Diphenyl Dithiophosphato- and Dicyclohexyldithiophosphinato-complexes of Rhodium(I)

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The reaction of [$\{Rh(CO)_2Cl\}_2$], [$Rh(PPh_3)_3Cl$], and [$\{Rh(cot)Cl\}_2$] with diphenyl dithiophosphate, $(PhO)_2PS_2^-$, and dicyclohexyldithiophosphinate, $(H_{11}C_6)_2PS_2^-$, ions gives neutral four-co-ordinate complexes [RhL_2(S–S)] and [Rh(cot)(S–S)] [L = CO or PPh_3; cot = η-cyclo-octa-1,5-diene; S–S$^-$ = $(PhO)_2PS_2^-$ or $(H_{11}C_6)_2PS_2^-$]. On treating rhodium(I) dithio-bonded complexes with CO or PPh_3 no five-co-ordinate complex has been obtained but only some substitution products of the neutral ligand. 1,2-Bis(diphenylphosphino)ethane and 1,2-bis-(diphenylarsino)ethane, L–L, react, cleaving the metal–sulphur bonds and giving new cationic five-co-ordinate species, [$Rh(L–L)_2CO$](S–S). These easily lose their CO affording cationic [$Rh(L–L)_2$](S–S) and these complexes may also be obtained as tetraphenylborate salts. On bubbling CO through a CH_2Cl_2 solution containing [$Rh(L–L)_2$](S–S) [S–S$^-$ = $(H_{11}C_6)_2PS_2^-$], neutral [$Rh(CO)_2$(S–S)] is formed. The possibility of identifying the mode of co-ordination of the dithio-ligands by i.r. spectra is briefly discussed. Some oxidative-addition reactions of [$Rh(CO)_2$(S–S)] complexes are also reported: [$\{Rh(CO)(S–S)X_2\}_2$] complexes have been obtained by treating [$Rh(CO)_2$(S–S)] with bromine or iodine, whereas the same reaction with MeI gives [Rh(CO)(COMe)-(S–S)I].

THE continuing interest in the study of metal complexes containing dithio-ligands is shown by the number of recent reports on this subject.[1-3] The potentially chelating anions dithiophosphate, $(RO)_2PS_2^-$, and dithiophosphinate, $R_2PS_2^-$, easily form complexes with metal ions,[2,3] but only recently some reports concerning the preparation and reactivity of various organometallic complexes containing dithio- and other ancillary co-ordinated ligands have been published. These reports concerned carbonyl and carbonylphosphine complexes of manganese(I),[4] rhenium(I),[4,5] iridium(III),[6] palladium(II),[7-9] platinum(II),[8-10] and ruthenium(II); [11] brief mention was also made of analogous complexes of rhodium and osmium, but no further details on the type of complexes have been given.[8,11]

I have studied the preparation and reactivity of [RhL_2(S-S)] and [Rh(cot)(S-S)] complexes [L = CO or PPh_3; cot = η-cyclo-octa-1,5-diene; S-S$^-$ = $(H_{11}C_6)_2$-PS_2^- and $(PhO)_2PS_2^-$]; † some of the oxidative-addition chemistry of these complexes is also reported. The synthesis and the reactions of analogous iridium(I) complexes will be discussed in a forthcoming paper.[12] Other Rh^I and Rh^{III} complexes containing dithio-ligands have been reported earlier,[13-18] but no information has been presented on their reactivity.

RESULTS AND DISCUSSION

The complexes [RhL_2(S-S)] and [Rh(cot)(S-S)] [L = CO or PPh_3; cot = η-cyclo-octa-1,5-diene; S-S$^-$ = $(H_{11}C_6)_2PS_2^-$ and $(PhO)_2PS_2^-$] were obtained by reacting [$\{Rh(CO)_2Cl\}_2$], [$Rh(PPh_3)_3Cl$], and [$\{Rh(cot)Cl\}_2$] with ammonium salts of diphenyl dithiophosphate and dicyclohexyldithiophosphinate in benzene solution as reported in the Experimental section. All the complexes are crystalline solids, non-conducting in dichloromethane or acetone solution, soluble in non-polar solvents, and quite stable both in the solid and solution state. Their colour ranges from orange-yellow for the complexes containing $(PhO)_2PS_2^-$ to red-brown for $(H_{11}C_6)_2PS_2^-$ complexes. The prepared complexes clearly indicate the bidentate nature of the dithio-ligands used and thus are monomers as indicated by molecular-weight measurements in benzene or dichloromethane solution. Associated structures in solution have been suggested [19,20] for some dithiophosphato- and dithiophosphinato-compounds and in some cases in the solid state these formulations have been derived from *X*-ray determinations.[21] On the basis of *X*-ray evidence given for dithiophosphato- and dithiophosphinato-complexes of the nickel group,[8,22,23] the complexes here reported are likely to have a square-planar arrangement of ligands. The

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† The abbreviations S–S and L–L represent bidentate ligands.

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i.r. spectra, in the CO-stretching region, of the complexes $[\mathrm{Rh(CO)_2(S{-}S)}]$ showed, as expected, two very strong bands at *ca.* 2 010 and 2 070 cm^{-1}.

Reactions with Neutral Ligands.—No five-co-ordinate complex was obtained when CO or $\mathrm{PPh_3}$ reacted with $[\mathrm{RhL_2(S{-}S)}]$ or $[\mathrm{Rh(cot)(S{-}S)}]$, nor any substitution of dithio-ligand. No reaction, in fact, was observed when CO was bubbled through a dichloromethane solution containing $[\mathrm{Rh(CO)_2(S{-}S)}]$. However, the complexes $[\mathrm{Rh(cot)(S{-}S)}]$ and $[\mathrm{Rh(PPh_3)_2(S{-}S)}]$ reacted, under the same conditions, with CO giving respectively $[\mathrm{Rh(CO)_2(S{-}S)}]$ and $[\mathrm{Rh(CO)(PPh_3)(S{-}S)}]$. The latter complexes were also obtained by treating directly $[\{\mathrm{Rh(CO)(PPh_3)Cl}\}_2]$ with ammonium salts of $\mathrm{(H_{11}C_6)_2PS_2^-}$ and $\mathrm{(PhO)_2PS_2^-}$. Triphenylphosphine reacted both with carbonyl and cot complexes giving substitution products of CO or cot. In no case was either formation of five-co-ordinate complexes or cleavage of rhodium–sulphur bonds observed. On the basis of the evidence given by the reactions described, it is possible to infer that the dithio-ligands used have a strong labilizing effect on the *trans*-groups. The high value of the CO-stretching frequencies in the carbonyl complexes could indicate strong back donation of electrons from the metal to the π-symmetry orbitals of the sulphur atoms in accord with a high π-acid character of the dithio-ligands co-ordinated.

It is interesting to note that, in some cases, tertiary phosphines react with dithiophosphato- and dithiophosphinato-complexes by cleavage of metal–sulphur bonds.[5,8,10,11] For example, the complexes $\mathrm{M(S{-}S)_2}$ [$\mathrm{M = Pd}$ or Pt; $\mathrm{S{-}S^- = Ph_2PS_2^-}$ or $\mathrm{(EtO)_2PS_2^-}$] react with tertiary phosphines by stepwise cleavage of metal–sulphur bonds to give four-co-ordinate adducts $[\mathrm{M(S{-}S)_2PR_3}]$ and $[\mathrm{M(S{-}S)(PR_3)_2}]\mathrm{(S{-}S)}$ with unidentate–bidentate and bidentate–ionic dithio-ligand co-ordination respectively.[8-10] Also the nature of the neutral reacting ligand can influence the type of reaction. Ammonia, for example,[5] reacts with $[\mathrm{(Et_2PS_2)Re(CO)_4}]$ to give $[\mathrm{(Et_2PS_2)Re(CO)_4NH_3}]$ by stepwise substitution of the originally bidentate $\mathrm{Et_2PS_2^-}$, whereas weak π-acceptors like $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, and $\mathrm{SbPh_3}$ react differently replacing CO. The strong σ-donor and weak π-acceptor 4-methylpyridine does not react, at room temperature, with $[\mathrm{Rh(CO)_2(S{-}S)}]$ complexes.

By adding to a pentane solution of $[\mathrm{Rh(CO)_2(S{-}S)}]$ an excess of the ligands L–L = 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(diphenylarsino)ethane (dpae), the complexes $[\mathrm{Rh(CO)(L{-}L)_2}]\mathrm{(S{-}S)}$ were obtained. By using other methods only the $[\mathrm{Rh(dppe)_2}]^+$ cation was obtained.[24] As expected, the i.r. spectra of $[\mathrm{Rh(CO)(L{-}L)_2}]\mathrm{(S{-}S)}$ complexes showed a strong ν(CO) band at *ca.* 1 970 cm^{-1}. The CO ligand in these complexes is very labile and is easily lost when the complexes are dissolved in a solvent or when the solid is left for a few hours. On adding $\mathrm{NaBPh_4}$ in methanol to a solution containing the cationic complexes $[\mathrm{Rh(CO)(L{-}L)_2}]\mathrm{(S{-}S)}$ or $[\mathrm{Rh(L{-}L)_2}]\mathrm{(S{-}S)}$ in the same solvent, $[\mathrm{Rh(L{-}L)_2}]\mathrm{BPh_4}$ (L–L = dppe or dpae) salts were obtained, and this confirms that (S–S) is not a co-ordinated ion. The five-co-ordinate CO adduct was not regenerated on passing CO into a solution containing the four-co-ordinate species $[\mathrm{Rh(L{-}L)_2}]\mathrm{(S{-}S)}$. Under these conditions, in fact, $[\mathrm{Rh(CO)_2\{S_2P(C_6H_{11})_2\}}]$ was regenerated from $[\mathrm{Rh(L{-}L)_2}][\mathrm{S_2P(C_6H_{11})_2}]$, probably by means of nucleophilic attack of $\mathrm{(H_{11}C_6)_2PS_2^-}$ on the rhodium centre favoured by the presence of carbon monoxide. The same reaction did not occur when the non-co-ordinated ion was $\mathrm{(PhO)_2PS_2^-}$ due to the lower nucleophilicity of $\mathrm{(PhO)_2PS_2^-}$ with respect to $\mathrm{(H_{11}C_6)_2PS_2^-}$. 2,2′-Bipyridyl (bipy) and 1,2-diphenylthioethane also did not react with $[\mathrm{Rh(CO)_2(S{-}S)}]$ or $[\mathrm{Rh(cot)(S{-}S)}]$ when heated under reflux in heptane. Partial substitution of the co-ordinated $\mathrm{Et_2PS_2^-}$ and formation of $[\mathrm{(Et_2PS_2)Re(CO)_3(L{-}L)}]$ was previously observed[5] in the reaction of $[\mathrm{(Et_2PS_2)Re(CO)_4}]$ with bipy and dppe. Although I have no spectroscopic evidence, it is reasonable to postulate that reactions of $[\mathrm{Rh(CO)_2(S{-}S)}]$ with bidentate ligands give, in a first stage, partial substitution of the co-ordinated dithio-ligand. Attempts to obtain the reaction intermediate by using $[\mathrm{Rh(CO)_2(S{-}S)}]$ and the dithio-ligand in a 1 : 1 molar ratio were unsuccessful.

Reactions with Anionic Ligands.—No reaction was observed when $[\mathrm{RhL_2(S{-}S)}]$ or $[\mathrm{Rh(cot)(S{-}S)}]$ (L = CO or $\mathrm{PPh_3}$) complexes were heated under reflux in acetone in the presence of LiCl or $[\mathrm{Ph_4As}]\mathrm{Cl}$.

Oxidative-addition Reactions.—The complexes $[\mathrm{RhL_2(S{-}S)}]$ and $[\mathrm{Rh(cot)(S{-}S)}]$ are co-ordinatively unsaturated rhodium(I) species and as such might be expected to undergo oxidative-addition reactions. This was confirmed in a detailed study of the reaction of $[\mathrm{Rh(CO)_2(S{-}S)}]$ complexes with iodine, bromine, chlorine, methyl iodide, allyl chloride, and hydrogen. Also some oxidative-addition reactions of $[\mathrm{Rh(PPh_3)_2(S{-}S)}]$ and $[\mathrm{Rh(cot)(S{-}S)}]$ complexes have been studied. Oxidative-addition reactions have been recently extensively studied using as substrate phosphine or carbonylphosphine complexes and it is generally found[25] that the σ-basicity and π-acidity of the ligands, if steric factors are not important,[26] are mainly responsible for the tendency to give oxidative additions and for the stability of the oxidized products. It was therefore of interest to examine the behaviour of complexes containing dithiophosphate and dithiophosphinate ligands.

Treatment of $[\mathrm{Rh(CO)_2(S{-}S)}]$ with iodine or bromine, in pentane, led to an immediate reaction to give a solid product which showed only a single carbon monoxide stretch in the i.r. spectrum at higher wavenumber than the starting rhodium(I) species. The stability of these reaction products appears to be dependent on the nature of the halogen and increases in the order $\mathrm{Cl < Br < I}$;

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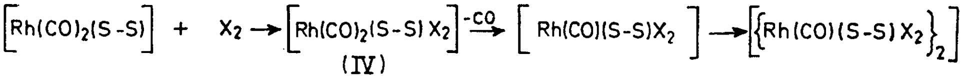
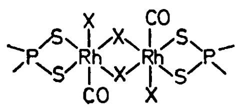
[26] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716; *J.C.S. Dalton*, 1972, 223.

furthermore, rhodium(III) complexes containing $(PhO)_2PS_2^-$ seem to be less stable than those containing $(H_{11}C_6)_2PS_2^-$. Addition products of chlorine soon became dark and it was not possible to isolate them as pure compounds. Molecular-weight and conductivity determinations and analytical data of oxidative-addition products of Br_2 and I_2 indicated a dimeric structure for these products and ruled out a structure having two CO groups in *trans*-positions. I.r. spectra in the 700—400 cm^{-1} region excluded also structures having bridging dithio-ligands.

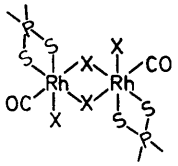
The most probable structures for complexes $[\{Rh(CO)(S\text{-}S)X_2\}_2]$, having C_{2h} and C_i symmetries, are shown below (X = halogen). Unfortunately, chloro-derivatives were not isolated in a pure state and this did not allow us to assign ν(Rh–Cl). ν(Rh–Br) And ν(Rh–I) could not be located since they fell beyond the range covered by the instrument used. A choice between these proposed structures is not feasible; since the CO-stretching vibration appears to be insensitive to changes in the (S–S) ligand, structure (III) could be excluded whereas (I) and (II) seem to be the most probable for these complexes. The formation of these dimeric rhodium(III) complexes may be conceptually rationalized *via* the Scheme. The initial step is assumed to be *trans*-oxidative addition of the halogen to the rhodium(I) substrate followed by loss of carbon monoxide to form a five-co-ordinate rhodium(III) species which then dimerizes to form the observed product. Qualitatively at least, the rate of reaction appears to be dependent on the nature of X_2 and increases in the order I < Br < Cl. Following the reaction, in CH_2Cl_2 solution, by i.r. spectroscopy, I observed that on adding Br_2 or I_2 three bands of medium intensity appeared in the CO-stretching region and, during the reaction, two of these, which belong to complex (IV), became very weak whereas the other increased in intensity. Moreover, by allowing halogens to react with analogous iridium(I) complexes, $[Ir(CO)_2(S\text{-}S)]$, $[Ir(CO)_2(S\text{-}S)X_2]$ complexes, which show two ν(CO) bands, can be isolated.[12] The complexes [Rh(cot)(S–S)] and $[Rh(PPh_3)_2(S\text{-}S)]$ reacted very easily with iodine giving $[Rh(cot)(S\text{-}S)I_2]$ and $[Rh(PPh_3)_2(S\text{-}S)I_2]$. The strength of the Rh–L bond is, therefore, responsible for the course of the reaction.



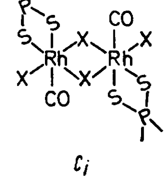
SCHEME



C_{2h}
(I)



C_i
(II)



C_i
(III)

An excess of MeI did not react with $[Rh(CO)_2(S\text{-}S)]$ complexes in CH_2Cl_2 or, at room temperature, in the absence of solvent. However, on heating $[Rh(CO)_2(S\text{-}S)]$ complexes with MeI under reflux for *ca.* 1 h the solution became brown and after evaporation of the solvent and crystallization it was possible to obtain brown solids which, on the basis of elemental analysis, molecular-weight and conductivity measurements, and i.r. spectra can be formulated as [Rh(CO)(S–S)(COMe)I]. Their i.r. spectra, in fact, showed a very strong band at *ca.* 2 080 cm^{-1}, attributed to the stretching frequency of the terminal CO, and a very strong and broad one at 1 710 cm^{-1} indicating the presence of a COMe group and excluding possible attack of the Me group on the sulphur atoms. However, i.r. spectra did not permit the structure of these five-co-ordinate rhodium(III) complexes to be established. It is possible that these reactions proceed through an oxidative addition giving six-co-ordinate rhodium(III) species and these rearrange forming, *via* methyl transfer, five-co-ordinate rhodium(III) acetyl complexes. Some complexes[27] of the type *trans*-$[Rh(CO)L_2X]$ react with MeI giving initially six-co-ordinate rhodium(III) complexes which then isomerize, *via* methyl transfer, to an acetyl complex.

Trimethyloxonium tetrafluoroborate did not react with the $[Rh(CO)_2(S\text{-}S)]$ complexes, in CH_2Cl_2, and this excludes that the reaction of the former complexes with MeI involve a five-co-ordinate intermediate cation, $[Rh(CO)_2(S\text{-}S)Me]I$. The trimethyloxonium cation is known to be an effective alkylating agent of ligands having lone pairs of electrons available, as the sulphur atom in the complexes here reported, and in reactions with co-ordinatively unsaturated complexes can also undergo oxidative additions.[28-30] Allyl chloride reacted with the $[Rh(CO)_2(S\text{-}S)]$ complexes, in CH_2Cl_2, as shown by the appearance of two bands at 2 088 and 1 725 cm^{-1} in the i.r. spectrum. Probably, as in the above reaction with MeI, formation of an acyclic complex occurs but, in

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[27] I. C. Douek and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2604.

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[30] P. R. Branson and M. Green, *J.C.S. Dalton*, 1972, 1303.

this case, an equilibrium is operating. All attempts to isolate the product gave intractable material or the starting substrate. Hydrogen and HCl did not react with the $[Rh(CO)_2(S\text{–}S)]$ complexes.

I.R. Spectra.—The assignment of ν(P–S) in dithiophosphato- and dithiophosphinato-complexes has been discussed by several authors.[31] Recently, due to extensive coupling of these vibrations, no attempt has been made to assign these bands to any specific mode of vibration and only characteristic bands of the co-ordination mode of the dithio-ligand in the ν(P–S) stretching region have been assigned.[8,9,11] An examination of the i.r. spectra of the complexes reported in this work suggests that the presence of certain bands in the 680—500 cm^{-1} region must be considered with caution as diagnostic of bidentate or ionic co-ordination of the dithio-ligand. Rhodium(I) complexes containing bidentate $(PhO)_2PS_2^-$ or $(H_{11}C_6)_2PS_2^-$ show a weak or medium band at *ca.* 600 cm^{-1} and a strong one at *ca.* 550 cm^{-1} characteristic of the mode of co-ordination of the ligand. In corresponding rhodium(III) complexes this last band, in certain instances, is 10—20 cm^{-1} to higher wavenumber. In $[Rh(L\text{–}L)_2](S\text{–}S)$ complexes, characteristic bands of the anionic dithio-ligand can be assigned at *ca.* 630 and 565 cm^{-1}; this assignment was based on a comparison of i.r. spectra of $[Rh(L\text{–}L)_2](S\text{–}S)$ and the analogous $[Rh(L\text{–}L)_2]BPh_4$.

Analytical data (%) and $\tilde{\nu}$(CO) stretching wavenumbers (cm^{-1})

		Found					Calc.					
Complex	Colour	C	H	S	Hal.	*M* [a]	C	H	S	Hal.	*M*	$\tilde{\nu}$(CO) [b]
$[Rh(CO)_2\{S_2P(C_6H_{11})_2\}]$	Red-violet	40·2	5·4	15·3		570	40·0	5·2	15·2		420	2 005vs 2 072vs
$[Rh(CO)_2\{S_2P(OPh)_2\}]$	Orange	38·2	2·3	14·4		512	38·2	2·3	14·5		440	2 015vs 2 078vs
$[Rh(cot)\{S_2P(C_6H_{11})_2\}]$	Red-brown	50·8	7·2	13·5		542	50·7	7·3	13·8		472	
$[Rh(cot)\{S_2P(OPh)_2\}]$	Yellow	48·9	4·7	13·2		563	48·8	4·5	13·0		492	
$[Rh(PPh_3)_2\{S_2P(C_6H_{11})_2\}]$	Red-brown	64·8	5·7	6·9		924	64·8	5·9	7·2		888	
$[Rh(PPh_3)_2\{S_2P(OPh)_2\}]$	Orange	63·5	4·4	7·2		932	63·4	4·4	7·0		908	
$[Rh(CO)(PPh_3)\{S_2P(C_6H_{11})_2\}]$	Orange	57·1	5·8	9·9		674	56·9	5·7	9·8		654	1 972vs
$[Rh(CO)(PPh_3)\{S_2P(OPh)_2\}]$	Orange	55·3	3·9	9·4		693	55·2	3·7	9·5		674	1 980vs
$[Rh(CO)(dppe)_2][S_2P(C_6H_{11})_2]$	Yellow											1 975vs
$[Rh(CO)(dppe)_2][S_2P(OPh)_2]$	Yellow											1 970vs
$[Rh(CO)(dpae)_2][S_2P(C_6H_{11})_2]$	Yellow											1 970vs
$[Rh(CO)(dpae)_2][S_2P(OPh)_2]$	Yellow											1 960s
$[Rh(dppe)_2][S_2P(C_6H_{11})_2]$	Yellow	66·3	6·1	5·6			66·2	6·1	5·5			
$[Rh(dppe)_2][S_2P(OPh)_2]$	Yellow	65·2	4·8	5·6			65·1	4·9	5·4			
$[Rh(dpae)_2][S_2P(C_6H_{11})_2]$	Yellow	57·7	5·3	4·9			57·5	5·3	4·8			
$[Rh(dpae)_2][S_2P(OPh)_2]$	Yellow	56·8	4·5	4·9			56·6	4·3	4·7			
$[Rh(dppe)_2]BPh_4$	Yellow	74·6	5·7				74·9	5·6				
$[Rh(dpae)_2]BPh_4$	Yellow	65·2	5·1				65·4	4·9				
$[\{Rh(CO)[S_2P(C_6H_{11})_2]I_2\}_2]$	Brown	24·3	3·6	9·5	39·5	1 449	24·1	3·4	9·9	39·3	1 292	2 088vs
$[\{Rh(CO)[S_2P(OPh)_2]I_2\}_2]$	Brown	23·2	1·7	9·5	38·4	1 374	23·4	1·5	9·6	38·1	1 332	2 093vs
$[\{Rh(CO)[S_2P(C_6H_{11})_2]Br_2\}_2]$	Yellow	28·4	4·3	11·8	29·2	1 162	28·3	4·0	11·6	28·9	1 104	2 102vs
$[\{Rh(CO)[S_2P(OPh)_2]Br_2\}_2]$	Brown	27·4	1·9	11·1	27·5	1 175	27·3	1·7	11·2	27·9	1 144	2 098vs
$[Rh(cot)\{S_2P(C_6H_{11})_2\}I_2]$	Brown	33·3	4·9	8·5	34·7	817 [c]	33·1	4·7	8·8	34·9	726	
$[Rh(cot)\{S_2P(OPh)_2\}I_2]$	Brown	32·1	2·7	8·8	34·3	762 [c]	32·2	2·9	8·6	34·0	746	
$[Rh(PPh_3)_2\{S_2P(C_6H_{11})_2\}I_2]$	Brown	50·2	4·8	5·6	22·5	1 184 [c]	50·4	4·6	5·6	22·2	1 142	
$[Rh(PPh_3)_2\{S_2P(OPh)_2\}I_2]$	Brown	52·1	3·8	5·6	23·4	1 126 [c]	52·4	3·6	5·8	23·0	1 100	
$[Rh(CO)(COMe)I\{S_2P(C_6H_{11})_2\}]$	Brown	32·2	4·6	11·1	22·7	630 [c]	32·0	4·5	11·4	22·6	562	2 075vs 1 705vs
$Rh(CO)(COMe)I\{S_2P(OPh)_2\}]$	Brown	31·1	2·4	11·1	21·4	645 [c]	30·9	2·2	11·0	21·8	582	2 082vs 1 710vs

[a] Measured osmometrically in benzene. [b] In CH_2Cl_2 solution. [c] In dichloromethane.

EXPERIMENTAL

The complexes $[\{Rh(CO)_2Cl\}_2]$,[32] $[\{Rh(cot)Cl\}_2]$,[33] $[\{Rh(CO)(PPh_3)Cl\}_2]$,[34] and $[Rh(PPh_3)_3Cl]$ [35] were prepared following methods reported in the literature. The salt $[H_4N][S_2P(OPh)_2]$ was prepared as described by Fletcher *et al.*[36] Other chemicals were reagent grade and were used without purification. I.r. spectra were recorded with a Perkin-Elmer 457 spectrometer. Molecular weights were determined with a Knauer vapour-pressure osmometer. A conductivity meter WTW LBR was used for conductivity measurements. Elemental analyses were by Bernhardt, Mulheim, Germany. All reactions were carried out under an atmosphere of oxygen-free nitrogen, although this precaution could probably be dispensed with in most cases. Analytical data and ν(CO) stretching frequencies are reported in the Table.

Dicarbonyl(diphenyl dithiophosphato)rhodium(I),$[Rh(CO)_2\{S_2P(OPh)_2\}]$.—To a solution of $[\{Rh(CO)_2Cl\}_2]$ (0·450 g, 1·15 mmol) in benzene, $[H_4N][S_2P(OPh)_2]$ (0·78 g, 2·6 mmol) was added and the mixture was left at 60 °C for *ca.* 1 h. The resulting yellow solution was evaporated to dryness; extraction with pentane gave, after partial evaporation of

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the solvent, the product as yellow *crystals* (yield 88%). *Dicarbonyl(dicyclohexyldithiophosphinato)rhodium*(I), $[\mathrm{Rh(CO)_2\{S_2P(C_6H_{11})_2\}}]$, was prepared in the same way from $[\{\mathrm{Rh(CO)_2Cl}\}_2]$ (0·450 g, 1·15 mmol) and $[\mathrm{H_4N}][\mathrm{S_2P(C_6H_{11})_2}]$ (0·70 g, 2·5 mmol) and was isolated as red-violet *crystals* (yield 92%).

(Diphenyl dithiophosphato)bis(triphenylphosphine)rhodium(I), $[\mathrm{Rh(PPh_3)_2\{S_2P(OPh)_2\}}]$.—A benzene suspension of $[\mathrm{Rh(PPh_3)_3Cl}]$ (0·350 g, 0·38 mmol) and $[\mathrm{H_4N}][\mathrm{S_2P(OPh)_2}]$ (0·126 g, 0·42 mmol) was heated under reflux, with stirring, for *ca.* 2 h. The solvent was evaporated off and the crude product extracted with pentane. After partial evaporation of the solvent, orange *crystals* were obtained (yield 81%). *(Dicyclohexyldithiophosphinato)bis(triphenylphosphine)rhodium*(I), $[\mathrm{Rh(PPh_3)_2\{S_2P(C_6H_{11})_2\}}]$, was prepared analogously from $[\mathrm{Rh(PPh_3)_3Cl}]$ (0·35 g, 0·38 mmol) and $[\mathrm{H_4N}][\mathrm{S_2P(C_6H_{11})_2}]$ (0·117 g, 0·42 mmol) and obtained as dark-red crystals (yield 84%).

(η-Cyclo-octa-1,5-diene)(diphenyl dithiophosphato)rhodium(I), $[\mathrm{Rh(cot)\{S_2P(OPh)_2\}}]$.—$[\mathrm{H_4N}][\mathrm{S_2P(OPh)_2}]$ (0·48 g, 1·6 mmol) Was added to a solution of $[\{\mathrm{Rh(cot)Cl}\}_2]$ (0·300 g, 0·61 mmol) in benzene and the mixture was heated under reflux, with stirring, for *ca.* 2 h. The solvent was then evaporated and the residue extracted with pentane. After reducing the volume of the pentane solution, yellow *crystals* of the product formed (yield 88%). *(η-Cyclo-octa-1,5-diene)(dicyclohexyldithiophosphinato)rhodium*(I), $[\mathrm{Rh(cot)\{S_2P(C_6H_{11})_2\}}]$, was similarly prepared from $[\{\mathrm{Rh(cot)Cl}\}_2]$ (0·300 g, 0·61 mmol) and $[\mathrm{H_4N}][\mathrm{S_2P(C_6H_{11})_2}]$ (0·42 g, 1·5 mmol) and was obtained as red-brown crystals (yield 86%).

Carbonyl(diphenyl dithiophosphato)triphenylphosphinerhodium(I), $[\mathrm{Rh(CO)(PPh_3)\{S_2P(OPh)_2\}}]$.—*Method* (a). Triphenylphosphine in excess was added to a solution of $[\mathrm{Rh(CO)_2\{S_2P(OPh)_2\}}]$ in pentane and the mixture was stirred for *ca.* 1 h. A yellow *solid* was formed and this was filtered off and washed several times with hot heptane. *Carbonyl(dicyclohexyldithiophosphinato)triphenylphosphinerhodium*(I), $[\mathrm{Rh(CO)(PPh_3)\{S_2P(C_6H_{11})_2\}}]$, was similarly obtained from $[\mathrm{Rh(CO)_2\{S_2P(C_6H_{11})_2\}}]$ and an excess of triphenylphosphine.

Method (b). To a solution of $[\{\mathrm{Rh(CO)(PPh_3)Cl}\}_2]$ (0·250 g, 0·29 mmol) in benzene, $[\mathrm{H_4N}][\mathrm{S_2P(OPh)_2}]$ (0·185 g, 0·62 mmol) was added and the mixture was left at *ca.* 60 °C for *ca.* 2 h. The solvent was then evaporated off. Extraction with diethyl ether gave, after evaporation of the solvent, the product as yellow *crystals* (yield 78%). Using this method, the complex *carbonyl(dicyclohexyldithiophosphinato)triphenylphosphinerhodium*(I) was also prepared.

Absorption of Carbon Monoxide.—When CO was bubbled through a dichloromethane solution containing $[\mathrm{Rh(cot)(S{-}S)}]$, the i.r. spectrum, in the CO-stretching region, showed the same bands found for $[\mathrm{Rh(CO)_2(S{-}S)}]$ complexes. On evaporating the solvent to a small volume and then adding pentane, $[\mathrm{Rh(CO)_2(S{-}S)}]$ complexes were obtained. Using the same method, the complexes $[\mathrm{Rh(CO)(PPh_3)(S{-}S)}]$ were obtained by bubbling CO into a dichloromethane solution containing $[\mathrm{Rh(PPh_3)_2(S{-}S)}]$.

Bis[1,2-bis(diphenylphosphino)ethane]carbonylrhodium(I) *Diphenyl Dithiophosphate*, $[\mathrm{Rh(CO)(dppe)_2}][\mathrm{S_2P(OPh)_2}]$.—Excess of 1,2-bis(diphenylphosphino)ethane was added to a solution containing $[\mathrm{Rh(CO)_2\{S_2P(OPh)_2\}}]$ in pentane and the mixture was left, with vigorous stirring, for *ca.* 30 min. A yellow *solid* was obtained; this was separated by filtration and washed several times with heptane in order to remove the excess of the ligand. *Bis[1,2-bis(diphenylphosphino)ethane]carbonylrhodium*(I) *dicyclohexyldithiophosphinate*, $[\mathrm{Rh(CO)(dppe)_2}][\mathrm{S_2P(C_6H_{11})_2}]$, *bis[1,2-bis(diphenylarsino)ethane]carbonylrhodium*(I) *diphenyl dithiophosphate*, $[\mathrm{Rh(CO)(dpae)_2}][\mathrm{S_2P(OPh)_2}]$, and *bis[1,2-bis(diphenylarsino)ethane]carbonylrhodium*(I) *dicyclohexyldithiophosphinate*, $[\mathrm{Rh(CO)(dpae)_2}][\mathrm{S_2P(C_6H_{11})_2}]$, were obtained similarly. All these complexes lose CO giving the corresponding cationic four-co-ordinate rhodium(I) complexes $[\mathrm{Rh(L{-}L)_2}](\mathrm{S{-}S})$.

Tetraphenylborate Salts.—The complexes $[\mathrm{Rh(L{-}L)_2}]\mathrm{BPh_4}$ ($\mathrm{L{-}L}$ = dppe or dpae) were prepared by adding $\mathrm{NaBPh_4}$ dissolved in methanol to a solution of $[\mathrm{Rh(L{-}L)_2}](\mathrm{S{-}S})$ in the same solvent.

Di-μ-iodo-bis[carbonyl(diphenyl dithiophosphato)iodorhodium(III)], $[\{\mathrm{Rh(CO)[S_2P(OPh)_2]I_2}\}_2]$.—A pentane solution of $\mathrm{I_2}$ was added dropwise to $[\mathrm{Rh(CO)_2\{S_2P(OPh)_2\}}]$ dissolved in the same solvent. The progress of the reaction was followed by i.r. spectroscopy. A brown precipitate was formed. This was separated by filtration and washed several times with pentane and dried. The complexes $[\{\mathrm{Rh(CO)[S_2P(C_6H_{11})_2]I_2}\}_2]$, $[\{\mathrm{Rh(CO)[S_2P(OPh)_2]Br_2}\}_2]$, $[\{\mathrm{Rh(CO)[S_2P(C_6H_{11})_2]Br_2}\}_2]$, $[\mathrm{Rh(cot)\{S_2P(OPh)_2\}I_2}]$, $[\mathrm{Rh(cot)\{S_2P(C_6H_{11})_2\}I_2}]$, $[\mathrm{Rh(PPh_3)_2\{S_2P(OPh)_2\}I_2}]$, and $[\mathrm{Rh(PPh_3)_2\{S_2P(C_6H_{11})_2\}I_2}]$ were prepared and isolated similarly.

Acetylcarbonyl(diphenyl dithiophosphato)iodorhodium(III), $[\mathrm{Rh(CO)(COMe)I\{S_2P(OPh)_2\}}]$.—MeI (3 cm³) and $[\mathrm{Rh(CO)_2\{S_2P(OPh)_2\}}]$ (0·180 g) were heated under reflux with stirring. The progress of the reaction was followed by i.r. spectroscopy in $\mathrm{CH_2Cl_2}$. After *ca.* 2 h the reaction was complete. The solvent was evaporated *in vacuo* and the crude product obtained was crystallized from $\mathrm{CH_2Cl_2}$–pentane to give a brown solid. Using the same procedure with $[\mathrm{Rh(CO)_2\{S_2P(C_6H_{11})_2\}}]$, *acetylcarbonyl(dicyclohexyldithiophosphinato)iodorhodium*(I), $[\mathrm{Rh(CO)(COMe)I\{S_2P(C_6H_{11})_2\}}]$, was obtained as a brown solid.

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