*Inorganica Chimica Acta*, 64 (1982) L39–L41
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# Interaction of Metal–Carbamoyl Derivatives with Organic Isothiocyanates

LUIGI BUSETTO and ANTONIO PALAZZI

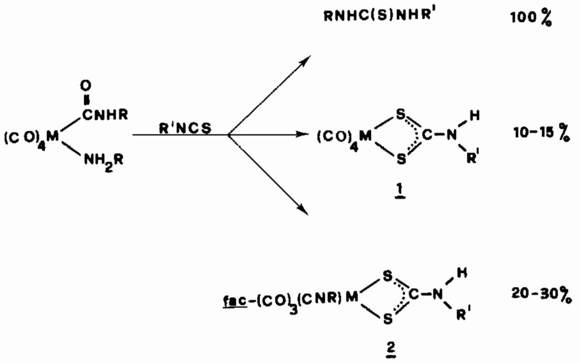
*Istituto di Tecnologie Chimiche Speciali, Facoltà di Chimica Industriale dell'Università, Bologna, Italy*

Received July 29, 1981

Unlike $CS_2$, which provides good yields of $M(CO)_4S_2CNHCH_3$ on treatment with $M(CO)_4(NH_2CH_3)(CONHCH_3)$ [1] (M = Mn, Re):

$$M(CO)_4(NH_2CH_3)CONHCH_3 + CS_2 \rightarrow M(CO)_4S_2CNHCH_3 + CO + NH_2CH_3 \qquad (1)$$

moderate yields of products arising from desulfurization and sulfur incorporation are obtained from $M(CO)_4(NH_2R)CONHR$ and R'NCS:



M = Mn; R = $CH_3$, $C_6H_{11}$; R' = $CH_3$, $C_6H_5$, $C_6H_{11}$, $CH_2C_6H_5$; M = Re; R = $CH_3$; R' = $CH_3$

In fact by reacting the carbamoyl derivative $Mn(CO)_4(NH_2CH_3)CONHCH_3$ with excess of $CH_3NCS$ in tetrahydrofuran at room temperature for several hours, we have obtained the stoichiometric amount of the disubstituted N,N-methylthiourea, $CH_3NHC(S)NHCH_3$, the dithiocarbamate complex $Mn(CO)_4S_2CNHCH_3$, (*1a*) in about 10% yield and the methyl isocyanide derivative *fac*-$Mn(CO)_3(CNCH_3)S_2CNHCH_3$, (*2a*), in about 25% yield. These two complexes have been recently obtained by Knox *et al.* [2] as unique products from the reaction between $[Mn(CO)_5]^-$ and $CH_3NCS$. Their formation has been explained in terms of a sulfur abstraction from methylisothiocyanate [3, 4] which leads to the formation of an intermediate anion $[Mn(CO)_4S_2CNCH_3]^-$ which, in agreement with the high nucleophilicity explicated by the nitrogen of the dithiocarbonimidate ligand [5], abstracts a proton from some source to give the corresponding dithiocarbamate complex (*1a*). The consequent evolution of methylisocyanide accounts for the isolation of the isocyanide derivative (*2a*).

Despite the striking similarities between our reaction products and those obtained from carbonyl anions and isothiocyanates, the mechanisms involved must be substantially different. These differences are well evidenced by the reaction scheme (2) which shows that the carbamoyl derivatives $M(CO)_4(NH_2CH_3)CONHCH_3$ react with R'NCS to produce together with N,N'-disubstituted thioureas the dithiocarbamate complexes (*1* and *2*) in which the dithioligand bears the alkyl or aryl group of the incoming R'NCS. In addition, the isocyanide coordinated in type *2* complexes must not be formed by simple sulfur abstraction from the R'NCS but more likely arises from the coordinated –CONHR group of the starting derivatives.

As an example, by reacting $Mn(CO)_4(NH_2CH_3)CONHCH_3$ and $C_6H_5NCS$ in benzene at room temperature, the thiourea $CH_3NHC(S)NHC_6H_5$ is quantitatively recovered together with $Mn(CO)_4S_2CNHC_6H_5$, (*1b*), and the isocyanide $Mn(CO)_3(CNCH_3)S_2CNHC_6H_5$ complex, (*2b*), which have been separated by column chromatography.

As shown in Table I, the i.r. spectrum of $Mn(CO)_3(CNCH_3)S_2CNHC_6H_5$ exhibits strong CO absorptions at 2020, 1950 and 1922 $cm^{-1}$ (consistent with a *fac*-$Mn(CO)_3$ arrangement), and a medium-strong band at 2200 $cm^{-1}$ attributable to the $\nu$CN of the coordinated $CNCH_3$ group. However the $^1H$ n.m.r. spectrum shows a singlet at $\tau$ 6.40 and a broad signal in the range $\tau$ 2.1–2.9, attributable to the $CH_3$ and $NHC_6H_5$ groups respectively. The mass spectrum of the isocyanide derivative reveals, together with the parent ion, signals due to the successive loss of the three CO and the base peak at 223 m/e corresponding to $[MnS_2CNHC_6H_5]^+$, which is also present as the most intense peak in the mass spectrum of $Mn(CO)_4S_2CNHC_6H_5$.

Additional evidence of this unusual reaction path comes from the reaction of $Mn(CO)_4(NH_2C_6H_{11})CONHC_6H_{11}$ with $CH_3NCS$ and from the reaction of $Mn(CO)_4(NH_2CH_3)CONHCH_3$ with $C_6H_{11}NCS$ which form (*1a*) and (*2e*) or (*1c*) and (*2c*) respectively. The different natures of the type *2* complexes *fac*-$Mn(CO)_3(CNCH_3)(S_2CNHC_6H_{11})$, (*2c*), and *fac*-$Mn(CO)_3(CNC_6H_{11})S_2CNHCH_3$, (*2e*), readily detectable by $^1H$ n.m.r. analysis (see Table I), is an indication that the coordinated isocyanide does not arise from a direct metal–isothiocyanate interaction. The latter would afford $M(CO)_3(CNR')S_2CNHR'$ complexes resulting from a disproportion of the heterocumulene R'NCS, as proposed in all the cases in which

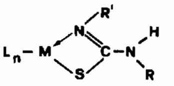
TABLE 1. Physical and Spectroscopic Data for the New Compounds.

| Compounds | | Colour | M.p. (°C) | I.r. bands (cm$^{-1}$)$^a$ | | $^1$H N.m.r. ($\tau$)$^b$ |
|---|---|---|---|---|---|---|
| | | | | $\nu$(C≡N) | $\nu$(C≡O) | |
| (*1a*) | $Mn(CO)_4S_2CN(H)CH_3$$^c$ | yellow | 81–82<br>(dec.) | | 2087m, 2012vs, 1998s<br>1958vs | 2.98(br, 1H), 6.90<br>(d, J 5 Hz, 3H) |
| (*1b*) | $Mn(CO)_4S_2CN(H)C_6H_5$$^c$ | yellow | 146<br>(dec.) | | 2088m, 2010vs, 1995s<br>1960vs | 2.60 (br) |
| (*1c*) | $Mn(CO)_4S_2CN(H)C_6H_{11}$ | brown | 132<br>(dec.) | | 2082m, 2003vs, 1995s<br>1945vs | 3.2 (br, 1H), 7.7–8.8<br>(br, 11H) |
| (*1d*) | $Mn(CO)_4S_2CN(H)CH_2C_6H_5$$^d$ | yellow | | | 2098m, 2032vs, 2005s<br>1973vs | |
| (*2a*) | $Mn(CO)_3(CNCH_3)S_2CN(H)CH_3$$^c$ | yellow | 125<br>(dec.) | 2190m | 2030vs, 1966vs, 1932vs | 3.0(br, 1H) 6.33 (s, 3H),<br>6.9(d, J5Hz, 3H) |
| (*2b*) | $Mn(CO)_3(CNCH_3)S_2CN(H)C_6H_5$ | yellow | 145<br>(dec.) | 2200m | 2020vs, 1950vs, 1922vs | 1.5(br, 1H), 2.1–2.9<br>(br, 5H), 6.4(s, 3H) |
| (*2c*) | $Mn(CO)_3(CNCH_3)S_2CN(H)C_6H_{11}$ | yellow | 138–140<br>(dec.) | 2198m | 2025vs, 1958vs, 1925vs | 3.1(br, 1H), 6.4(s, 3H)<br>7.6–8.8(br, 11H) |
| (*2d*) | $Mn(CO)_3(CNCH_3)S_2CN(H)CH_2C_6H_5$ | yellow | 125–127<br>(dec.) | 2200m | 2028vs, 1960vs, 1930vs | 2.1(br, 1H), 2.26(br, 5H)<br>5.46(br, 2H), 6.61(s, 3H) |
| (*2e*) | $Mn(CO)_3(CNC_6H_{11})S_2CN(H)CH_3$ | yellow | 115–118<br>(dec.) | 2160m | 2020vs, 1968vs, 1925vs | 3.3(br, 1H), 7.0(d, J 5Hz,<br>3H), 7.7–8.8(br, 11H) |
| | $Re(CO)_4S_2CN(H)CH_3$$^c$ | white | 78–79<br>(dec.) | | 2013m, 2005vs, 1988s<br>1948vs | 3.35(br, 1H), 7.05(d,<br>J5Hz, 3H) |
| | $Re(CO)_3(CNCH_3)S_2CN(H)CH_3$$^c$ | pale-yellow | 108<br>(dec.) | 2200m | 2022vs, 1950vs, 1918vs | 3.2(br, 1H), 6.44(s, 3H)<br>6.94(d, J5Hz, 3H) |

[a] In $CCl_4$. [b] In $CDCl_3$, $\tau$ in ppm, TMS as internal standard. [c] See references 1 and 2. [d] Obtained in impure form.

similar reactions have been studied and mixed isocyanide–dithiocarbamate complexes such as $Pt(PPh_3)(CNPh)(S_2CNPh)$ [4], $[Rh[X\text{-}C(Z)\text{-}Y](CNR)(S_2CNR)(PPh_3)$, ([X-C(Z)-Y] = an unsaturated hetero-allylic chelate group [6]), and $M(CO)_3CNR)S_2CNHR$ [2] have been obtained. On the other hand, the quantitative formation of N,N'-disubstituted thioureas which probably arise from the reaction of the amine and the R'NCS, excludes the possibility that the coordinated $NH_2R$ group is the source of the isocyanide complex.

Although we cannot at present develop a complete explanation for the reactions studied, the results obtained may substantiate the idea of a nucleophilic attack on the electrophilic carbon atom of the isothiocyanate by the nitrogen of the coordinated CONHR group. Thus by analogy with the known reactivity of $CS_2$ toward the same carbamoyl derivatives [1], formation of a probable intermediate of the type:



may occur, which by interaction with a second R'NCS molecule ejects the isocyanide CNR group to afford complexes of the type $M(CO)_4S_2CNHR'$ which in turn are the source of $M(CO)_3(CNR)S_2CNHR'$ complexes on carbon monoxide substitution by the formed isocyanide.

## Experimental

The carbamoyl derivatives $M(CO)_4(NH_2R)(CONHR)$, M = Mn, Re, were prepared according to literature methods [7, 8]. I.r. and $^1H$ n.m.r. spectra were recorded on Perkin-Elmer 180 and on JEOL C-60 ML or on Varian XL-100 spectrophotometers respectively. Mass spectra were recorded on a JEOL JMS–D100 working at 75 eV.

All the reactions were carried out in inert atmosphere and the products reported in scheme 2 have been fully characterized by elemental analysis and spectroscopic properties.

General preparative procedures are described as follows: One mmol of $M(CO)_4(NH_2R)(CONHR)$ dissolved in 100 ml of tetrahydrofuran was treated at room temperature with a tenfold excess of R'NCS. After stirring for several hours the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was slurried in $CH_2Cl_2$ and placed on a 2 × 30 column of silica gel. Elution with a 2:1 mixture of $CH_2Cl_2$–hexane gave the products in the following sequence: thiourea, tetracarbonyldithiocarbamate complex, and tricarbonylisocyanide-dithiocarbamate complex. The complexes were recrystallized from $CH_2Cl_2$ by addition of hexane.

*Anal.*: $[Mn(CO)_3(CNCH_3)S_2CN(H)C_6H_5]$: Found: C, 41.2; H, 2.7; N, 8.1%; $C_{12}H_9N_2O_3MnS_2$ requires: C, 41.38; H, 2.60; N, 8.04%. $[Mn(CO)_3(CNCH_3)S_2CN(H)C_6H_{11}]$: Found: C, 40.5; H, 4.3; N, 7.8%; $C_{12}H_{15}N_2O_3MnS_2$ requires: C, 40.68; H, 4.27; N, 7.91%. $[Mn(CO)_3(CNC_6H_{11})S_2CN(H)CH_3]$: Found: C, 40.6; H, 4.1; N, 7.8%; $C_{12}H_{15}N_2O_3MnS_2$ requires: C, 40.68; H, 4.27; N, 7.91%. $[Mn(CO)_3(CNCH_3)S_2CN(H)CH_2C_6H_5]$: Found: C, 43.2; H, 3.1; N, 7.6%; $C_{13}H_{11}N_2O_3MnS_2$ requires: C, 43.09; H, 3.06; N, 7.73%.

## Acknowledgement

The National Council of Research (CNR) and the Ministero della Pubblica Instruzione have provided partial support for this study.

## References

1 L. Busetto, A. Palazzi and V. Foliadis, *Inorg. Chim. Acta, 40,* 147 (1980).
2 S. R. Finnimore, R. Goddard, S. D. Killops, S. A. R. Knox and P. Woodward, *J. Chem. Soc. Dalton,* 1247 (1978).
3 T. A. Manuel, *Inorg. Chem., 3,* 1703 (1964).
4 F. L. Bowden, R. Giles and R. N. Haszeldine, *J. Chem. Soc. Chem. Comm.,* 578 (1974).
5 R. O. Harris, J. Powell, A. Walker and P. V. Yaneff, *J. Organometal. Chem., 141,* 217 (1977).
6 D. H. M. W. Thewissen and H. L. M. Van Gaal, *J. Organometal. Chem., 172,* 69 (1979).
7 R. J. Angelici and A. Kruse, *J. Organometal. Chem., 22,* 461 (1970).
8 R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta, 2,* 398 (1968).