# Organosulphur–Transition-metal Chemistry. Part 3.[1] Methyl Thiocyanate Complexes: Crystal and Molecular Structure of Pentacarbonyl(methyl thiocyanate)chromium

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Treatment of $[N(PPh_3)_2][M(NCS)(CO)_5]$ (M = Cr, Mo, or W) with $SFO_2(OMe)$ yields methyl thiocyanate complexes $[M(CO)_5(NCSMe)]$ (M = Cr or W) in *ca.* 50% yield. The molybdenum analogue is unstable and could not be purified. Displacement of acetonitrile from $[Cr(CO)_5(NCMe)]$ by MeSCN also gives $[Cr(CO)_5(NCSMe)]$, while the isocyanide $[Cr(CO)_5(CNMe)]$ is formed on attempted displacement by MeNCS. Several reactions of $[M(CO)_5(NCSMe)]$ have been studied, but only that with $PPh_3$ was successful, affording $[M(CO)_5(PPh_3)]$. Methylation of a mixture of $[Fe(SCN)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe(NCS)(CO)_2(\eta\text{-}C_5H_5)]$ does not yield a cationic complex of either MeNCS or MeSCN, and addition of $SFO_2(OMe)$ to $[N(PPh_3)_2][Cr(NCO)(CO)_5]$ gives only a low yield of unstable $[Cr(CO)_5(NCOMe)]$, identified by its i.r. spectrum. Crystals of the title complex are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 6.462(6)$, $b = 11.891(12)$, $c = 13.618(18)$ Å, and $\beta = 96.46(9)°$. The structure has been elucidated by conventional heavy-atom methods from 2 720 independent reflections measured on a four-circle diffractometer at a low temperature (203 K), and refined to *R* 0.032. The atomic sequence Cr–N–C–S–Me has been established with geometry: Cr–N 2.059, N≡C 1.145, and C–S 1.688 Å; C–S–C 98.7°. Chromium is octahedrally co-ordinated, with the carbonyl group *trans* to the MeSCN ligand having Cr–C shorter (0.073 Å) and C–O longer (0.02 Å) than the four co-planar carbonyl groups, a reflection of the low $\pi$-acceptor capacity of MeSCN.

In Part 2 [1] of this series we reported an investigation of, primarily, the reactivity of MeNCS towards $[Mn(CO)_5]^-$. The formation of a dithiocarbamato-complex and a methyl isocyanide derivative thereof brought into focus the instability of the S–C bond within isothiocyanates RNCS, and also within thiocyanates RSCN, where transition metals are concerned. Complexes of both RNCS and RSCN as ligands are rare due to this instability, which is clearly shown by the reactions of PhNCS with $[Fe_3(CO)_{12}]$ and $[Mo(CO)_6]$, affording $[Fe(CO)_4(CNPh)]$ and $[Mo(CO)_3(CNPh)_3]$ respectively.[2] Further illustration is provided by the reaction of MeSCN with $[Fe_3(CO)_{12}]$ which yields $[\{Fe(CO)_3(\mu_2\text{-}SMe)\}_2]$,[3] and of PhNCS with $[Pt(PPh_3)_4]$ which yields *inter alia* an iminomethanedithiolato-complex $[Pt(CNPh)(PPh_3)(S_2C{:}NPh)]$.[4]

Known complexes are restricted to alkyl thiocyanate and isothiocyanate adducts of the type $[TaCl_5(SCNMe)]$ [5] and $[TiCl_4(NCSEt)_2]$,[6] and to $[Pt(PPh_3)_2(\eta^2\text{-}SCNPh)]$ and $[RhCl(\sigma\text{-}SCNPh)(\eta^2\text{-}SCNPh)(PPh_3)_2]$, identified 10 years ago.[7] However, the advent of $SFO_2(OMe)$ as a powerful methylating agent presented the opportunity of developing a simple direct route to such complexes. Species $[M(NCS)(CO)_5]^-$ (M = Cr, Mo, or W),[8] $[Fe(NCS)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe(SCN)(CO)_2(\eta\text{-}C_5H_5)]$,[9] for example, contain the 'backbone' of an organic thiocyanate or isothiocyanate, and their methylation might be expected to generate these as ligands. This paper describes such a study; after its completion the synthesis of various organic thiocyanate derivatives of chromium and tungsten was reported, [10] obtained by

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[1] Part 2, preceding paper.

[2] T. A. Manuel, *Inorg. Chem.*, 1964, **3**, 1703.

[3] R. L. Downs, A. Wojcicki, and P. J. Pollick, *Abs. 148th Amer. Chem. Soc. Meeting*, Chicago, 1964, 31–0.

[4] F. L. Bowden R. Giles, and R. N. Haszeldine, *J.C.S. Chem. Comm.*, 1974, 578.

[5] H. Böhland and F. M. Schneider, *Z. Chem.*, 1972, **12**, 63.

[6] S. C. Jain and R. Rivest, *Canad. J. Chem.*, 1965, **43**, 787.

[7] M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 864.

[8] A. Wojcicki and M. F. Farona, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2289.

[9] T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1268.

[10] M. H. Quick and R. J. Angelici, *Inorg. Chem.*, 1976, **15**, 160.

reaction (1). Phenyl cyanate and selenocyanates were similarly prepared. Alkylation of $[W(NCS)(CO)_5]^-$ was

$$[NEt_4][MI(CO)_5] + Ag[BF_4] + RSCN \longrightarrow [M(CO)_5(NCSR)] + AgI + [NEt_4][BF_4] \quad (1)$$

also briefly mentioned, but in contrast to our findings only poor yields of $[W(CO)_5(NCSR)]$ (R = Me or Et) were obtained.

## RESULTS AND DISCUSSION

The anions $[M(NCS)(CO)_5]^-$ (M = Cr, Mo, or W) contain an *N*-bonded thiocyanate ion and methylation might therefore be expected to occur at sulphur, generating a methyl thiocyanate ligand similarly *N*-bonded. It is conceivable, however, that an MeSCN ligand so formed could rearrange to an *S*-bonded form, or even that methylation could occur at nitrogen to give a methyl isothiocyanate ligand, either *N*- or *S*-bonded, or that MeSCN or MeNCS are $\pi$-bonded. The intriguing possibility of methylation at carbon and formation of a 'nitrene' complex $[M(CO)_5\{NC(S)Me\}]$, although extremely unlikely, was also considered.

In the event, methylation of $[N(PPh_3)_2][M(NCS)(CO)_5]$ occurred rapidly in dichloromethane solution on addition of methyl fluorosulphonate, $SFO_2(OMe)$, to give low-melting yellow diamond-shaped crystals of the methyl thiocyanate complexes $[M(CO)_5(NCSMe)]$ (M = Cr or W) in *ca.* 50% yield. Each is thermally stable at room temperature but decomposition takes place within hours on exposure to air, with the chromium derivative less stable in this respect. The molybdenum complex was too unstable to isolate and only i.r. evidence for its existence could be obtained. Such behaviour is not uncommon; molybdenum complexes have been noted to be less stable than their chromium or tungsten analogues for the species $[M(CO)_5(NCMe)]$,[11] $[M(CO)_5(CNR)]$,[12] and, significantly for this work, for $[NEt_4][M(NCS)(CO)_5]$.[8] Attempted phenylation of $[Cr(NCS)(CO)_5]^-$ with $[PhN_2][BF_4]$ was unsuccessful.

Methylation was clearly revealed to have occurred at the sulphur atom of $[M(NCS)(CO)_5]^-$ by the $^1H$ n.m.r. spectra of $[M(CO)_5(NCSMe)]$ (M = Cr or W) which showed a signal at *ca.* $\tau$ 7.4, characteristic of SMe rather than NMe, which would be expected at lower field. The observation of $\nu(C{\equiv}N)$ in the i.r. spectra provides unequivocal confirmation, as does the independent synthesis of $[Cr(CO)_5(NCSMe)]$ described below. Whether the methyl thiocyanate ligand is *N*- or *S*-bonded is not so easily established. For reasons which Quick and Angelici [10] have explained well, the value of $\nu(C{\equiv}N)$ is not a satisfactory determinant of the mode of bonding. The carbonyl-stretching bands of $[Cr(CO)_5(NCMe)]$, however, are very similar in energies to those of $[Cr(CO)_5(NCSMe)]$, implying *N*-bonding of the latter. In order to establish firmly the mode of bonding of MeSCN in these complexes a low-temperature *X*-ray diffraction study of $[Cr(CO)_5(NCSMe)]$ was initiated. While this manuscript was in preparation Angelici and his co-workers [13] described the structure of this complex at room temperature.

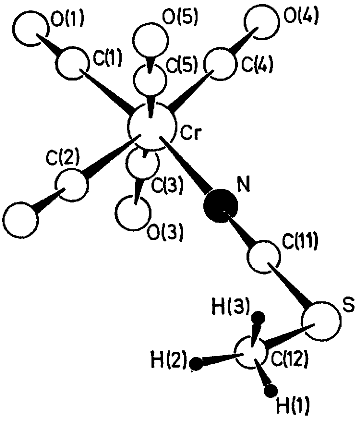

FIGURE 1 The molecular structure of $[Cr(CO)_5(NCSMe)]$, showing the atom-numbering system

The title complex consists of discrete monomeric molecules in which a methyl thiocyanate ligand is $\sigma$-bonded through the nitrogen atom to a $Cr(CO)_5$ group. The configuration and atom-numbering system are shown in Figure 1, the packing of molecules within the monoclinic unit cell in Figure 2, while Tables 1 and 2 summarise the crystallographic results. The co-ordination around the chromium atom is approximately octahedral. The carbonyl group *trans* to the MeSCN ligand differs from the four co-planar carbonyl groups in that the Cr–C bond

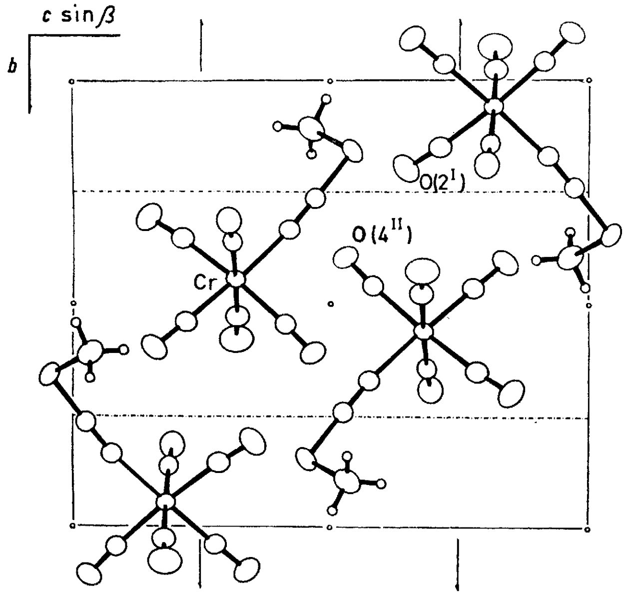

FIGURE 2 The contents of the monoclinic unit cell seen in projection down *a* looking towards the origin

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[11] D. L. Ross, J. G. Graselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 1023.

[12] J. A. Connor, E. M. Jones, G. K. McEwan, M. K. Lloyd, and J. A. McCleverty, *J.C.S. Dalton*, 1972, 1246.

[13] B. J. Helland, M. H. Quick, R. A. Jacobson, and R. J. Angelici, *J. Organometallic Chem.*, 1977, **132**, 95.

length is 0.073 Å shorter, and the C–O length 0.02 Å longer, reflecting a poor $\pi$-acceptor capability for the methyl thiocyanate ligand. This is further shown by the long Cr–N bond length [2.059(2) Å] and the short C≡N bond length [1.145(3) Å], which can be compared with that in aliphatic nitriles [1.158(2) Å].[14] The internal structure of the MeSCN ligand is, in fact, effectively identical to that of the free molecule.[15,16] The atoms C(1), O(1), Cr, N, C(11), and S are substantially collinear; their deviations from the unweighted least-squares line are Cr 0.102, C(1) 0.015, O(1) 0.117, N 0.158, C(11) 0.043, and S 0.171 Å. The angle between the MeS bond and this line is 99°. When the molecule is viewed along the axis of the thiocyanate ligand the methyl group is asymmetrically staggered with respect to the four carbonyl groups [C(2),O(2)—C(5),O(5)]; this appears to be due to crystal-packing forces, for both lone pairs on the sulphur atom bisect angles made at the sulphur by O(2$^{\mathrm{I}}$), O(4$^{\mathrm{II}}$) and O(2$^{\mathrm{I}}$), S$^{\mathrm{III}}$,* which are atoms in other molecules in the crystal. These three atoms, O(2$^{\mathrm{I}}$), O(4$^{\mathrm{II}}$), and S$^{\mathrm{III}}$, are at distances from sulphur [O(2$^{\mathrm{I}}$) • • • S 3.324(2), O(4$^{\mathrm{II}}$) • • • S 3.499(2), and S$^{\mathrm{III}}$ • • • S 3.981(1) Å] comparable with the sums of their van der Waals radii.[17] The small distortion around the chromium atom, and more significantly around the carbon atoms C(2), C(4), can also be attributed to the intermolecular interaction between S, O(2), and O(4).

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cr | 0.155 09(4) | 0.442 68(2) | 0.318 12(2) |
| N | 0.072 1(2) | 0.331 8(1) | 0.423 0(1) |
| C(11) | 0.024 2(3) | 0.261 6(2) | 0.473 5(1) |
| S | −0.048 93(8) | 0.156 10(4) | 0.544 93(4) |
| C(12) | −0.274 7(4) | 0.107 3(2) | 0.465 3(2) |
| H(1) | −0.319(5) | 0.040(3) | 0.494(2) |
| H(2) | −0.247(5) | 0.101(3) | 0.400(3) |
| H(3) | −0.382(5) | 0.163(3) | 0.466(2) |
| C(1) | 0.233 5(3) | 0.537 3(2) | 0.221 8(1) |
| O(1) | 0.283 7(3) | 0.594 5(1) | 0.160 1(1) |
| C(2) | 0.017 3(3) | 0.352 1(2) | 0.214 8(1) |
| O(2) | −0.063 6(3) | 0.304 8(1) | 0.148 5(1) |
| C(3) | 0.407 6(3) | 0.359 3(2) | 0.311 8(1) |
| O(3) | 0.558 0(2) | 0.312 3(1) | 0.304 5(1) |
| C(4) | 0.291 6(3) | 0.542 6(2) | 0.415 2(1) |
| O(4) | 0.372 1(5) | 0.607 0(1) | 0.468 5(1) |
| C(5) | −0.098 1(3) | 0.525 0(2) | 0.321 9(2) |
| O(5) | −0.247 5(3) | 0.575 5(2) | 0.320 0(2) |

TABLE 2

Bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| (*a*) Distances | | | |
| Cr–C(1) | 1.842(2) | C(2)–O(2) | 1.140(3) |
| Cr–C(2) | 1.911(2) | C(3)–O(3) | 1.135(3) |
| Cr–C(3) | 1.920(2) | C(4)–O(4) | 1.140(2) |
| Cr–C(4) | 1.917(2) | C(5)–O(5) | 1.135(3) |
| Cr–C(5) | 1.912(2) | C(11)–N | 1.145(3) |
| Cr–N | 2.059(2) | C(12)–H(1) | 0.95(3) |
| S–C(11) | 1.688(2) | C(12)–H(2) | 0.93(4) |
| S–C(12) | 1.813(3) | C(12)–H(3) | 0.96(4) |
| C(1)–O(1) | 1.156(3) | | |
| (*b*) Angles | | | |
| Co-ordination around Cr | | | |
| C(1)–Cr–C(2) | 87.86(8) | C(1)–Cr–C(3) | 88.87(8) |
| C(1)–Cr–C(4) | 88.33(8) | C(1)–Cr–C(5) | 90.63(9) |
| C(2)–Cr–C(3) | 90.21(8) | C(3)–Cr–C(4) | 91.36(8) |
| C(4)–Cr–C(5) | 89.60(8) | C(5)–Cr–C(2) | 88.80(8) |
| N–Cr–C(2) | 90.78(7) | N–Cr–C(3) | 89.39(8) |
| N–Cr–C(4) | 93.09(7) | N–Cr–C(5) | 91.09(8) |
| Methyl thiocyanate ligand | | | |
| Cr–N–C(11) | 172.6(1) | S–C(11)–N | 178.4(2) |
| C(11)–S–C(12) | 98.7(1) | S–C(12)–H(1) | 106(2) |
| H(1)–C(12)–H(2) | 115(3) | S–C(12)–H(2) | 112(2) |
| H(2)–C(12)–H(3) | 106(3) | S–C(12)–H(3) | 108(2) |
| H(3)–C(12)–H(1) | 109(3) | | |
| Carbonyl groups | | | |
| Cr–C(1)–O(1) | 178.4(2) | Cr–C(2)–O(2) | 174.8(2) |
| Cr–C(3)–O(3) | 177.1(2) | Cr–C(4)–O(4) | 175.7(2) |
| Cr–C(5)–O(5) | 177.0(2) | | |

Detailed comparison † of the structural parameters reported here with those of Helland *et al.*[13] show that there are no significant differences within the molecule; the bond lengths measured at low temperature are all within 3$\sigma$ of the room-temperature values. The lattice parameters and the atomic fractional co-ordinates are, of course, different and these reflect the somewhat closer packing of the molecules at low temperature. As might be expected, the low-temperature study gives a somewhat better *R* value and lower estimated standard deviations. Also, the effects of secondary extinction mentioned by the authors of the room-temperature study were not evident in the present work.

The complex [Cr(CO)$_5$(NCSMe)] was also obtained on heating readily prepared [Cr(CO)$_5$(NCMe)][11] with MeSCN briefly in hexane. Quantitative conversion appeared to occur, but the product was isolated in only *ca.* 20% yield. A corresponding attempt to produce a methyl isothiocyanate complex by treating [Cr(CO)$_5$(NCMe)] with MeNCS in heptane gave a 10% yield of [Cr(CO)$_5$(CNMe)],[12] yet another example of the cleavage of an isothiocyanate on reaction with a transition-metal complex. Similar reaction of [Cr(CO)$_5$(thf)] (thf = tetrahydrofuran) with MeNCS gave only [Cr(CO)$_6$].

The lability of MeSCN as a ligand was investigated by treating [M(CO)$_5$(NCSMe)] with PPh$_3$ (M = Cr), CS$_2$ (M = W), C$_2$H$_4$ (M = W), and cyclo-octatetraene (M = Cr); only the first reaction yielded a product other than [M(CO)$_6$], [Cr(CO)$_5$(PPh$_3$)] being produced quantitatively.

Methylation of *N*-bonded thiocyanate ion having led to a methyl thiocyanate ligand, it was of interest to determine the course of methylation of the *S*-bonded ion. This could either generate an elusive methyl isothiocyanate ligand through methylation at non-bonded

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* Roman superscripts refer to the following symmetry operations: I $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; II $1-x, 1-y, 1-z$; III $-x, -y, -z$.

† In order to compare co-ordinates in the two studies it is necessary to renumber the atoms and to effect the transformation $x = \frac{1}{2} - x'$, $y = y'$, $z = \frac{1}{2} - z'$ where the primes refer to the study by Helland *et al.*[13]

[14] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

[15] S. Nakagawa, S. Takahashi, T. Kojima, and C. C. Lin, *J. Chem. Phys.*, 1965, **43**, 3583.

[16] A. Bjorseth and K. M. Marstokk, *J. Mol. Struct.*, 1972, **11**, 15.

[17] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

nitrogen, or attack at sulphur could again occur with probable subsequent rearrangement to give *N*-bonded methyl thiocyanate. Unfortunately, there appears to be no known example of the preferred candidate for methylation, *i.e.* an anionic carbonylmetal *S*-bonded thiocyanato-complex. There are, however, several neutral complexes with the required orientation of thiocyanate of which $[\mathrm{Fe(SCN)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ [9] was chosen for study.

The reaction of $[\{\mathrm{Fe(CO)_2}(\eta\text{-}\mathrm{C_5H_5})\}_2]$ with $\mathrm{K[SCN]}$–$\mathrm{HBF_4}$ provides a mixture of $[\mathrm{Fe(SCN)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Fe(NCS)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ as thermally stable complexes, interconvertible only on u.v. irradiation.[9] These were chromatographically inseparable and the mixture (*ca.* 2 : 1 *S*- and *N*-bonded) was therefore treated with $\mathrm{SFO_2(OMe)}$. Little reaction was observed, shown by the lack of development of high-energy carbonyl bands commensurate with cationic complex formation. After allowing contact of the reagents for 1 h, sodium tetrahydroborate was added in an attempt to generate a neutral species from any cation which had been formed on methylation. Once again little sign of a reaction was apparent, but trace amounts of two complexes were isolated on chromatography. The first was unstable, but exhibited an i.r. spectrum with bands at 2 158 [$\nu(\mathrm{C{\equiv}N})$] and 2 027s and 1 983vs cm$^{-1}$ [$\nu(\mathrm{C{\equiv}O})$], the carbonyl bands being consistent with $[\mathrm{Fe(SMe)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$.[18] The absorption at 2 158 cm$^{-1}$ can be attributed to MeNC contaminant, generated by cleavage of thiocyanate ion on $\mathrm{SFO_2(OMe)}$ attack. The second complex had bands at 2 112m [$\nu(\mathrm{C{\equiv}N})$] and 2 063ms and 2 020ms cm$^{-1}$ [$\nu(\mathrm{C{\equiv}O})$], characteristic of $[\mathrm{Fe(CN)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$.[19] The reaction mixture also bore the smell of a thiol, encouraging a belief in the following sequence:

$$\begin{aligned}
&[\mathrm{Fe(NCS)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})] \xrightarrow{\mathrm{Me^+}} \\
&\qquad [\mathrm{Fe(NCSMe)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]^+ \\
&\qquad\quad \big\downarrow \mathrm{H^-} \\
&\qquad [\mathrm{Fe(NC)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})] + \mathrm{MeSH} \\
&\qquad\quad \big\downarrow \\
&\qquad [\mathrm{Fe(CN)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]
\end{aligned}$$

Reaction of RNCS (R = Me or Ph) with $[\mathrm{Mn(CO)_5}]^-$ was described in Part 2,[1] and as a somewhat exotic extension of this work a mixture of $[\mathrm{Fe(NCS)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Fe(SCN)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ was treated with the manganate anion. Should $[\mathrm{Fe(NCS)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ react in the same way as MeNCS then a dimetal complex $[\mathrm{(OC)_4Mn}\{\mu_2\text{-}\mathrm{S_2CN(H)}\}\mathrm{Fe(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ was expected. No such reaction was observed, however, and only $[\mathrm{Mn_2(CO)_{10}}]$ was obtained on subsequent methylation.

The preparation of a methyl cyanate complex *via* the methylation process was attempted, providing evidence for unstable $[\mathrm{Cr(CO)_5(NCOMe)}]$. Addition of $\mathrm{SFO_2(OMe)}$ to $[\mathrm{N(PPh_3)_2}][\mathrm{Cr(NCO)(CO)_5}]$ yielded mainly $[\mathrm{Cr(CO)_6}]$, but also present and inseparable was a small quantity of a very air-sensitive product with carbonyl bands at 2 068mw, 1 951vs, and 1 928s cm$^{-1}$ in hexane, a pattern comparing well with that of $[\mathrm{Cr(CO)_5(NCSMe)}]$. Similar treatment of the anion with $[\mathrm{OEt_3}][\mathrm{BF_4}]$ has been reported [10] to provide an equally low quantity of unstable $[\mathrm{Cr(CO)_5(NCOEt)}]$.

## EXPERIMENTAL

*Synthetic Studies.*—Instrumentation and general experimental techniques were as described in Part 1.[20] Methyl fluorosulphonate was used as supplied by Aldrich Chemical Co. Ltd. The anions $[\mathrm{M(NCS)(CO)_5}]^-$ (M = Cr, Mo, or W) were prepared as described in the literature,[8] but isolated as the $[\mathrm{N(PPh_3)_2}]^+$ salts.

*Methylation.*—(*a*) *Of* $[\mathrm{N(PPh_3)_2}][\mathrm{Cr(NCS)(CO)_5}]$.—A mixture of K[SCN] (0.405 g, 4.17 mmol) and $[\mathrm{Cr(CO)_6}]$ (0.96 g, 4.37 mmol) was heated in diglyme (25 cm$^3$) under reflux for 10 min, care being taken to clear sublimed hexacarbonyl from the condenser mouth. The now yellow solution was allowed to cool and a dichloromethane (25 cm$^3$) solution of $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (2.4 g, 4.19 mmol) added. After stirring for 1 h light petroleum (b.p. 60—80 °C) was added, precipitating a yellow-green solid. This was washed, after decanting the supernatant liquid, and passed down a 10-cm alumina column, eluting with dichloromethane. The yellow solution obtained was evaporated to yield 2.3 g (70%) of yellow-brown powder identified as $[\mathrm{N(PPh_3)_2}][\mathrm{Cr(NCS)(CO)_5}]$ by its i.r. spectrum {2 086mw,br [$\nu(\mathrm{C{\equiv}N})$], 2 051mw, 1 931s,br, and 1 854m,br cm$^{-1}$ [$\nu(\mathrm{C{\equiv}O})$] in $\mathrm{CH_2Cl_2}$; lit.,[8] 2 115m, 2 066w, 1 934s, and 1 882m cm$^{-1}$ for $[\mathrm{NMe_4}][\mathrm{Cr(NCS)(CO)_5}]$ in $\mathrm{CHCl_3}$}. The salt was dissolved in dichloromethane (75 cm$^3$) and stirred with excess of $\mathrm{SFO_2(OMe)}$ (1 cm$^3$) for 0.5 h, the yellow solution darkening substantially. Removal of solvent at reduced pressure left a yellow-brown residue which was extracted with hexane. The resulting yellow solution provided a bright yellow powder on evaporation. Sublimation at 30 °C ($10^{-1}$ Torr) * followed by crystallisation from hexane gave 0.26 g {47% based on $[\mathrm{N(PPh_3)_2}]^+$ salt} of yellow diamond-like $[\mathrm{Cr(CO)_5(NCSMe)}]$, m.p. 36—37 °C (Found: C, 31.9; H, 1.3; N, 5.5; S, 12.1%; *M* 265. $\mathrm{C_7H_3CrNO_5S}$ requires C, 31.7; H, 1.1; N, 5.3; S, 11.9%); $\nu(\mathrm{C{\equiv}N})$ at 2 176w cm$^{-1}$, $\nu(\mathrm{C{\equiv}O})$ at 2 072w, 1 954vs, and 1 930m cm$^{-1}$ in hexane; $^1$H n.m.r. $\tau$ 7.38(s) in $\mathrm{CDCl_3}$.

(*b*) *Of* $[\mathrm{N(PPh_3)_2}][\mathrm{Mo(NCS)(CO)_5}]$.—Similar treatment of $[\mathrm{Mo(CO)_6}]$ (1.38 g, 5.23 mmol) with K[SCN] (0.5 g, 5.2 mmol) and then $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (2.98 g, 5.19 mmol) yielded 2.25 g (52%) of $[\mathrm{N(PPh_3)_2}][\mathrm{Mo(NCS)(CO)_5}]$ {2 099mw,br [$\nu(\mathrm{C{\equiv}N})$], 2 067mw, 1 933s,br, and 1 866m,br cm$^{-1}$ [$\nu(\mathrm{C{\equiv}O})$] in $\mathrm{CH_2Cl_2}$; lit.,[8] 2 105m, 2 073w, 1 941s, and 1 876m cm$^{-1}$ for $[\mathrm{NMe_4}][\mathrm{Mo(NCS)(CO)_5}]$ in $\mathrm{CHCl_3}$}. Methylation with $\mathrm{SFO_2(OMe)}$ as above, followed by evaporation and hexane extraction, gave mainly $[\mathrm{Mo(CO)_6}]$ but contaminated with a small amount of unstable $[\mathrm{Mo(CO)_5(NCSMe)}]$, identified by its i.r. spectrum {2 075w, 1 954s, and 1 929m cm$^{-1}$ [$\nu(\mathrm{C{\equiv}O})$] in hexane}.

(*c*) *Of* $[\mathrm{N(PPh_3)_2}][\mathrm{W(NCS)(CO)_5}]$. Treatment of $[\mathrm{W(CO)_6}]$ (1.76 g, 5.0 mmol) with K[SCN] (0.5 g, 5.2 mmol) and then $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ (2.86 g, 5.0 mmol) as above gave 2.25 g (49%) of yellow powdery $[\mathrm{N(PPh_3)_2}][\mathrm{W(NCS)(CO)_5}]$ {2 104mw,br [$\nu(\mathrm{C{\equiv}N})$], 2 067mw, 1 924s,br, and 1 864m,

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* Throughout this paper: 1 Torr = (101. 325/760) Nm$^{-2}$.

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br cm$^{-1}$ [ν(C≡O)] in $CH_2Cl_2$; lit.,[8] 2 105m, 2 067w, 1 920s, and 1 873m cm$^{-1}$ for $[NMe_4][W(NCS)(CO)_5]$ in $CHCl_3$}. This was treated with $SFO_2(OMe)$ as above, then following removal of dichloromethane solvent the residue was extracted with hexane. Filtration, concentration, and cooling of this extract crystallised 0.42 g {43% based on $[N(PPh_3)_2]^+$ salt} of yellow diamond-like $[W(CO)_5(NCSMe)]$, m.p. 61—63 °C (Found: C, 21.5; H, 0.8; N, 3.5; S, 9.1%; *M* 397. $C_7H_3NO_5SW$ requires C, 21.2; H, 0.8; N, 3.5; S, 8.1%; *M* 397); ν(C≡N) at 2 166w cm$^{-1}$, ν(C≡O) at 2 074w, 1 947vs, and 1 929m cm$^{-1}$ in hexane; $^1H$ n.m.r. τ 7.35(s) in $CDCl_3$.

(*d*) *Of* $[N(PPh_3)_2][Cr(NCO)(CO)_5]$. The complex $[Cr(CO)_6]$ (2.4 g, 10.9 mmol) and $Na[N_3]$ (0.65 g, 10.06 mmol) were heated in diglyme (25 cm$^3$) under reflux for 15 min, then to the cooled dark yellow-brown cloudy solution $[N(PPh_3)_2]Cl$ (6.13 g, 10.69 mmol) in dichloromethane (25 cm$^3$) was added, the whole being stirred for 1 h. Addition of light petroleum (b.p. 60—80 °C) precipitated a bright yellow-green powder, which was passed through a 5-cm alumina column in dichloromethane, to yield 1.5 g (19%) of yellow $[N(PPh_3)_2][Cr(NCO)(CO)_5]$ {2 070w, 1 924m, and 1 854w cm$^{-1}$ [ν(C≡O)] in $CH_2Cl_2$; *cf.* $[AsPh_4][W(NCO)(CO)_5]$,[21] 2 067w, 1 927s, and 1 868m cm$^{-1}$ in acetone}. Treatment of the salt with $SFO_2(OMe)$ (1 cm$^3$) in dichloromethane (20 cm$^3$) as above, followed by solvent evaporation and hexane extraction, gave a solution containing mainly $[Cr(CO)_6]$ together with a small amount of unstable i.r.-identified $[Cr(CO)_5(NCOMe)]$ [ν(C≡O) at 2 068mw, 1 951vs, and 1 928s cm$^{-1}$ in hexane].

(*e*) *Of* $[Fe(SCN)(CO)_2(\eta\text{-}C_5H_5)]$–$[Fe(NCS)(CO)_2(\eta\text{-}C_5H_5)]$. A *ca.* 2 : 1 mixture of $[Fe(SCN)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe(NCS)(CO)_2(\eta\text{-}C_5H_5)]$ (1.5 g, 6.38 mmol) was prepared by the literature method,[9] and stirred in dichloromethane (25 cm$^3$) with $SFO_2(OMe)$ (1 cm$^3$) for 1 h, without the appearance of having reacted. Excess of $Na[BH_4]$ (3 g) was then added and stirring continued for another hour. No colour change occurred, and after removal of solvent the red-brown residue was introduced to a 30-cm alumina column. Elution with dichloromethane–hexane (1 : 1) removed a faint yellow band which yielded a trace amount of yellow solid exhibiting ν(C≡N) at 2 158m cm$^{-1}$ and ν(C≡O) at 2 027s and 1 983vs cm$^{-1}$ in hexane, tentatively identified as $[Fe(SMe)(CO)_2(\eta\text{-}C_5H_5)]$ (lit.,[17] 2 029 and 1 981 cm$^{-1}$ in $CCl_4$). Neat dichloromethane eluted essentially the initial quantity of unchanged thiocyanatoiron complexes, preceded by a trace amount of a yellow product with an i.r. spectrum showing ν(C≡N) at 2 112m and ν(C≡O) at 2 063s and 2 020s cm$^{-1}$ in $CH_2Cl_2$, similar to that of $[Fe(CN)(CO)_2(\eta\text{-}C_5H_5)]$ (lit.,[18] 2 125s, 2 060vs, and 2 020vs cm$^{-1}$ in $CHCl_3$).

*Reactions of* $[Cr(CO)_5(NCMe)]$.—(*a*) *With* MeSCN. As in the literature,[11] $[Cr(CO)_6]$ (1.0 g, 4.57 mmol) was heated under reflux in acetonitrile (50 cm$^3$) for 6 h, after which time monitoring of CO evolution indicated the displacement of 1 equivalent of the gas. The dark yellow solution was evaporated to dryness to give bright yellow $[Cr(CO)_5(NCMe)]$, identified by its i.r. spectrum, which was stirred with excess of MeSCN (2 cm$^3$) in hexane (50 cm$^3$) for 2 h. No reaction occurred in this time, but on bringing the solution to reflux temperature the reaction was completed within 15 min. Infrared monitoring indicated essentially quantitative formation of $[Cr(CO)_5(NCSMe)]$. Evaporation of solvent and excess of MeSCN and crystallisation of the residue from hexane gave 0.24 g {20% based on $[Cr(CO)_6]$} of $[Cr(CO)_5(NCSMe)]$, identified by its i.r. spectrum.

(*b*) *With* MeNCS. A quantity of $[Cr(CO)_5(NCMe)]$ prepared as above from $[Cr(CO)_6]$ (1.0 g, 4.57 mmol) was heated under reflux in heptane (50 cm$^3$) with MeNCS (1.81 g, 24.8 mmol) for 45 min. The mixture was filtered while warm, solvent removed under reduced pressure, and the residue placed on a 15-cm alumina column. Elution with hexane yielded first $[Cr(CO)_6]$ and then a white powder, sublimed (30 °C, $10^{-1}$ Torr) as white needle-like $[Cr(CO)_5(CNMe)]$ (0.108 g, 10%) (Found: C, 35.8; H, 1.2; N, 6.0%; *M* 233. $C_7H_3CrNO_5$ requires C, 36.1; H, 1.3; N, 6.0%; *M* 233), further identified by i.r. and n.m.r. spectroscopy.[12]

*Reactions of* $[M(CO)_5(NCSMe)]$ (M = Cr *or* W).—To a refluxing hexane (25 cm$^3$) solution of $[Cr(CO)_5(NCSMe)]$ (0.105 g, 0.38 mmol) was added dropwise a warm hexane solution of triphenylphosphine until i.r. monitoring indicated that all the starting complex had been consumed. The cloudy brown solution was then filtered, concentrated, and cooled to yield 0.17 g (96%) of white crystalline $[Cr(CO)_5(PPh_3)]$, identified by its i.r. spectrum [ν(C≡O) at 2 064mw, 1 988vs, and 1 944s cm$^{-1}$ in hexane; lit.,[22] 2 066, 1 988, and 1 942 cm$^{-1}$ in $CCl_4$].

Further reactions of $[Cr(CO)_5(SCNMe)]$ with cyclooctatetraene and of $[W(CO)_5(SCNMe)]$ with ethylene or carbon disulphide, each in hexane at reflux, gave only the appropriate $[M(CO)_6]$.

*X-Ray Data Collection and Structure Determination.*—Crystals of $[Cr(CO)_5(NCSMe)]$ grow as low-melting (*ca.* 36 °C) yellow rhombs. Diffracted intensities were collected at 203 K from a crystal of dimensions 0.36 × 0.35 × 0.37 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[23] The low temperature of the crystal was maintained by a stream of cold dry nitrogen gas (10 cu. ft h$^{-1}$) passing through an annular nozzle (0.7 cm in diameter) electrically heated to prevent serious icing. Nitrogen gas was conducted through a heat exchanger immersed in a Dewar tank of liquid nitrogen. The cooled gas was transferred through glass Dewar tubing swivel-jointed so that it was affixed to the χ circle, and the jet was directed along the φ axis throughout data collection. The unit cell was defined by inspection of the real-space vectors produced by the autoindexing program from 15 randomly chosen reflections (with $15 < 2\theta < 25°$); data collection (with equatorial bisecting geometry and a θ—2θ scan in 96 steps) employed graphite-monochromatised Mo-$K_\alpha$ *X*-radiation (λ 0.710 69 Å), $2.9 \leqslant 2\theta \leqslant 60.0°$. The scan rate = 0.001 34*C*, where *C* was a preliminary 2-s peak count (for $100 \leqslant C \leqslant 1\,000$); for $C < 100$, scan rate = 0.03° s$^{-1}$ and for $C > 1\,000$ scan rate = 1.0° s$^{-1}$. Scan interval: 1° below θ for $K_{\alpha1}$ to 1° above θ for $K_{\alpha2}$. Background count (before and after each scan) to give total background time = scan time. Three check reflections (every 30 reflections) showed no significant variance over the 105-h *X*-ray exposure. Number of reflections measured: 3 166; number observed 2 720 [according to the criterion $I > 2.5\sigma(I)$].

*Crystal data.* $C_7H_3CrNO_5S$, $M = 265.2$, Monoclinic, $a = 6.462(6)$, $b = 11.891(12)$, $c = 13.618(18)$ Å, $\beta = 96.46(9)°$, $D_c = 1.69$ g cm$^{-3}$, $Z = 4$, $D_m = 1.67$ g cm$^{-3}$, $F(000) = 528$, space group $P2_1/n$, Mo-$K_\alpha$ *X*-radiation, λ 0.710 69 Å, μ(Mo-$K_\alpha$) = 13.4 cm$^{-1}$, 203 K.

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The data were corrected for Lorentz and polarisation effects, but not for *X*-ray absorption. The structure was solved by conventional heavy-atom methods and refined by full-matrix least squares to *R* 0.032, with anisotropic thermal parameters for all the non-hydrogen atoms. The use of free-atom, spherically symmetric, scattering factors for hydrogen, and an isotropic thermal parameter, results in a C–H bond length which is unrealistically short. Churchill [24] has estimated that the true $sp^3$ C–H single bond should be 1.08 Å, which implies that the individual values reported here are probably *ca.* 0.13 Å too short.

Individual weights were applied according to the scheme $1/w = (a + b|F| + c|F|^2 + d|F|^3)$ where $a = 0.71$, $b = -0.057$, $c = 0.002\,2$, and $d = -0.000\,007$; whence $R'$ 0.040. All the computational work was carried out with the '*X*-Ray System' of programs.[25] Atomic scattering factors are those of refs. 26 (Cr), 27 (S, N, C, and O), and 28 (H). Observed and calculated structure factors, and the atomic thermal parameters, are listed in Supplementary Publication No. SUP 22260 (13 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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