Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

ANIONIC THIOCYANATE COMPLEXES OF MANGANESE AND RHENIUM

P. M. TREICHEL AND W. M. DOUGLAS
Department of Chemistry, University of Wisconsin, Madison, Wisconsin (U.S.A.)

(Received March 5th, 1969)

Anionic halocarbonylmetallates of manganese and rhenium, having the general formula $M(CO)_4X_2^-$, were described several years ago by two groups[1-3]. A complex $Re(CO)_3I_3^{2-}$ has also been reported, in the latter reference[3], to be formed in a prolonged reaction of $Re(CO)_5I$ and iodide ion. Analogous dicyanotetracarbonyl complexes, $M(CO)_4(CN)_2^-$, are also reported for these two elements (Mn[1,4], Re[5]). For manganese further substitution of CO by CN^- is reported to occur using forcing conditions to give $Mn(CO)_3(CN)_3^{2-}$ (ref. 6). There is no report yet of an anionic thiocyanatocarbonylmanganate complex however, and only one report of a thiocyanatocarbonylrhenate whose structure is uncertain*. We wish to describe here the preparation and characterization of the complexes, $Mn(CO)_4(NCS)_2^-$ and $Re(CO)_3(NCS)_3^{2-}$, which are formed by substitution of halide ion and carbonyl (or triphenylphosphine) ligands by the thiocyanate anion. Brief mention is made of analogous reactions of the Group VI metal carbonyls, and $C_5H_5Fe(CO)_2I$.

EXPERIMENTAL

Manganese and rhenium carbonyls were obtained commercially; molybdenum carbonyl was a gift of the Climax Company.

IR spectra were recorded on a Beckman IR-10 or Perkin–Elmer-457 Spectrometer. The IR data are recorded in Table 1. Microanalyses were performed by the Bernhardt Laboratory, Muhlheim, Germany, and Galbraith Laboratory, Knoxville, Tennessee.

Reactions were run under nitrogen, and solvents deoxygenated by bubling nitrogen through them. The manganese and rhenium compounds were handled in a dry bag, under nitrogen.

Tetraethylammonium bis(isothiocyanato)tetracarbonylmanganate(I)

Manganese pentacarbonyl bromide (1.0 g, 3.6 mmoles) and KSCN (0.73 g,

---

* Cotton *et al.*[7] report a complex $[(C_4H_9)_3N]_3Re_2(CO)_2(SCN)_{10}$ and suggest that it may involve two anions $Re(NCS)_6^{2-}$ and $Re(CO)_2(NCS)_4^-$, cocrystallized in equal amounts.

7.4 mmoles) were refluxed in 60 ml of anhydrous methanol for 2.5 h. After cooling the solvent was removed with a water aspirator. The residue that remained was extracted with 40 ml chloroform to remove any unreacted manganese pentacarbonyl bromide and then dried *in vacuo*. The material was then dissolved in a minimum of methanol, filtered, and added to a saturated aqueous solution of tetraethylammonium bromide. The yellow flocculent precipitate was collected, dried and recrystallized from nitromethane and ethyl ether ($\sim$0.15 g, $\sim$10% yield). Because of the sensitivity of the complex to oxygen, and probably light, only fair elemental analyses were obtained*. (Found: C, 38.9; H, 5.16; N, 11.2; O, 16.8; S, 17.1. $C_{14}H_{20}MnN_3O_4S_2$ calcd.: C, 40.1, H, 4.84; N, 10.2; O, 15.5; S, 15.5%.)

The reaction of $Mn(CO)_4[(C_6H_5)_3P]Br$ (0.9 mmoles) and KSCN (0.38 g, 3.8 mmoles) under the same conditions gave $Mn(CO)_4[(C_6H_5)_3P]SCN$ as the only organometallic product in small yield. This compound had previously been reported to be formed in the reaction of $Mn(CO)_5SCN$ and triphenylphosphine[8].

Bis(tetraethylammonium) tris(isothiocyanato)tricarbonylrhenate(I)

The reaction of $Re(CO)_5Br$ (1.0 g, 2.5 mmole) and KSCN (0.51 g, 5.3 mmoles) was run in refluxing anhydrous methanol, and the product worked up in a manner similar to that for the manganese system. The product, $[(C_2H_5)_4N]_2Re(CO)_3(NCS)_3$, was obtained as a white powder in 37% yield (0.45 g). The compound is thermally stable, and unreactive to air and moisture, in distinct contrast to the manganese compound. (Found: C, 38.1; H, 6.26; N, 9.68; O, 6.62; S, 13.14. $C_{22}H_{40}N_5O_3ReS_3$ calcd.: C, 37.6; H, 5.67; N, 9.94; O, 6.82; S, 13.6%.)

The reaction of $Re(CO)_4[(C_6H_5)_3P]Br$ and KSCN in diglyme (96°, 2 h) and the reaction of $Re(CO)_3[(C_6H_5)_3P]_2Br$ and KSCN in diglyme (105°, 2 h) also produced the anion $Re(CO)_3(NCS)_3^{2-}$ as the only organometallic product. These reactions were followed by the change in IR spectra.

Other reactions

In the course of this study, we also carried out reactions of KSCN with $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, using the conditions described above, and followed these reactions by their IR spectrum. After initial formation of the $M(CO)_5NCS^-$ ion on further substitution was observed to occur. We had hoped that by analogy to the rhenium reaction above that a compound such as $W(CO)_4(NCS)_2^{2-}$ would form. Analogous complexes, $W(CO)_4(CN)_2^{2-}$ and $Cr(CO)_4(CN)_2^{2-}$ were recently prepared photochemically by Ruff[9]. We also confirmed that the reaction of $C_5H_5Fe(CO)_2I$ and KSCN[10] on prolonged reflux (18 h) gave a small amount of $C_5H_5Fe(CO)_2SCN$, but no anionic complex. In contrast the reaction of KCN and $C_5H_5Fe(CO)_2Br$, reported by Coffey[11], gives $C_5H_5Fe(CO)(CN)_2^-$.

RESULTS AND DISCUSSION

A brief report that the reaction of KSCN and $Mn(CO)_5Br$ failed to give a thiocyanato–manganese complex is found[12]; however, substantially milder condi-

---

* M. F. Farona and L. M. Frazee, reacting a substantial excess of KSCN with $Mn(CO)_5Cl$ obtained a different, and very stable, product (see next paper, this journal). We saw no evidence of their compound. We suspect, on discussion with these authors, that the key to the differences is in the excess KSCN used.

tions and a different stoichiometry were employed in that study. The reaction of these reagents described here was carried out in refluxing anhydrous methanol, in a manner similar to that used by Angelici to prepare other $Mn(CO)_4X_2^-$ anions[1]. The anion $Mn(CO)_4(NCS)_2^-$ is similar to other $Mn(CO)_4X_2^-$ ions reported ($X=Cl$, Br, I, CN)[1]; it has a *cis* geometry, with localized C_{2v} symmetry around the metal atom. The carbonyl stretching frequencies are similar to those reported[1] for the analogous complexes, although the B_1 and A_1^b (CO's *trans* to NCS) bands (2015 cm^{-1}) not resolved using a medium resolution instrument. The frequencies of the bands observed are a few wavenumbers below those for the halide and cyanide complexes, but the difference did not appear substantial, and the fact that different solvents were used precludes direct comparison.

One would anticipate that this complex $Mn(CO)_4(NCS)_2^-$ will have N-bonded thiocyanate groups, since this mode of bonding is found for $Cr(CO)_5NCS^-$, and probably associated with negative charge on the metal[13]. The IR evidence, though not conclusive, certainly supports this assignment. A weak band at 780 cm^{-1} [ν(CS)] falls within the range 780–860 cm^{-1} associated with this structure[13,14]. A band at 470 cm^{-1} [δ(NCS)] is also appropriate for this isomer[15]. There is no band in the 410–440 cm^{-1} or 690–720 cm^{-1} regions expected for an S-bonded group[14–16]. The value of ν(CN) falls at 2130 cm^{-1}, which though high is not unacceptable for the N-bonded form.

In the reaction of $Mn(CO)_5Br$ and KSCN no evidence was obtained for a further substitution of CO by SCN^- giving $Mn(CO)_3(NCS)_3^{2-}$. This observation contrasts with the facile reaction, described below, giving the analogous rhenium complex. The only known anion of manganese which is strictly analogous is $Mn(CO)_3(CN)_3^{2-}$, described by Behrens and coworkers[17].

Formation of the anion $Re(CO)_3(NCS)_3^{2-}$ under relatively mild conditions was somewhat unexpected. Only in the reaction of $Re(CO)_5I$ and iodide ion over a substantially longer time (8 *vs.* 2.5 h) and at higher temperature (80° *vs.* 65°), had disubstitution been shown to occur[3]. In this work, the anion $Re(CO)_4(NCS)_2^-$ apparently had a transitory existence since the reaction could not be stopped at that point. The analogous compound $Re(CO)_4I_2^-$ was isolated by Abel and coworkers[3].

The anion $Re(CO)_3(NCS)_3^{2-}$ was also obtained from the reactions of $Re(CO)_{5-n}[(C_6H_5)_3P]_nBr$ ($n=1, 2$) and thiocyanate. Triphenylphosphine was displaced in each reaction.

For the ion $Re(CO)_3(NCS)_3^{2-}$ peaks in the IR spectrum at 2090 [ν(CN)], 2005 and 1890 [ν(CO)] are seen (dichloromethane). The 1890 cm^{-1} peak is split in a mull spectrum. These data are similar to the ν(CO) values reported for $Re(CO)_3I_3^{2-}$ (ref. 3) and $Mn(CO)_3(CN)_3^{2-}$ (ref. 6), and support a *fac* substituted C_{3v} geometry. The IR absorptions also support the existence of N-bonded thiocyanate groups in this complex. In the appropriate ν(CS) and δ(CNS) regions two absorptions are noted.

ACKNOWLEDGEMENT

We are pleased to acknowledge support by the National Science Foundation (Grant GP-8140).

REFERENCES

1 R. J. Angelici, *Inorg. Chem.*, 3 (1964) 1099.
2 E. W. Abel and I. S. Butler, *J. Chem. Soc.*, (1964) 434.
3 E. W. Abel, I. S. Butler, M. C. Ganorkar, C. R. Jenkins, and M. H. B. Stiddard, *Inorg. Chem.*, 5 (1966) 25.
4 W. Hieber and W. Schropp. *Z. Naturforsch.*, *B*, 14 (1959) 460.
5 W. Hieber and L. Schuster, *Z. Anorg. Allgem. Chem.*, 287 (1956) 214.
6 H. Behrens, E. Ruyter and E. Lindner, *Z. Anorg. Allgem. Chem.*, 349 (1967) 251.
7 F. A. Cotton, W. R. Robinson, R. A. Walton and R. Whyman, *Inorg. Chem.*, 6 (1967) 929.
8 M. F. Farona and A. Wojcicki, *Inorg. Chem.*, 4 (1965) 1402.
9 J. K. Ruff, *Inorg. Chem.*, 8 (1969) 86.
10 T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 7 (1968) 1268.
11 C. E. Coffey, *J. Inorg. Nucl. Chem.*, 25 (1963) 179.
12 M. F. Farona and A. Wojcicki, *Inorg. Chem.*, 4 (1965) 857.
13 A. Wojcicki and M. F. Farona, *J. Inorg. Nucl. Chem.*, 26 (1964) 2289.
14 A. Turco and C. Pecile, *Nature*, 191 (1961) 66.
15 J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.*, (1961) 4590.
16 I. Bertini and A. Sabatini, *Inorg. Chem.*, 5 (1966) 1025.