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Unidentate Dithiocarbamate Complexes of Rhodium and Iron: Dithiocarbamate and Dithiocarbonate Complexes of Ruthenium †

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The interaction of sodium dimethyldithiocarbamate with acetone solutions of chlorotris(triphenylphosphine)rhodium(I) and *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) leads to the new complexes $Rh^{I}(S_2CNMe_2)(PPh_3)_2$, $Rh^{I}(S_2CNMe_2)(CO)PPh_3$, $Rh^{III}(S_2CNMe_2)_3(PPh_3)$, and $Rh^{III}(S_2CNMe_2)_3(CO)PPh_3$. I.r. and n.m.r. spectra of the last two complexes suggest the presence of a unidentate dithiocarbamate group.

From chlorodicarbonyl-π-cyclopentadienyl-iron(II) a similar unidentate complex $(\pi\text{-}C_5H_5)Fe(CO)_2(S_2CNMe_2)$ has been obtained.

Dichlorotris(triphenylphosphine)ruthenium(II) reacts with sodium dimethyldithiocarbamate, the corresponding diethyl and diphenyl salts, and also sodium *O*-methyl and -ethyl dithiocarbonates to form ruthenium(II) chelate complexes of the type $Ru(Me_2NCS_2)_2(PPh_3)_2$ and $Ru(MeOCS_2)_2(PPh_3)_2$.

Interaction of Chlorotris(triphenylphosphine)rhodium(I) *with Sodium Dithiocarbamates*.—The interaction of chlorotris(triphenylphosphine)rhodium(I) with sodium dimethyldithiocarbamate in acetone solution produces different dithiocarbamate complexes, depending upon the conditions. With stoicheiometric amounts and short reaction times (30 min.), the main component of the resulting orange solution, after chromatography on alumina, is the chelate complex of rhodium(I), $Rh(S_2CNMe_2)(PPh_3)_2$. This has a band in the infrared spectrum (Table) commonly assigned as a C–N stretching frequency characteristic of dithiocarbamate complexes.[1] The n.m.r. spectrum has a peak corresponding to the phenyl group at τ 2·52 with that for the methyl group at τ 7·3 with the relative areas 5 : 1 as expected for (I). It is hence quite similar to the dicarbonyl chelate complex, $Rh(CO)_2(S_2CNMe_2)_2$, prepared from chlorocarbonylrhodium dimer, $Rh_2(CO)_4Cl_2$ and sodium dimethyldithiocarbamate.[1]

If an excess of the dithiocarbamate is used and the reaction time is *ca.* 24 hr. chromatographic separation

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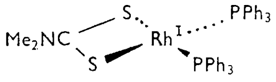
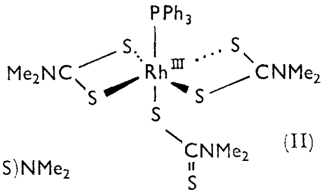
† No reprints available.

[1] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.

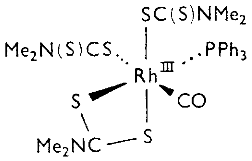
of the components of the resulting orange solution leads to the isolation of triphenylphosphine sulphide (characterised by analysis and the band corresponding to the P=S bond in the i.r. spectrum at 642 cm.$^{-1}$), the tris(dimethyldithiocarbamato)rhodium(III)[1] and



(I)



(II)



(III)

an orange yellow complex characterised as $Rh(S_2CNMe_2)_3(PPh_3)$. It is evident that unless the normal octahedral co-ordination of rhodium(III) is exceeded in the latter, one of the dithiocarbamate groups must be bound by only one sulphur atom. There is only one previously known example of a unidentate dithiocarbamate, namely $Ru(NO)(S_2CNEt_2)_3$, whose *X*-ray crystal structure has been determined.[2] While the rhodium complex shows a band in the 1460—1470 cm.$^{-1}$ region of the i.r. spectrum suggested[2] as being associated with a unidentate dithiocarbamate, the clearest proof is found from n.m.r. spectrum. This shows a band due to the phenyl peak at τ 2·63 together with two peaks showing complex splitting centred at τ 6·72 and 7·24, the relative areas being 3 : 2 : 1, consistent with two chelate and one unidentate group as in (II) or an isomer thereof. A similar diethyldithiocarbamate complex can be obtained and this also has an n.m.r. spectrum consistent with the presence of six ethyl groups per triphenylphosphine and a non-chelate dithiocarbamate; it also has a band at 1720 cm.$^{-1}$ together with other weak bands not found in the spectrum of the corresponding tris(diethyldithiocarbamato)rhodium(III) or of $RhCl(PPh_3)_3$.

I.r. spectra of dithiocarbamato-complexes (cm.$^{-1}$, in Nujol or hexachlorobutadiene mulls)

Compound	ν(CO)	ν(CN) (chelate)	ν(CN) (unidentate)[a]
$Rh(S_2CNMe_2)(PPh_3)_2$		1520	
$Rh(S_2CNMe_2)(CO)(PPh_3)$	1920s	1525	
$Rh(S_2CNMe_2)_3$		1520	
$Rh(S_2CNMe_2)_3PPh_3$		1515	1478
$Rh(S_2CNMe_2)_3(CO)(PPh_3)$	2100s	1530	1490
$(\pi\text{-}C_5H_5)Fe(CO)_2S_2CNMe_2$	2030, 1990s		1480
$Ru(S_2CNMe_2)_2(PPh_3)_2$ ...		1504	
$Ru(S_2CNMe_2)_2(PPh_3)_2$ ...		1487	
$Ru(S_2CNPh_2)_2(PPh_3)_2$ ...		1488	

[a] *Cf.* $Na[S_2CNMe_2],H_2O$, ν_{CN} 1480.

Interaction of trans-*Chlorocarbonylbis(triphenylphosphine)rhodium*(I) *with Sodium Dimethyldithiocarbamate.*—In a similar way, but using *trans*-$RhCl(CO)(PPh_3)_2$ and one equivalent of dithiocarbamate, the carbonyl-substituted analogue of (I), namely $Rh(S_2CNMe_2)(CO)(PPh_3)$, is obtained. The n.m.r. spectrum shows only two main bands (with some splitting) at τ 2·50 and 6·95 due to phenyl and methyl groups.

Using excess dithiocarbamate and a 24 hr. reaction period the tris(dithiocarbamato)rhodium(III) complex was again isolated, together with a second, carbonyl-containing complex of formula $Rh(S_2CNMe_2)_3(CO)(PPh_3)$. The latter is rather sparingly soluble in deuteriochloroform, but the n.m.r. spectrum shows bands due to phenyl groups at τ 2·68 and two resonances due to methyl groups at τ 6·75 and 7·22, the relative areas being 1 : 1. The complex again is formulated as one with unidentate dithiocarbamato-groups, *e.g.* (III). Isomers are possible but we have no evidence for more than one, though which particular one has not been ascertained. The frequency of the C–O stretch is raised in this Rh^{III} complex, compared with that for the Rh^{I} carbonyl complex, as expected.

Dimethyldithiocarbamatodicarbonyl-π-cyclopentadienyliron(II).—In order to obtain another example of a unidentate dithiocarbamate, we treated $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ in acetone solution with sodium dimethyldithiocarbamate. The complex subsequently isolated was $(\pi\text{-}C_5H_5)Fe(CO)_2(S_2CNMe_2)$ which again clearly had a unidentate group according to its i.r. spectrum (Table). The n.m.r. spectrum shows peaks due to the cyclopentadienyl group at τ 4·98 (relative area 5) and to the methyl group at τ 6·50 (relative area 6). It may be noted that the interaction of the dimer $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with tetramethylthiuramdisulphide gives[1] a normal chelate complex $(\pi\text{-}C_5H_5)Fe(CO)(S_2CNMe_2)$. However, unidentate trithiocarbonate complexes $(\pi\text{-}C_5H_5)Fe(CO)_2S(CS)SR$ (R = Me or Et) have been prepared.[3]

It is possible that other unidentate dithiocarbamato-complexes may be obtained by interaction of a halide complex L_nMX with sodium dialkyldithiocarbamate provided that the reaction conditions are sufficiently mild for a ligand not to be displaced, which would result in the formation of the chelate complex.

Interaction of Sodium Dithiocarbamates and Dithiocarbonates with Dichlorotris(triphenylphosphine)ruthenium(II).—The interaction of $RuCl_2(PPh_3)_3$ with two equivalents of sodium dimethyldithiocarbamate in acetone solutions leads to yellow-orange crystals of the complex $Ru(S_2CNMe_2)_2(PPh_3)_2,Me_2CO$. If only one equivalent of the dithiocarbamate is used a mixture of the bis-complex and unreacted $RuCl_2(PPh_3)_3$ is obtained; a similar result has been noted previously[4] in the preparation of the dicarbonyl complexes $Ru(S_2CNR_2)_2(CO)_2$, to which the phosphine complexes are related. Corresponding reactions with sodium diethyl- and diphenyl dithiocarbamates give similar

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[2] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 1966, 476.

[3] R. Bruce and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 67.

[4] J. V. Kingston and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2709.

complexes while sodium *O*-methyl and -ethyl dithiocarbonates give the complexes $Ru(S_2COR)_2(PPh_3)_2$.

Neither the dithiocarbamates nor the dithiocarbonates react with carbon monoxide, even under pressure; $Ru(S_2CNMe_2)_2(PPh_3)_2$ does not react with pyridine and was recovered unchanged after refluxing in carbon disulphide for 12 hr.

Although it is not possible to be certain on the basis of spectroscopic evidence, it seems reasonable to assume that in these complexes the triphenylphosphine groups are *trans* to each other with dithiocarbamato- or dithiocarbonato-groups acting as chelates. The CN stretching frequency of the dimethyl dithiocarbamate complex is in the region for the chelate complexes but the diethyl and diphenyl complexes have values overlapping the region for the unidentate group (Table). Hence, in the absence of other evidence the position of the stretching frequency as a diagnostic test for the bonding of the dithiocarbamate group cannot be relied upon.

The n.m.r. spectrum of $Ru(S_2CNMe_2)_2(PPh_3)_2,Me_2CO$ also shows some splitting of the methyl resonance with peaks at τ 7·18 and 7·30 (ratio *ca.* 2 : 4); since there is only one C–N stretch however it seems most reasonable to attribute this to differing orientations of the methyl groups, possibly due to steric hindrance by the bulky triphenylphosphine groups. The other bands in the n.m.r. spectrum are at τ 2·7 (Ph, 15) and 7·95 (Me_2CO, 3). The bands due to diethyldithiocarbamate also showed some signs of splitting of the methylene quartet at τ 6·60. Although the *O*-methyl dithiocarbonate had only a singlet at τ 6·32, the *O*-ethyl complex had two slightly displaced quartets at τ 5·7 and a triplet at 8·7.

The far i.r. spectra of $Ru(S_2CNMe_2)(PPh_3)_2$ had strong bands at 340 and 318 $cm.^{-1}$ not found in similar triphenylphosphine complexes, which may tentatively be assigned as the symmetric and asymmetric Ru–S stretching frequencies; in the ethyl complex these appear at 345 and 322 (split) and in the phenyl complex at 306 and 265 $cm.^{-1}$. In the *O*-methyl and -ethyl dithiocarbonates the respective bands are at 348s, 318s, and 320s, and 300m $cm.^{-1}$.

EXPERIMENTAL

Microanalysis and molecular weights (Perkin-Elmer-Hitachi osmometer at 35°) were obtained by the Microanalytical Laboratory, Imperial College.

Materials and Apparatus.—N.m.r. spectra were measured on a Perkin-Elmer model R 14 at 100 Mc./sec. I.r. spectra were measured on a Perkin-Elmer grating i.r. spectrometer. M.p.'s were determined on a Köfler hot-stage microscope.

The petroleum used had b.p. 40—60°.

Dimethyldithiocarbamatobis(triphenylphosphine)rhodium(I).—Chlorotris(triphenylphosphine)rhodium(I) (0·368 g.) and an equivalent of sodium dimethyldithiocarbamate (0·072 g.) in acetone (50 ml.) were shaken for 30 min. The precipitated sodium chloride was filtered off from the orange solution and petroleum (50 ml.) was added to the filtrate. The solid was collected, dissolved in the minimum of benzene, and the solution chromatographed on alumina using benzene–dichloromethane (1 : 1 v/v) as eluant. Only one band was obtained, some decomposition products remaining on the column. The eluant was evaporated, the oil dissolved in benzene, and petroleum was added to precipitate the yellow *complex* (*ca.* 50%), m.p. (decomp.) 112° [Found: C, 62·4; H, 4·7; N, 1·95%; *M* (benzene), 670. $C_{39}H_{36}NP_2RhS$ requires C, 62·6; H, 4·8; N, 1·9%; *M*, 748].

Tris(dimethyldithiocarbamato)triphenylphosphinerhodium(III).—Chlorotris(triphenylphosphine)rhodium(I) (0·72 g.) and an excess (6 moles) of sodium dimethyldithiocarbamate (0·864 g.) in acetone (100 ml.) was shaken for 24 hr. The precipitated sodium chloride was filtered off from the orange solution, the filtrate was evaporated, and the residue dissolved in benzene and transferred to an alumina column.

Elution with benzene–petroleum (1 : 1 v/v) gives two bands, the first yellow-green band being triphenylphosphine sulphide (m.p. 155—157°). The yellow solution from the second band was evaporated, and the residue washed with diethyl ether to remove any triphenylphosphine sulphide, leaving trisdithiocarbamatorhodium(III) [Found: C, 24·8; H, 3·8; N, 8·8%; *M* (benzene) 460. Calc. for $C_9H_{18}N_3RhS_6$: C, 23·3; H, 3·9; N, 9·0%; *M*, 464].

On further elution with benzene–dichloromethane (1 : 1 v/v) the main product obtained is a yellow solution, with some decomposition products remaining on the column. The solvent was removed, the solid dissolved in the minimum of benzene, and petroleum was added to give orange-yellow crystals of the *complex* (*ca.* 50%), m.p. 108—110° [Found: C, 45·4; H, 4·7; N, 5·5; S, 25·6%; *M* (benzene) 670. $C_{27}H_{33}N_3PRhS_6$ requires C, 44·7; H, 4·6; N, 5·8; S, 26·5%; *M*, 726]. The complex is a non-conductor in nitromethane, (10^{-3}M).

In an analogous way, using sodium diethyl dithiocarbamate but dissolving the solid after elution in acetone and cooling to −10°, we obtained orange-yellow crystals of *tris(diethyldithiocarbamato)triphenylphosphinerhodium*(III) [Found: C, 48·8; H, 6·0; N, 4·8%; *M* (benzene) 780. $C_{33}H_{45}N_3PRhS_6$ requires C, 49·0; H, 5·6; N, 5·2%; *M*, 810].

Dimethyldithiocarbamatocarbonyltriphenylphosphinerhodium(I).—The complex *trans*-$RhCl(CO)(PPh_3)_2$ (0·276 g.) and one equivalent of sodium dimethyl dithiocarbamate (0·072 g.) in acetone (50 ml.) was shaken for 30 min. Treatment as before and elution with benzene–dichloromethane gives a single band which on evaporation gives the *complex* as brown crystals (*ca.* 70%), m.p. 83—85° [Found: C, 51·4; H, 4·1; N, 2·1; S, 10·3%; *M* (benzene) 560. $C_{22}N_{21}NOPRhS_2$ requires C, 51·5; H, 4·1; N, 2·8; S, 12·5%; *M*, 513].

Trimethyldithiocarbamatocarbonyl(triphenylphosphine)-rhodium(III).—The complex *trans*-$RhCl(CO)(PPh_3)_3$ (0·69 g.) and an excess (6 moles) of sodium diethyldithiocarbamate in acetone were shaken for 24 hr.; the colour changes from yellow to orange-brown and sodium chloride is precipitated. Treatment as before and elution with benzene–petroleum gives an orange band of $Rh(S_2CNMe_2)_3$ while elution with benzene–dichloromethane yields the *complex* (*ca.* 30%) as orange-yellow crystals, m.p. 135—138° (Found: C, 45·8; H, 4·4; N, 5·4; S, 21·5. $C_{26}H_{33}N_3OPRhS_6$ requires C, 44·6; H, 4·4; N, 5·5; S, 25·5).

Dimethyldithiocarbamatodicarbonyl-π-cyclopentadienyl-iron(II).—The compound π-$C_5H_5Fe(CO)_2Cl$ (0·213 g.) and one equivalent of sodium dimethyldithiocarbamate (0·179 g.) in acetone (100 ml.) was shaken for 24 hr. when the colour changes from red-brown to brown and sodium chloride is precipitated. The filtered solution was evaporated, dissolved in benzene, and transferred to an alumina column. Elution with benzene–dichloromethane (1 : 1 v/v) gives first a small quantity of an unstable substance and then the major product as a dark orange band. Recovery by evaporation and precipitation from benzene by petroleum gives the brown-orange *complex* (*ca.* 70%), m.p. 102—104° [Found: C, 40·9; H, 4·2; N, 4·3%; *M* (benzene) 295. $C_{10}H_{11}FeNO_2S_2$ requires C, 40·4; H, 3·7; N, 4·7%; *M*, 297].

Bis(dimethyldithiocarbamato)bis)triphenylphosphine)-ruthenium(II) *Acetone Solvate*.—Dichlorotris(triphenylphosphine)ruthenium(II) (0·5 g.) and sodium dimethyldithiocarbamato hydrate (0·15 g.) were refluxed in degassed acetone (50 ml.) for *ca.* 12 hr. The solution was filtered, the orange crystals washed with water (to remove sodium chloride) and with diethyl ether, then dried *in vacuo* at 60° to give the *complex* (0·4 g., 90%), m.p. 153° (decomp.) [Found: C, 57·4; H, 5·1; N, 3·1%; *M* (dichloromethane) 860. $C_{42}H_{42}N_2P_2RuS_4,Me_2CO$ requires C, 57·6; H, 5·1; N, 3·0%; *M*, 865]. The complex is soluble in carbon disulphide and dichloromethane, less readily soluble in benzene, acetone, and methanol and insoluble in diethyl ether. The solid is stable to aerial oxidation but the solutions slowly darken on exposure to air.

Bis(diethyldithiocarbamato)bis(triphenylphosphine)ruthenium(II).—This was prepared as for the dimethyldithiocarbamate compound but using sodium diethyldithiocarbamate (0·2 g.) in degassed acetone (50 ml.) for *ca.* 12 hr. giving yellow-orange crystals of the *complex* (0·39 g., 85%), m.p. 182—183° (decomp.) [Found: C, 59·2; H, 5·3; N, 3·2; S, 14·5%; *M*, 918 (dichloromethane). $C_{46}H_5ON_2P_2RuS_4$ requires C, 59·9; H, 5·4; N, 3·2; S, 13·9%; *M*, 921]. The compound has properties similar to those of the dimethyldithiocarbamate compound.

Bis(diphenyldithiocarbamato)bis(triphenylphosphine)-ruthenium(II).—This was prepared as for the dimethyldithiocarbamate compound but using sodium diphenyldithiocarbamate (0·28 g.) in acetone (50 ml.) to give the *complex* (*ca.* 80%) which blackens before melting (Found: C, 66·6; H, 4·3; N, 2·6; S, 12·0. $C_{62}H_{50}N_2P_2RuS_4$ requires C, 66·8; H, 4·5; N, 2·5; S, 11·5%).

Bis-(O-*methyl dithiocarbonato*)*bis*(*triphenylphosphine*)*ruthenium*(II).— Dichlorotris(triphenylphosphine)ruthenium(II) (0·5 g.) and potassium *O*-methyl dithiocarbonate (0·16 g.) were refluxed in degassed acetone (50 ml.) for *ca.* 12 hr. The precipitate was washed with water and diethyl ether to leave orange crystals of the *complex* (0·25 g., 60%), m.p. 165—169° (decomp.) (Found: C, 58·0; H, 4·1; S, 14·8. $C_{40}H_{36}O_2P_2RuS_4$ requires C, 57·2; H, 4·3; S, 14·3%). The complex is soluble in dichloromethane, carbon disulphide, and benzene, less soluble in methanol and acetone and insoluble in diethyl ether and petroleum. The solid is stable to oxidation but the solutions darken fairly readily in air.

Bis-(O-*ethyl dithiocarbonato*)*bis*(*triphenylphosphine*)*ruthenium*(II).—This was prepared as for the dimethyl compound but using potassium *O*-ethyl dithiocarbonate (0·17 g.) in degassed acetone (50 ml.) to give yellow-orange crystals of the *complex* (*ca.* 80%), m.p. 175—176° (decomp.) (Found: C, 57·6; H, 5·1; S, 14·1%; *M*, 800. $C_{42}H_{40}O_2P_2RuS_4$ requires C, 58·1; H, 4·6; S, 14·7%; *M*, 867). The solubilities are similar to those of the methyl complex.

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