tive species could be a di- or trisulfato substitution product.

All the green species have the same high absorption band at around 360 nm (which is not found in hexaaquomolybdenum(III)[5-8]). This band is probably characteristic of the di-μ-ol-molybdenum(III) structure. The two peaks of the aquo ion at 571 and 624 nm are shifted toward the red in the chloro and sulfato species in agreement with the position of these ligands in the spectrochemical series.

The similarities of the spectra in H_2SO_4 and HCl misled Hartmann and Schmidt to interpret them as belonging to the same species (see ref 2, Figures 7 and 9). One can observe several differences between these spectra, some of which were noted by the authors themselves, such as the disappearance of the peak at 580 nm in 2 *M* HCl. These and other spectral differences can be understood by considering the change in the relative concentrations of the different species which compose these solutions.

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Registry No. I, 51567-86-3.

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New Route to Thiocarbonyl Complexes of Iridium(III) and Rhodium(III)

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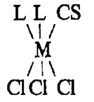
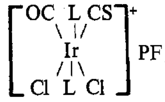
The recent report[1] of the syntheses of thiocarbonyl complexes of chromium, molybdenum, and tungsten utilizing thiophosgene ($CSCl_2$) as thiocarbonylating agent prompts us to report our studies of reactions of thiophosgene with some complexes of group VIII metals. Ethyl (or methyl) thiochloroformate has been used to synthesize the thiocarbonyl cation $C_5H_5Fe(CO)_2CS^+$.[2] Reactions of metal complexes with carbon disulfide and triphenylphosphine have been previously employed to synthesize thiocarbonyl complexes of rhodium, ruthenium, and iridium.[3-5]

We now report the facile and relatively high yield syntheses of thiocarbonyl complexes of iridium(III) and rhodium(III) by the three-fragment oxidative addition of thiophosgene to $Ir(PPh_3)_2(N_2)Cl$, $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$, and $Rh(PPh_3)_3Cl$. The addition of the three fragments of thiophosgene and the loss of the labile ligands dinitrogen, acetonitrile, and triphenylphosphine lead to the formation of the six-coordinated products **1A**, **2**, and **1B**. The proposed structures for the thiocarbonyl complexes are depicted.



1A, M = Ir; L = PPh_3
1B, M = Rh; L = PPh_3



2, L = PPh_3

The CS stretching frequencies in the mull spectra of the iridium(III) complexes (at 1368 cm^{-1} for **1A** and at 1409 cm^{-1} for **2**) are increased from 1332 cm^{-1} for $Ir(PPh_3)_2(CS)Cl$ due to decreased back-donation from the Ir(III) as compared to Ir(I). The ν(CS) at 1409 cm^{-1} for **2** is at a higher frequency than the ν(CS) observed in the 1263-1381-cm^{-1} region for cationic five-coordinated iridium(I) thiocarbonyl complexes $[Ir(CO)_2(CS)(PR_3)_2]^+$ where R = phenyl or cyclohexyl.[6] The ν(CS) at 1409 cm^{-1} for $[Ir(PPh_3)_2(CO)(CS)Cl_2]^+$ is the highest frequency yet reported for metal–thiocarbonyl complexes. This high frequency reflects the small amount of back-donation from Ir(III) to CS in the cationic complex. The ν(CO) at 2127 cm^{-1} for **2** is also much higher than the ν(CO) in the 2036- to 2066-cm^{-1} region observed for cationic iridium(I) complexes $[Ir(CO)_2(CS)(PR_3)_2]^+$.[6] The significantly higher frequency for the ν(CO) band at 2127 cm^{-1} in $[Ir(PPh_3)_2(CO)(CS)Cl_2]^+$ than in $[Ir(PPh_3)_2(CO)_2Cl_2]^+$ [7] (at 2050 and 2007 cm^{-1}) is also indicative of the greater effectiveness of the thiocarbonyl group compared to the carbonyl group in removing electron density from the central metal. The rhodium(III) compound **1B** similarly has ν(CS) at 1364 cm^{-1} increased from 1299 cm^{-1} for $Rh(PPh_3)_2(CS)Cl$. Compound **1B** can be prepared by the oxidative addition reaction of chlorine and $Rh(PPh_3)_2(CS)Cl$.[8] The proposed structures for **1A**, **1B**, and **2** are suggested from the dependence of the metal-chlorine stretching frequencies on ligands trans to the chlorine ligand.[9] The Cl ligand trans to CO or CS gives rise to ν(Ir–Cl) in the 290-310-cm^{-1} region, whereas Cl trans to PPh_3 gives ν(Ir–Cl) in the 270-280-cm^{-1} region.

The reactions of thiophosgene with other group VIII metal complexes were explored briefly. Reactions of $CSCl_2$ with $[Rh(CO)_2Cl]_2$ and with $[Rh(CO)_2(PPh_3)_2Cl]_2$ in benzene gave immediately dark-brown solids which had ν(CO) in the 2090-2100-cm^{-1} region but no strong absorption in the 1000-1420-cm^{-1} region other than bands due to triphenylphosphine. The reaction of $CSCl_2$ with $Ir(CO)(PPh_3)_2Cl$ in benzene gave a red-brown Ir(III) complex with ir frequencies at 1358 (vs), 2014 (s), and 2065 (c) cm^{-1}. Similarly, the reaction of $CSCl_2$ with $Rh(CO)(PPh_3)_2Cl$ in benzene or dichloromethane gave red-brown solids with ir frequencies at 1364 and 2085 cm^{-1} expected for a Rh(III) complex with CO and CS ligands. The rhodium(III) complex additionally had bands at 1102 (m) and 1112 (sh) cm^{-1} which may be ascribed to π-CS_2 coordination. Attempts to recrystallize these products from various solvents gave solids which had the ν(CS) band at 1358 and 1364 cm^{-1} diminished in intensity, and further characterization of these compounds was not pursued.

The reaction of $CSCl_2$ and $Pt(PPh_3)_3$ in benzene gave two isolable products: one which was brown and had ir bands characteristic of the PPh_3 ligand and a second lighter brown solid which in addition to PPh_3 bands had a ν(CS) band at

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1400 cm^{-1} and a weaker band at 2100 cm^{-1}. The reaction of $CSCl_2$ and $Pt(PPh_3)_2(C_2H_4)$ gave a green solid with bands due to the PPh_3 ligand and a yellow solid which had a strong band at 1400 cm^{-1} and a weak band at 2105 cm^{-1}. The reaction of $CSCl_2$ with $Pt(PPh_3)_2(C_2H_4)$ in the presence of halide acceptor BCl_3 in benzene gave a brown solid with a very intense ir band at 1400 cm^{-1} and a weaker band at 2100 cm^{-1}. This latter band which may be due to Pt-H stretching arising from hydrolysis of a Pt(II)-CS complex was diminished in intensity when stringent procedures were adopted to exclude water and oxygen, but a product completely free from the 2100-cm^{-1} band could not be prepared. We suggest that the product with the intense band at 1400 cm^{-1} is $[Pt(PPh_3)_2(CS)Cl]^+$, but attempts to recrystallize this compound in various solvents and in the presence of PF_6^- and BPh_4^- resulted in the disappearance of the ν(CS) band at 1400 cm^{-1} and evolution of hydrogen sulfide. Cationic platinum(II) carbonyl complexes are highly susceptible to nucleophilic attack at CO,[10] and the CS ligand is more readily attacked by nucleophiles than the CO ligand.[1,11]

Experimental Section

Thiophosgene from Aldrich Chemical Co. was used without further purification. Previously reported procedures were used to prepare $Ir(PPh_3)_2(N_2)Cl$, $Ir(CO)(PPh_3)_2Cl$, $Rh(PPh_3)_3Cl$, $[Rh(CO)_2Cl]_2$, $[Rh(CO)_2Cl]_2$, $[Rh(CO)_2(PPh_3)Cl]_2$, $Rh(PPh_3)_2(CO)Cl$, $Pt(PPh_3)_3$, $Pt(PPh_3)_2(C_2H_4)_2$, and $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$.[12] Benzene was distilled from P_4O_{10} and stored over molecular sieves. All reactions were conducted in a nitrogen atmosphere. Infrared spectra were obtained in Nujol and hexachlorobutadiene (hcb) mulls with a Perkin-Elmer Model 621 spectrophotometer. Only frequencies other than those due to the PPh_3 ligand are reported herein, and frequencies reported herein are for Nujol mulls except in the 1370-cm^{-1} region where hcb mulls were employed. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

Trichlorobis(triphenylphosphine)thiocarbonyliridium(III), $[Ir(PPh_3)_2(CS)Cl_3]$. Thiophosgene (0.18 ml, 2.3 mmol) was added to 720 mg (0.93 mmol) of $Ir(PPh_3)_2(N_2)Cl$ in 30 ml of benzene. The tan solid which formed was recrystallized twice from dichloromethane–ethanol to give 680 mg (80%) of pale-yellow crystals, mp 193° dec. *Anal.* Calcd for $IrC_{37}H_{36}Cl_3P_2S{\cdot}CH_2Cl_2$: C, 47.93; H, 3.38; Cl, 18.6; S, 3.36. Found: C, 47.45; H, 3.52; Cl, 20.5; S, 3.45. ν(CS) 1368 (hcb) (vs); ν(Ir–Cl) 308 (w), 273 (w), 282 (sh) cm^{-1}.

Dichlorobis(triphenylphosphine)thiocarbonylcarbonyliridium(III) Hexafluorophosphate, $[Ir(PPh_3)_2(CO)(CS)Cl_2]PF_6$. A solution of 668 mg (0.72 mmol) of $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$ and 0.08 ml (1.0 mmol) of thiophosgene in 20 ml of dichloromethane was stirred for 20 min. The solvent was evaporated under reduced pressure to 5 ml and 40 ml of diethyl ether was added to precipitate 630 mg of pale-white solid. The product was recrystallized from dichloromethane–diethyl ether to give 480 mg (67%) of bone-white crystals, mp 135° dec: ν(CS) 1409 (vs); ν(CO) 2127 (s); $\nu(PF_6)$ 842 (vs); ν(Ir–Cl) 305 (w), 295 (w) cm^{-1}. *Anal.* Calcd for $IrC_{38}H_{30}OCl_2F_6P_3S$: C, 45.46; H, 3.01; Cl, 3.19; S, 7.07. Found: C, 45.61; H, 2.98; Cl, 3.62; S, 6.77.

Trichlorobis(triphenylphosphine)thiocarbonylrhodium(III), $[Rh(PPh_3)_2(CS)Cl_3]$. Thiophosgene (0.08 ml, 1.0 mmol) was added to 463 mg (0.50 mmol) of $Rh(PPh_3)_3Cl$ in 15 ml of benzene. The reaction mixture was stirred at room temperature for 1 hr. The red-brown solid (252 mg, 65%) was recrystallized from dichloromethane–benzene and washed with diethyl ether, mp 141° dec: ν(CS) 1364 (hcb) (vs) (lit. value 1362 cm^{-1} (C_6H_6))[8]; ν(Rh–Cl) 295 (w), 282 (w), 270 (w) cm^{-1}. *Anal.* Calcd for $RhC_{37}H_{30}Cl_3P_2S$: C, 57.14; H, 3.88; Cl, 13.68; S, 4.11. Found: C, 56.92; H, 3.63; Cl, 13.50; S, 4.98.

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Registry No. **1A**, 51540-60-4; **2**, 51540-62-6; **1B**, 51607-40-0; $CSCl_2$, 463-71-8; $Ir(PPh_3)_2(N_2)Cl$, 15695-36-0; $[Ir(PPh_3)_2(CO)(CH_3CN)]PF_6$, 51540-63-7; $Rh(PPh_3)_3Cl$, 14694-95-2.

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Convenient Synthesis of Tellurium Chloride Pentafluoride

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Tellurium chloride pentafluoride was first prepared in low yield by Fraser, Peacock, and Watkins[1] by the reaction of fluorine and tellurium tetrachloride. More recently[2] $TeClF_5$ was produced as one of the products of the reaction of chlorine monofluoride and bis(perfluoroethyl) telluride and ditelluride. We wish to report the convenient synthesis of $TeClF_5$ in good yield, by the reaction of chlorine monofluoride with TeF_4, $TeCl_4$, or TeO_2.

Experimental Section

Apparatus and Materials. Techniques and apparatus are described in ref 3. Te, TeF_6, $TeCl_4$, TeO_2, and ClF were used without further purification. Tellurium tetrafluoride was prepared by the reaction of tellurium hexafluoride and tellurium metal[4] in a Monel vessel at 160–170° for 3 days. Crystalline tellurium tetrafluoride product was sublimed into the cooled top of the Monel reactor.

Tellurium Tetrafluoride and Chlorine Monofluoride. Chlorine monofluoride (7.9 mmol) was condensed in small aliquots onto tellurium tetrafluoride (3.54 mmol) in a Kel-F vessel. The reactants were warmed to room temperature after each addition and finally left overnight. Solid TeF_4 was consumed; the reaction product was a yellow liquid. Materials volatile at −78° were condensed from the reaction vessel for about 1 min and shown to contain ClF, $TeClF_5$, SiF_4, and fluorocarbons. The involatile fraction was clear liquid $TeClF_5$ (2.76 mmol).

Tellurium Tetrachloride and Chlorine Monofluoride. In a typical experiment chlorine monofluoride (31 mmol) was condensed in small aliquots onto $TeCl_4$ (5.5 mmol). The reactants were warmed to room temperature after each addition. Liquid ClF reacted with $TeCl_4$ with bubbling. The yellow liquid product consisted of a mixture of $TeClF_5$, chlorine, and impurities such as SiF_4. The ^{19}F nmr[1] of the product showed that the only tellurium species present was $TeClF_5$. Relatively pure material was obtained by condensing out about two-thirds by volume of the liquid product. The last traces of chlorine were removed by agitation with mercury giving 4.6 mmol of clear colorless liquid $TeClF_5$. The volatile products of reactions, in which less than a stoichiometric amount of ClF had been added, were examined by infrared and ^{19}F nmr. Only $TeClF_5$ was detected by these techniques, although chlorine was also present. X-Ray powder photographs of the solid showed the presence of TeF_4, but its mass spectrum showed peaks attributable to both $TeCl_4$ and TeF_4 molecular ions and fragments.

Reaction of Tellurium Dioxide and Chlorine Monofluoride. In a typical reaction chlorine monofluoride (39.5 mmol) was condensed in small aliquots onto TeO_2 (3.36 mmoles). After the first additions a deep red liquid (probably ClO_2) and oxygen were formed. The

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