Tricarbonyldichloro(thiocarbonyl)ruthenium(II) and related Complexes: Synthesis and Réactions to give Aminomercaptocarbene and Isocyanide Complexes

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Thiocarbonyl chloride reacts with $[Ru_3(CO)_{12}]$ in refluxing heptane solution giving $[Ru(CO)_3(CS)Cl_2]$ (1). Reaction of (1) with PPh_3 affords $[Ru(CO)_2(CS)Cl_2(PPh_3)]$ (2); the cationic complex $[Ru(CO)_2(CS)(CNC_6H_{11})_2Cl]^+$ is obtained by treating (1) with $C_6H_{11}NC$. A mixture of species has been obtained from the reaction of (1) with the bidentate ligands $Ph_2EC_2H_4EPh_2$ (E = P or As); only $[Ru(Ph_2AsC_2H_4AsPh_2)(CO)_2(CS)Cl][BPh_4]$ has been isolated in a pure form. Isocyanide complexes of the type $[Ru(CNR)(CO)_2Cl_2L]$ (L = CO or PPh_3; R = Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*, or C_6H_{11}) have been obtained from the reaction of (1) and (2) with primary amines NRH_2. The ^1H n.m.r. and i.r. spectra of these species are discussed.

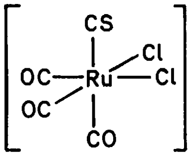
THIOCARBONYL complexes are few in number and are commonly prepared by activation of CS_2 by transition-metal complexes in the presence of an efficient sulphur acceptor such as triphenylphosphine.[1] Unfortunately this synthetic route is not general. Recently, thiocarbonyl chloride has been successfully used as a thiocarbonylating agent in reactions with carbonylmetallate anions[2] and in oxidative-addition reactions when there is a group weakly bound to the metal.[3] By this route, we have succeeded in preparing the first Group 8 metal thiocarbonyl complex containing only terminal CS and CO groups as co-ordinated neutral ligands. In fact, the complex $[Ru(CO)_3(CS)Cl_2]$ can be readily obtained by treating $[Ru_3(CO)_{12}]$ with $CSCl_2$.

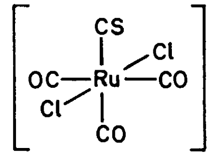
Although much effort has been devoted to the synthesis of thiocarbonyl complexes, comparatively little is known of their reactivity.[2,4-6] On the other hand, there is currently considerable emphasis on developing preparative methods for transition-metal carbene and isocyanide complexes. Recently, Dombek and Angelici[2] found that a co-ordinated thiocarbonyl group is susceptible to nucleophilic attack by amines giving aminomercaptocarbene or isocyanide complexes. We have studied the reactions of $[Ru(CO)_2(CS)Cl_2L]$ (L = CO or PPh_3) complexes with different primary amines in order to ascertain the role played by the metal and the ancillary ligands in the reactivity of the thiocarbonyl ligand. The reactions with secondary amines and other nucleophiles will be discussed in a forthcoming paper.

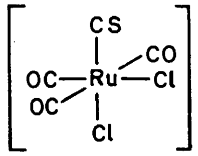
RESULTS AND DISCUSSION

A refluxing solution of $[Ru_3(CO)_{12}]$ in heptane reacted rapidly with $CSCl_2$ to give, in excellent yields, $[Ru(CO)_3(CS)Cl_2]$ (1) as a yellow solid which dissolves in benzene or chlorinated solvents but only slightly in diethyl ether; in air the complex smells of H_2S and must be stored under dinitrogen. Under the same conditions $[Os_3(CO)_{12}]$ failed to give $[Os(CO)_3(CS)Cl_2]$.

The i.r. spectrum of (1) shows, in the ν(CO) stretching region, three bands of which that at highest wavenumber is medium-weak whereas the remaining two are strong; ν(CS) can be assigned at 1 365 cm^{-1}. The far-i.r. spectrum has medium-broad bands at *ca.* 322 and 280 cm^{-1} which are assignable to Ru–Cl stretching modes. All the possible isomers of (1) are shown below and they are consistent with the number of ν(CO) bands observed. However, for isomer (1a) the vibration modes will all be of similar high intensity; in contrast, in the isomers (1b) and (1c), A_{1b} and A_b' respectively would be weak and at higher wavenumbers than the other strong vibration modes. The presence of two ν(Ru–Cl) bands in the far-i.r. spectrum supports the configuration *mer-cis*-(Ic) for complex (1). Moreover, considering the nature of the products obtained in the reactions of (1) with neutral ligands (see below) and the strong *trans* influence of CO and CS groups, it seems unlikely that these groups would be *trans* to each other as in (1b).


(1a) (C_s; $2A'+A''$)


(1b) (C_{2v}; $2A_1+B_1$)


(1c) (C_s; $2A'+A''$)

Complex (1) reacted with PPh_3 giving $[Ru(CO)_2(CS)Cl_2(PPh_3)]$ (2) as a yellow solid, soluble in benzene and chlorinated solvents. The i.r. spectrum has very strong ν(CO) bands at 2 062 and 1 998 cm^{-1} in CH_2Cl_2 and ν(CS) at 1 310 cm^{-1}, while the far-i.r. spectrum has two ν(Ru–Cl) bands at 300 and 275 cm^{-1}. Since the complex is obtained from (1c), it seems reasonable to assign to it the

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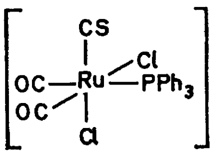
structure (2). Other thiocarbonyl(triphenylphosphine)ruthenium(II) complexes of formula $[Ru(CO)(CS)Cl_2(PPh_3)_2]$ have been described and can exist in different geometrical configurations.[7,8] Cyclohexyl isocyanide reacted with (1) giving the cationic complex $[Ru(CNC_6H_{11})_2(CO)_2(CS)Cl]^+$ which was isolated analytically pure as the tetraphenylborate salt. The i.r. spectrum contains two very strong ν(CO) bands at 2 060 and 2 005 cm^{-1} and a broad ν(CN) band at 2 190 cm^{-1}; the thiocarbonyl stretching frequency occurs at 1 325 cm^{-1}.



(2)

Complex (1) reacted with bidentate ligands $Ph_2EC_2H_4EPh_2$ (E = P or As) to give a mixture of at least two species, which we were not able to characterize fully. Reaction of (1) with $Ph_2AsC_2H_4AsPh_2$ in CH_2Cl_2, followed by solvent removal, gave a solid mixture from which the portion soluble in methanol, by adding $Na[BPh_4]$ in the same solvent, gave $[Ru(Ph_2AsC_2H_4AsPh_2)(CO)_2(CS)Cl][BPh_4]$ (3) as a yellow solid. The residue has an i.r. spectrum similar to that of (3) but it does not conduct in CH_2Cl_2 and its analysis is not consistent with any rational formulation. The compound $Ph_2PC_2H_4PPh_2$ probably reacts in a similar manner, but we were not able to isolate pure products.

The pattern of behaviour exibited by (1) seems to indicate that CS is a better π acceptor than CO and so should be more strongly bound to ruthenium; also, the nature and the spectral properties of the products obtained in the reactions of (1) with neutral ligands confirm structure (1c) for the starting complex. A structure of the type (1b), in the absence of isomerization processes, should give rise to complexes with a *trans*-dicarbonyl configuration. It is interesting to note that the complexes $[M(CO)_5(CS)]$ (M = Cr or W) undergo[2] CO-substitution reactions with PPh_3 or pyridine (py) giving *trans*-$[M(CO)_4(CS)L]$ (L = PPh_3 or py).

Reactions with Amines.—In the last few years the reactions of nucleophilic attack at co-ordinated ligands containing unsaturated carbon atoms such as carbon monoxide, olefins, acetylenes, and isocyanides have been extensively studied and by this route, in some cases, metal carbene complexes have been obtained.[9-11] On the other hand, the electrophilic character of the thiocarbonyl carbon atom in metal complexes has been demonstrated and, in some cases, it appears significantly higher than that of the carbonyl carbon atom.[2,4,12] On the basis of these findings, it is reasonable to extend to thiocarbonyl metal complexes some of the reported nucleophilic reactions at co-ordinated CO in order to compare the reactivity of the two systems.

We studied the reactions of primary amines with complexes (1) and (2). These complexes reacted with primary amines NRH_2 (R = C_6H_{11}, Ph, C_6H_4Me-*p*, or C_6H_4OMe-*p*) giving as final products the isocyanide complexes $[Ru(CNR)(CO)_2Cl_2L]$ (L = CO or PPh_3); these are yellow or yellow-brown solids, non-conducting in benzene solution, stable to air, and soluble in benzene, diethyl ether, and chlorinated solvents. These reactions probably proceed through the formation of labile aminomercaptocarbene species which give the final isocyanide complexes by fast elimination of H_2S. Qualitatively, the reaction of (1) with primary amines was faster than the analogous reaction of complex (2). Mixed carbonylisocyanideruthenium(II) complexes containing only one co-ordinated isocyanide are not known and the possibility of obtaining them by treating a ruthenium carbonyl complex with isocyanide ligand seems unlikely.

When co-ordinated to certain metals isocyanide is susceptible to attack by nucleophilic reagents, such as amines, to give carbene complexes.[13,14] The carbon atom of the co-ordinated isocyanide ligand in $[Ru(CNR)(CO)_2Cl_2L]$ complexes appears to be insufficiently electrophilic to react with amines and diaminocarbene complexes were not isolated. Other neutral isocyanideruthenium(II) complexes of the type $[Ru(CNR)_2Cl_2L_2]$ (L = PMe_2Ph, $PPr^n{}_2Ph$, or $PBut^n{}_2Ph$) do not react with amines.[15]

EXPERIMENTAL

All the amines were purified before use by distillation or sublimation; other chemicals were reagent grade. Infrared spectra were recorded on a Perkin-Elmer model 457 spectrometer using a polystyrene film for calibration. A Perkin-Elmer R 24 A (60 MHz) spectrometer was used to obtain ^1H n.m.r. spectra. Molecular weights were determined with a Knauer vapour-pressure osmometer. A WTW LBR conductivity meter was used for conductivity measurements. All the reactions were carried out under an atmosphere of oxygen-free dinitrogen. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Characteristic stretching frequencies of the prepared complexes are reported in the Table.

Preparations.— *Tricarbonyldichloro(thiocarbonyl)ruthenium*(II). To a refluxing solution of $[Ru_3(CO)_{12}]$ (0.38 g, 0.59 mmol) in heptane (80 cm^3) was added $CSCl_2$ (1 cm^3) with vigorous stirring. A yellow *precipitate* was immediately formed. After *ca.* 2 min this was filtered off under dinitrogen and then washed several times with pentane and

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dried (yield 87%) (Found: C, 16.0; Cl, 23.55; O, 15.9; S, 10.55. $C_4Cl_2O_3RuS$ requires C, 16.0; Cl, 23.65; O, 16.0; S, 10.7%).

Characteristic ^1H n.m.r. and i.r. data

Complex	N.m.r.[a] τ (C_6H_4Me) or τ(C_6H_4OMe)	I.r. (cm^{-1}) ν(CO)[b]	ν(CS)[c]	ν(CN)[b]
$[Ru(CO)_3(CS)Cl_2]$		2 118m, 2 078vs, 2 035vs	1 365vs	
$[Ru(CO)_2(CS)Cl_2(PPh_3)]$		2 062vs, 1 998vs	1 310s	
$[Ru(Ph_2AsC_2H_4AsPh_2)(CO)_2(CS)Cl][BPh_4]$		2 050vs, 1 995vs	1 305s	
$[Ru(CNC_6H_{11})_2(CO)_2(CS)Cl][BPh_4]$		2 062vs, 2 008vs	1 325s	2 198 vs
$[Ru(CNC_6H_{11})(CO)_3Cl_2]$		2 080w, 2 035vs, 1 955vs, br		2 145s
$[Ru(CNPh)(CO)_3Cl_2]$		2 130w, 2 055vs, 1 995vs		2 180s
$[Ru(CNC_6H_4Me\text{-}p)(CO)_3Cl_2]$	7.73 (s)	2 140w, 2 060vs, 1 996vs		2 182m
$[Ru(CNC_6H_{11})(CO)_2Cl_2(PPh_3)]$		2 040vs, 1 975vs		2 160m
$[Ru(CNC_6H_4Me\text{-}p)(CO)_2Cl_2(PPh_3)]$	7.82 (s)	2 062vs, 1 995vs		2 155m
$[Ru(CNC_6H_4OMe\text{-}p)(CO)_2Cl_2(PPh_3)]$	6.30 (s)	2 060vs, 1 992vs		2 152m

[a] In $CDCl_3$ solution. [b] In CH_2Cl_2 solution. [c] In Nujol mull.

Dicarbonyldichloro(thiocarbonyl)(triphenylphosphine)ruthenium(II). To a solution of $[Ru(CO)_3(CS)Cl_2]$ (0.32 g, 1.06 mmol) in dichloromethane (60 cm^3) was added PPh_3 (0.34 g, 1.3 mmol) and the mixture was stirred, at room temperature, for *ca.* 6 h. The red solution was evaporated to dryness and the crude product was washed several times with light petroleum (b.p. 40—70 °C) and chromatographed on a Florisil column, eluting with dichloromethane–diethyl ether (4 : 1). A yellow fraction was eluted which, after evaporation of the solvent at reduced pressure and crystallization from dichloromethane–hexane, gave the *product* as a yellow solid (yield 82%) (Found: C, 47.2; H, 2.85; Cl, 13.3; S, 5.90. $C_{21}H_{15}Cl_2O_2PRuS$ requires C, 47.2; H, 2.85; Cl, 13.25; S, 6.00%).

Dicarbonylchlorobis(cyclohexyl isocyanide)(thiocarbonyl)ruthenium(II) *tetraphenylborate*. To a suspension of $[Ru(CO)_3(CS)Cl_2]$ (0.28 g, 0.93 mmol) in diethyl ether (80 cm^3) was added $C_6H_{11}NC$ (0.21 g, 2 mmol) and the reaction mixture was stirred overnight. The solid was filtered off, washed with diethyl ether, and then extracted with methanol; by adding $Na[BPh_4]$ dissolved in the same solvent, the *product* was obtained as a yellow solid (Found: C, 63.55; H, 5.50; Cl, 4.65; N, 3.60. $C_{41}H_{42}BClN_2O_2RuS$ requires C, 63.6; H, 5.45; Cl, 4.60; N, 3.60%).

[1,2-*Bis(diphenylarsino)ethane*]*dicarbonylchloro(thiocarbonyl)ruthenium*(II) *tetraphenylborate*. To a solution of $[Ru(CO)_3(CS)Cl_2]$ (0.35 g, 1.16 mmol) in dichloromethane (60 cm^3) was added $Ph_2AsC_2H_4AsPh_2$ (0.585 g, 1.2 mmol) and the reaction mixture was stirred, at room temperature, until the ν(CO) bands of the starting material disappeared. The solution became red and removal of solvent left a yellow residue which was washed with diethyl ether. Extraction with methanol gave a yellow solution from which, by adding $Na[BPh_4]$ dissolved in the same solvent, the *product* was obtained as a yellow solid (Found: C, 60.35; H, 4.25; Cl, 3.35; S, 2.95. $C_{53}H_{44}As_2BClO_2RuS$ requires C, 61.1; H, 4.25; Cl, 3.40; S, 3.05%).

Tricarbonyldichloro(phenyl isocyanide)ruthenium(II). To a suspension of $[Ru(CO)_3(CS)Cl_2]$ (0.30 g, 1.0 mmol) in diethyl ether (50 cm^3) was added $NPhH_2$ (1 cm^3) and the reaction mixture was stirred for *ca.* 7 h. The solvent was then removed leaving a yellow residue which was washed with light petroleum (b.p. 40—70 °C) and dried. Extraction with benzene, evaporation of the solvent, and recrystallization from dichloromethane–hexane gave the *product* as a yellow solid (Found: C, 33.35; H, 1.40; Cl, 19.6; N, 3.75. $C_{10}H_5Cl_2NO_3Ru$ requires C, 33.45; H, 1.40; Cl, 19.75; N, 3.90%).

Working-up as above and using the appropriate amine, in diethyl ether (slight excess), the following complexes were obtained as yellow solids: $[Ru(CNC_6H_4Me\text{-}p)(CO)_3Cl_2]$ (Found: C, 35.45; H, 1.90; Cl, 18.85; N, 3.70. $C_{11}H_7Cl_2NO_3Ru$ requires C, 35.4; H, 1.90; Cl, 19.0; N, 3.75%); $[Ru(CNC_6H_{11})(CO)_3Cl_2]$ (Found: C, 32.85; H, 3.05; Cl, 19.35; N, 3.80. $C_{10}H_{11}Cl_2NO_3Ru$ requires C, 32.9; H, 3.05; Cl, 19.4; N, 3.85%); $[Ru(CNC_6H_4Me\text{-}p)(CO)_2Cl_2(PPh_3)]$ (Found: C, 55.4; H, 3.65; Cl, 11.7; N, 2.30. $C_{28}H_{22}Cl_2NO_2PRu$ requires C, 55.35; H, 3.65; Cl, 11.65; N, 2.30%); $[Ru(CNC_6H_4OMe\text{-}p)(CO)_2Cl_2(PPh_3)]$ (Found: C, 53.9; H, 3.50; Cl, 11.3; N, 2.30. $C_{28}H_{22}Cl_2NO_3PRu$ requires C, 53.95; H, 3.55; Cl, 11.35; N, 2.25%); and $[Ru(CNC_6H_{11})(CO)_2Cl_2(PPh_3)]$ (Found: C, 54.15; H, 4.35; Cl, 11.8; N, 2.30. $C_{27}H_{26}Cl_2NO_2PRu$ requires C, 54.1; H, 4.35; Cl, 11.85; N, 2.35%).

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