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Preliminary communication

DITHIOCARBENE COMPLEXES DERIVED FROM CS_2-BRIDGED DINUCLEAR COMPLEXES

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Summary

Stable dithiocarbene complexes $\{Cp(CO)_2FeC(SCH_3)[SML_n]\}^+$ (ML_n = $Re(CO)_5$, $Fe(CO)_2Cp$) are formed when monodentate ferrodithiocarboxylate—metal complexes $Cp(CO)_2FeC(=S)[SM'L_n]$ ($Cp = \eta^5$-C_5H_5) are treated with $CH_3SO_3CF_3$.

Although transition-metal complexes containing the dithiocarbene ligand $[C(SR)_2]$ have been isolated [1—5], it was only recently [6] that a neutral carbene complex, $W(CO)_5\{C(SCH_3)[SFe(CO)_2Cp]\}$ was obtained in which the dithiocarbene unit is bridging between two metal atoms; this complex was made from $[W(CO)_5C(=S)(SCH_3)]^-$ and $[CpFe(CO)_2(THF)]^+$. Efforts to prepare other examples of such complexes both from different metal cations or from Group 4A metal halides proved unsuccessful [6].

One route used to prepare dithiocarbene complexes involved the alkylation of the thione sulfur atom in dithioesters complexes $L_nMC(=S)(SR)$ by $CH_3SO_3CF_3$, and it seemed likely that unidentate CS_2-bridged dinuclear complexes might act similarly. We now describe such reactions, which provide cationic metallodithiocarbene—metal complexes $\{Cp(CO)_2FeC(SCH_3)$-$[SML_n]\}^+$ [ML_n = $Re(CO)_5$, $Fe(CO)_2Cp$] starting from the iron dithioesters $Cp(CO)_2FeC(=S)[SML_n]$.

We recently found [7] that treatment of a tetrahydrofuran solution of the carbon disulfide adduct of the dicarbonyl(cyclopentadienyl) ferrate $[Cp(CO)_2FeCS_2]^-$, with $Re(CO)_5Br$ at —78°C for 40 min gives the dithioester derivative $Cp(CO)_2FeC(=S)[SRe(CO)_5]$ (I), which is contaminated by small variable amounts of the chelato complex $Cp(CO)_2FeCS_2Re(CO)_4$ (II) [8]. Complex I is readily methylated at room temperature in CH_2Cl_2 with methyltrifluoromethane sulfonate to give the dithiocarbene cation $\{Cp(CO)_2FeC(SCH_3)[SRe(CO)_5]\}^+$, which after anion exchanges gives the

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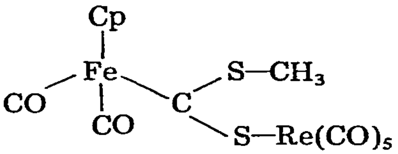
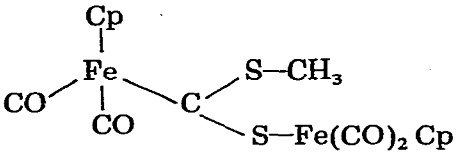
yellow PF_6^- salt III in an almost quantitative yield (ν(CO) (CH_2Cl_2): 2142m, 2085w, 2040 vs, 2010s cm^{-1} ; ^{1}H NMR (acetone-d_6)τ 6.51 (CH_3), 4.43 (C_5H_5)). There is no splitting of these ^{1}H singlets upon cooling an acetone-d_6 solution of III to −60°C, indicating that only one isomer is present.



(III)



(IV)

Such dithiocarbene formation could also be expected from the CS_2-bridged complex $[CpFe(CO)_2]_2CS_2$, in which the ferrodithiocarboxylate acts as a monohapto-S ligand [9]. Its reaction in CH_2Cl_2 with $CH_3SO_3CF_3$ does indeed, immediately produce IV, which was isolated as the PF_6^- salt (60%). (ν(CO) (CH_2Cl_2): 2047s, 2041s, 2003s cm^{-1} ; ^{1}H NMR (acetone-d_6):τ 6.65(CH_3), 4.49 (C_5H_5), 4.57 (C_5H_5); ^{13}C NMR (acetone-d_6): ppm 315.4 (carbene C), 206.3 (CO), 89.0 (C_5H_5), 88.3 (C_5H_5), 29.3 (SCH_3)). Analytical data and conductivity measurements support the proposed structures for both III and IV dithiocarbene complexes.

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