

SOME REACTIONS OF MANGANESE AND RHENIUM PENTACARBONYL HALIDES WITH SULPHUR-CONTAINING LIGANDS

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SUMMARY

The interaction of manganese and rhenium pentacarbonyl bromides with 4,5-dicyano-2,2-dimethyl-1,3-dithia-2-stannacyclopentene is reported. The reaction of the pentacarbonyl halides with (methylthio)- and (phenylthio)trimethylsilane has also been investigated and the possible structure of the products is discussed.

Recent investigations on the interaction of manganese and rhenium carbonyl and nitrosyl halides with sulphur ligands^{1,2} prompts this report of observations on some mercapto derivatives of Group VII metal carbonyls.

The anion *cis*-1,2-dicyanoethylene-1,2-dithiolate, $[S_2C_2(CN)_2]^{2-}$, forms numerous complexes with transitional metals in apparently high oxidation states³. However, few examples of the interaction of this ligand with metal ions in low oxidation states have been reported^{1,2}. Similarly, the reactions of 1,3-dithia-2-stannacyclopentenes with transitional metal salts have been studied⁴, but there have been no reports of the reactions of these ring compounds with carbonyl species. Herein is reported the interaction of manganese and rhenium pentacarbonyl halides with the compound 4,5-dicyano-2,2-dimethyl-1,3-dithia-2-stannacyclopentene.

Heating the carbonyl halides with the tin-sulphur ring compound, followed by the addition of a tetraphenylarsonium salt, yields red or orange crystals of tetraphenylarsonium tetracarbonyl(dicyanoethylene-1,2-dithiolato)manganate(I) or -rhenate(I).

TABLE 1

INFRARED CARBONYL STRETCHING FREQUENCIES IN $[M(CO)_4S_2C_2(CN)_2]^-$

M	Solvent	Modes ^a (cm ⁻¹)				Ref.
Mn	CHCl ₃	2075 w	2010 vs	1982 s	1933 m	1
	CHCl ₃ ^b		2009 vs		1917 s (bd)	This work
	CHCl ₃ ^c	2074 w	2003 vs	1978 s	1928 m	This work
	Nujol		1999 vs	1915 vs	1908 vs	This work
Re	CHCl ₃	2020 m	2003 vs		1897 vs (bd)	This work
	Nujol	2022 m	2006 vs	1911 vs	1898 vs	This work

^a w=weak; m=medium; s=strong; vs=very strong; bd=broad. ^b Immediate run. ^c After 24 h.

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$\text{Ph}_4\text{As}[\text{M}(\text{CO})_4\text{S}_2\text{C}_2(\text{CN})_2]$, where $\text{M} = \text{Mn}$ or Re , compounds formally containing $\text{M}(\text{I})$. The manganese anion has previously been produced by the reaction of disodium 1,2-dicyanoethylene-1,2-dithiolate with pentacarbonylmanganese bromide¹. A novel aspect of the dithiolato-manganese compound is that its IR spectrum, in chloroform solution, initially showed only two broad, strong absorptions in the carbonyl stretching region (Table 1). However, on standing, in the absence of air, a spectrum identical to that previously reported¹ was observed. The ionic nature of the complexes precludes the use of a more suitable solvent for IR analysis. The alteration in intensity pattern of the carbonyl stretching modes on replacement of the manganese atom by rhenium in the anion is noteworthy but presently inexplicable.

Considerable interest has recently attached to the organothio/seleno-carbonyl derivatives of manganese and rhenium. In particular, studies on the cleavage of organotin-sulphur and organotin-selenium compounds by carbonyl halides have yielded complexes of some novelty^{5,6}.

Without exception, the interaction of organotin-sulphur compounds with manganese and rhenium pentacarbonyl halides led⁵ to the corresponding organotin halides and the tricarbonyl species $[\text{RSM}(\text{CO})_3]_n$. In contrast, alkyl/arylselenotins yielded the dimers $[\text{RSeM}(\text{CO})_4]_2$ with the pentacarbonyl halides. Efforts to produce the direct formation of $[\text{RSeM}(\text{CO})_3]_n$ by paralleling the use of bis(alkylthio)tin compounds with $\text{Me}_2\text{Sn}(\text{SePh})_2$ led only to the dimeric tetracarbonyls⁶.

In view of the contrasting behaviour of the sulphur- and selenium-tin derivatives with carbonyl halides, manganese and rhenium pentacarbonyl halides were treated with thiosilanes under conditions similar to those employed for the synthesis of the dimeric selenium-bridged complexes. However, only the tricarbonyl species, $[\text{RSM}(\text{CO})_3]_n$ ($\text{R} = \text{Me}$ or Ph), could be isolated, again in good yield. IR spectroscopic examination during the course of the reactions failed to detect any tetracarbonyl dimers.

(Organothio)tricarbonyls were originally reported to be trimeric from osmometric molecular weight measurements, and a structure involving a triangular metal atom cluster was proposed^{5,7}. Subsequent mass spectral studies, however, indicated that, in the vapour phase, a tetrameric formulation rather than a trimeric one is more correct⁸⁻¹⁰. For the compound $[\text{Re}(\text{CO})_3\text{SPh}]_n$, mass spectrometry has fully characterised the existence of both the trimeric and tetrameric species in the gas phase⁹. These apparently contradictory results prompted a closer examination of the molecular weights of the tricarbonyl(organothio)manganese and -rhenium complexes in solution (Table 2).

The apparent sensitivity of the degree of aggregation of the complexes to the nature of the solvent, and even the method of preparation, has been demonstrated by various researchers (see Table 2). The (organothio)tricarbonyl species, obtained from thiosilanes, again show varied polymery. The manganese complexes appear to be tetrameric in solution as does (phenylthio)tricarbonylrhenium, while the (methylthio)rhenium complex appears to be pentameric in both benzene and chloroform.

The IR carbonyl stretching modes observed for the tricarbonyl species derived from thiosilanes are in good agreement with those previously reported (Table 3).

From the analysis of the combination spectrum of (ethylthio)tricarbonylmanganese, it has been proposed¹² that the structure of these tricarbonyls in solution is one in which the metal atoms form a regular tetrahedron, with a sulphur atom sym-

TABLE 2

MOLECULAR WEIGHTS OF $[M(CO)_3SR]_n$ AND $[M(CO)_3SeR]_n$

Compound	<i>M</i> (calcd.)		<i>M</i> (found)	Solvent	Reference
	Trimer	Tetramer			
Mn(CO) ₃ SMe	558	744	693, 710, 719, 725, 750, 803	CHCl ₃	10
			548, 785	C ₆ H ₆	5,8
			738	C ₆ H ₆	This work
			781	C ₆ H ₁₂	This work
Mn(CO) ₃ SEt	600	800	647, 637	C ₆ H ₆	5,11
			827	C ₆ H ₁₂	11
			815	EtOAc	11
			812, 718	CHCl ₃	10, 11
			876	C ₆ H ₆	6
Mn(CO) ₃ SeMe	699	932	876	C ₆ H ₆	6
Mn(CO) ₃ SPh	744	992	721, 982	C ₆ H ₆	7, 8
			910	CHCl ₃	This work
			734	C ₆ H ₆	5
Mn(CO) ₃ STol	789	1049	1062	C ₆ H ₁₂	11
			927	CHCl ₃	11
			912	EtOAc	11
			896, 983	C ₆ H ₆	6, 11
			1091	C ₆ H ₁₂	11
Mn(CO) ₃ SePh	885	1180	956	CHCl ₃	11
			970, 1231	C ₆ H ₆	5, 11
			1502	C ₆ H ₆	This work
Re(CO) ₃ SMe	952	1269	1516	CHCl ₃	This work
			1143, 1521	C ₆ H ₆	7, 11
			1615	C ₆ H ₆	This work
			1637	CHCl ₃	This work
Re(CO) ₃ SPh	1137	1516	1166	C ₆ H ₆	5
			1306, 1722	C ₆ H ₆	6, 11
Re(CO) ₃ STol	1180	1573	1709	CHCl ₃	11
Re(CO) ₃ SePh	1278	1704			

metrically situated above each face. The large number of bands in the combination spectrum proves that the paucity of IR-active fundamentals is due to the operation of selection rules rather than accidental degeneracy.

The proton magnetic resonance spectra of the (methylthio)tricarbonyls of manganese and rhenium have recently been reported^{6,10}. Only one methyl resonance could be observed at room temperature, indicating either the formation of one stable isomer, or rapid interconversion of different configurations. In an attempt to elucidate which of these situations exists, the behaviour of the methyl resonance of $[MeSMn(CO)_3]_n$ in solution at low temperature was observed. Although the intensity of the resonance decreased markedly as the temperature was reduced, no significant line broadening was detected; raising the temperature restored the intensity. It seems, therefore, that although rapid interconversion of species may be occurring, lower temperatures ($< -20^\circ$) than those employed here must be used to achieve detection of any conformers.

A previous attempt to study possible equilibria between $[M(CO)_3SR]$ units in solution, using (methylthio)- and (ethylthio)manganese derivatives, also failed to detect any mixed complexes which would be expected if equilibrium between species of varying polymery were established¹⁰.

TABLE 3

INFRARED SPECTRA OF $[M(CO)_3SR]_n$ IN THE CARBONYL STRETCHING REGION

Solvent: cyclohexane

Compound	Modes ^a (cm ⁻¹)				Reference
Mn(CO) ₃ SMe	2019 vs	2010 w	1947 vs	1905 vw	5
	2048 vw	2016 m	1952 vs	1910 vw	10
	2024 vw	2006 (sh)			
		1986 vw			
	2020 vs	2011 w	1947 vs	1906 vw	This work
Mn(CO) ₃ SPh	2038 vs	2020 w	1960 s		7
	2028 vs	2020 w (sh)	1954 s		This work
Re(CO) ₃ SMe	2028 vs	2019 w	1944 vs	1902 vw	5
	2030 vs	2020 w	1950 s		7
	2029 vs	2019 w	1944 vs	1903 vw	This work
Re(CO) ₃ SPh	2038 vs	2020 w	1950 s		7
	2032 vs	2022 w	1945 s		This work

^a Symbols as in Table 1.

EXPERIMENTAL

Analyses were performed by the Microanalytical Laboratory of the University of Bristol. Molecular weights were measured at Imperial College, University of London, using a vapour pressure osmometer.

IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer with scale expansion; calibration was by reference to the peak of liquid benzene at 2208 cm⁻¹. Proton magnetic resonance studies were conducted on a Varian Associates A-60 spectrometer, in carbon tetrachloride solution.

(Methylthio)trimethylsilane¹³, (phenylthio)trimethylsilane¹⁴, pentacarbonylmanganese and pentacarbonylrhenium bromide¹⁵ and 4,5-dicyano-2,2-dimethyl-1,3-dithia-2-stannacyclopentene⁴ were prepared by literature methods.

Interaction of pentacarbonylmanganese and pentacarbonylrhenium bromide with 4,5-dicyano-2,2-dimethyl-1,3-dithia-2-stannacyclopentene

The pentacarbonyl bromide (0.55 g, 1 mol) and the stannacyclopentene (1 mol) were heated in methanol (60 ml) under nitrogen. After refluxing 6 h, tetraphenylarsonium chloride (as its hydrochloride, 1 mol) was added. The resultant red or orange precipitate was filtered off, washed with cold methanol (10 ml) and dried, to give tetraphenylarsonium tetracarbonyl(1,2-dicyanoethylene-1,2-dithiolato)manganate (yield 31%) (Found: C, 55.6; H, 3.1; N, 4.1; S, 9.1. C₃₂H₂₀AsMnN₂O₄S₂ calcd.: C, 55.7; H, 2.9; N, 4.1; S, 9.3%) or tetraphenylarsonium tetracarbonyl(1,2-dicyanoethylene-1,2-dithiolato)rhenate. (Found: C, 46.5; H, 2.4; N, 3.5; S, 7.7. C₃₂H₂₀AsN₂O₄ReS₂ calcd.: C, 46.8; H, 2.4; N, 3.4; S, 7.8%.)

Interaction of pentacarbonylmanganese bromide with (methylthio)- and (phenylthio)-trimethylsilane

The carbonyl halide (0.55 g, 1 mol) was heated at 50° under nitrogen with excess of the thiosilane in 1,2-dimethoxyethane (20 ml) for 30 min, and then at above 70°. The resultant orange solution was filtered hot under nitrogen, and concentrated under reduced pressure. Addition of methanol gave orange crystals of (methylthio)tricarbonylmanganese (0.26 g, 70%) (Found: C, 26.2; H, 1.5; mol. wt. in benzene, 738, in cyclohexane, 781. $[C_4H_3O_3MnS]_4$ calcd.: C, 25.8; H, 1.6%; mol. wt., 744) or (phenylthio)tricarbonylmanganese (0.33 g, 55%). (Found: C, 44.0; H, 1.8; S, 12.7; mol. wt. in chloroform, 910. $[C_9H_5O_3MnS]_4$ calcd.: C, 43.6; H, 2.0; S, 12.9%; mol. wt., 992.)

Interacción of pentacarbonylrhenium bromide with (methylthio)- and (phenylthio)-trimethylsilane

The carbonyl halide (0.65 g, 1 mol) was heated at 85° with excess of the thiosilane for 1½ h in 1,2-dimethoxyethane (25 ml) under nitrogen. The resultant solution was filtered hot under nitrogen, and on cooling and addition of methanol yielded off-white (methylthio)tricarbonylrhenium (0.29 g, 62%) (Found: C, 15.5; H, 0.8; O, 15.0; S, 9.8; mol. wt. in benzene, 1502, in chloroform, 1516. $[C_4H_3O_3ReS]_n$ calcd.: C, 15.1; H, 1.0; O, 15.1; S, 10.1%; mol. wt. of tetramer, 1269; of pentamer, 1575) or pale-cream (phenylthio)tricarbonylrhenium (0.26 g, 56%). (Found: C, 28.6; H, 1.1; O, 12.7; S, 8.3; mol. wt. in benzene, 1615, in chloroform, 1637. $[C_9H_5O_3ReS]_4$ calcd.: C, 28.5; H, 1.3; O, 12.8; S, 8.4%; mol. wt., 1516.)

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REFERENCES

- 1 J. LOCKE AND J. A. MCCLEVERTY, *Chem. Commun.*, (1965) 102.
- 2 J. LOCKE, J. A. MCCLEVERTY, E. J. WHARTON AND C. J. WINSKOM, *Chem. Commun.*, (1966) 677; J. A. MCCLEVERTY, N. M. ATHERTON, J. LOCKE, E. J. WHARTON AND C. J. WINSKOM, *J. Amer. Chem. Soc.*, 89 (1967) 6082.
- 3 H. B. GRAY, *Transitional Metal Chemistry*, Vol. 1, Arnold, London, 1965, p. 279.
- 4 E. W. ABEL AND C. R. JENKINS, *J. Chem. Soc., A*, (1967) 1344.
- 5 E. W. ABEL AND B. C. CROSSE, *J. Chem. Soc., A*, (1966) 1141.
- 6 E. W. ABEL, B. C. CROSSE AND G. V. HUTSON, *Chem. Ind. (London)*, (1966) 238; *J. Chem. Soc., A* (1967) 2014.
- 7 A. G. OSBORNE AND F. G. A. STONE, *J. Chem. Soc., A*, (1966) 1143.
- 8 M. AHMAD, G. R. KNOX, F. J. PRESTON AND R. I. REED, *Chem. Commun.*, (1967) 138.
- 9 K. EDGAR, B. F. G. JOHNSON, J. LEWIS, I. G. WILLIAMS AND J. M. WILSON, *J. Chem. Soc., A*, (1967) 379.
- 10 B. F. G. JOHNSON, P. J. POLLICK, I. G. WILLIAMS AND A. WOJCICKI, *Inorg. Chem.*, 7 (1968) 831.
- 11 E. W. ABEL, Personal Communication, 1967.
- 12 P. S. BRATERMAN, *Chem. Commun.*, (1968) 91.
- 13 E. W. ABEL, D. A. ARMITAGE AND D. B. BRADY, *J. Organometal. Chem.*, 5 (1966) 130.
- 14 K. A. HOOTON AND A. L. ALLRED, *Inorg. Chem.*, 4 (1965) 671.
- 15 R. B. KING, *Organometallic Syntheses*, Vol. 1, Academic Press, New York, 1965, p. 174.