarbamate (0·2 g) and carbonylchlorohydridotris(triphenylphosphine)osmium (0·4 g) in 2-methoxyethanol (40 cm^3) was heated under reflux for 1 h. After concentrating to half volume, the solution was cooled to room temperature, diluted with methanol (40 cm^3), and set aside to crystallise. The required product was filtered off, recrystallised from dichloromethane–methanol, washed with ethanol then hexane, and dried *in vacuo* as pale yellow *crystals* (0·29 g, 87%). The following were similarly prepared from the appropriate sodium dialkyldithiocarbamate or *O*-alkyl dithiocarbonate: *carbonyl(diethyldithiocarbamato)hydridobis(triphenylphosphine)osmium*(II) as pale yellow crystals (36%); *carbonylhydrido*(O-*methyl dithiocarbonato*)*bis(triphenylphosphine)osmium*(II) as yellow needles (33%); and *carbonyl*(O-*ethyl dithiocarbonato*)*hydridobis(triphenylphosphine)osmium*(II) as yellow crystals (66%).

Carbonylchloro(dimethyldithiocarbamato)bis(triphenylphosphine)osmium(II).—A solution of sodium dimethyldithiocarbamate (0·2 g) and carbonylchloro(trifluoroacetato)-tris(triphenylphosphine)osmium (0·4 g) in acetone (60 cm^3) was heated under reflux for 1·5 h. The solution was cooled to room temperature, diluted with methanol (40 cm^3), and set aside to crystallise. The required product was filtered off, recrystallised from dichloromethane–methanol, washed with ethanol then hexane, and dried *in vacuo* as pale yellow *crystals* (0·13 g, 32%). Similarly prepared was *carbonylchloro(diethyldithiocarbamato)bis(triphenylphosphine)osmium*(II) as yellow microcrystals (64%).

Carbonylbis(dimethyldithiocarbamato)(triphenylphosphine)-iridium(III) *Chloride*.—A solution of tetramethylthiuram disulphide (0·4 g) and carbonylchlorobis(triphenylphosphine)iridium (0·4 g) in benzene (60 cm^3) was heated under reflux for 1 h. After cooling to room temperature, the required product was filtered off, washed with benzene then hexane, and dried *in vacuo* as pale yellow *microcrystals* (0·20 g, 62%).

Carbonylbis(dimethyldithiocarbamato)(triphenylphosphine)-iridium(III) *Tetraphenylborate*.—*Anion-exchange experiment*. A solution of carbonylbis(dimethyldithiocarbamato)(triphenylphosphine)iridium chloride (0·1 g) in methanol (10 cm^3) was added to a solution of sodium tetraphenylborate (0·1 g) in methanol (10 cm^3). The resulting precipitate was filtered off, washed with methanol and hexane, and dried *in vacuo* as a pale yellow *powder* (0·1 g, 73%).

(*Dimethyldithiocarbamato)dihydridobis(triphenylphosphine)iridium*(III).—A solution of sodium dimethyldithiocarbamate (0·2 g) and acetatodihydridotris(triphenylphosphine)iridium (0·4 g) in acetone (60 cm^3) was heated under reflux for 1 h, then evaporated to dryness under reduced pressure, and the residue extracted with dichloromethane (20 cm^3). The extract, after filtration, was diluted with methanol (20 cm^3) and set aside to crystallise. The required product was filtered off, washed with ethanol then hexane, and dried *in vacuo* as pale yellow *crystals* (0·11 g, 68%). The following were similarly prepared using the appropriate sodium dialkyldithiocarbamate or *O*-alkyl dithiocarbonate: (*diethyldithiocarbamato)dihydridobis(triphenylphosphine)-iridium*(III) as pale yellow crystals (74%); *dihydrido*(O-*methyl dithiocarbonato*)*bis(triphenylphosphine)iridium*(III) as pale yellow crystals (69%); and (O-*ethyl dithiocarbonato*)-*dihydridobis(triphenylphosphine)iridium*(III) as white platelets (79%).

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