

Journal of Organometallic Chemistry, 91 (1975) 65-70
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CYCLOPENTADIENYLMANGANESE THIOCARBONYL NITROSYL COMPLEXES

AVI EFRATY*, RÜZA ARNERI* and JOSEPH SIKORA

Rutgers University, School of Chemistry, New Brunswick, New Jersey, 08903 (U.S.A.)

(Received October 7th, 1974)

Summary

The air-stable yellow-orange complexes of cyclopentadienylmanganese carbonyl thiocarbonyl nitrosyl cations $[\text{RC}_5\text{H}_4\text{Mn}(\text{CO})(\text{CS})\text{NO}]^+\text{X}^-$ ($\text{R} = \text{H}, \text{CH}_3$; $\text{X} = \text{SbF}_6^-, \text{PF}_6^-$) were prepared by the reaction of $\text{RC}_5\text{H}_4\text{Mn}(\text{CO})_2\text{CS}$ ($\text{R} = \text{H}, \text{CH}_3$) with either $\text{NO}^+\text{SbF}_6^-$ or NO^+PF_6^- . These complexes undergo facile monocarbonyl substitution reactions with various Lewis bases (L) to afford products of the type $[\text{RC}_5\text{H}_4\text{Mn}(\text{CS})(\text{NO})\text{L}]^+\text{SbF}_6^-$ ($\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}$ and Ph_3Sb).

Introduction

Despite the growing interest in the synthesis and properties of transition metal thiocarbonyl complexes, relatively few such compounds have been prepared and studied [1]. Recently, Butler et al. [2] have reported the synthesis of the manganese thiocarbonyl complexes $\text{RC}_5\text{H}_4\text{Mn}(\text{CO})_n(\text{CS})_{3-n}$ ($\text{R} = \text{H}, \text{CH}_3$) and some of their chemical and spectroscopic properties. For example, the monothiocarbonyl complex, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{CS}$, has been shown to react with various Lewis bases (L) [3] under photolytic conditions to afford products of the type $\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{CS})\text{L}$ and $\text{C}_5\text{H}_5\text{Mn}(\text{CS})\text{L}_2$; $\text{L} =$ phosphines, phosphites, Ph_3As , Ph_3Sb . Attempts to prepare the cationic complex $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{CS})(\text{NO})]^+$ by the reaction of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{CS}$ with NaNO_2 and HCl under thermal conditions were apparently unsuccessful [2]. As a possible explanation for this it has been suggested that the highly π -acidic CS ligand would destabilize a cationic state with respect to a neutral one [2]. However, this explanation is somewhat doubtful in view of the existence of several well-defined and stable cationic metal thiocarbonyl complexes such as $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CS}]^+\text{PF}_6^-$ [4], $[\text{IrCl}(\text{CS})(\text{NO})(\text{PR}_3)_2]^+\text{BF}_4^-$ ($\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_{11}$) [5] and others [1]. The synthesis of the cationic iridium complexes, the only known metal nitrosyl thiocarbonyl

* On leave from the University of Zagreb, Yugoslavia (1973-5).

complexes, by the oxidative addition of NO^+ to *trans*- $\text{IrCl}(\text{CO})(\text{PR}_3)_2$ [5] and the facile formation of the cations $[\text{QM}(\text{CO})_2\text{NO}]^+$ ($\text{Q} = \text{C}_4\text{H}_4$, $\text{M} = \text{Fe}$ [6]; $\text{Q} = \text{C}_5\text{H}_5$, $\text{M} = \text{Mn}$ [7]; $\text{Q} = \text{C}_6\text{Me}_{6-n}\text{H}_n$, $\text{M} = \text{Cr}$ [8]) in the reaction between $\text{QM}(\text{CO})_3$ and NO^+ have indicated the rather distinct possibility of preparing the cationic manganese complex $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{CS})(\text{NO})]^+$ by a similar route. This work describes the reactions between $\text{RC}_5\text{H}_4\text{Mn}(\text{CO})_2\text{CS}$ ($\text{R} = \text{H}, \text{CH}_3$) and the nitrosylating agents $\text{NO}^+\text{SbF}_6^-$ and $\text{NO}_2^+\text{PF}_6^-$.

Experimental

The preparation of the cyclopentadienylmanganese thiocarbonyl nitrosyl cations is described below. Microanalyses (Table 1) were carried out by Schwarzkopf Microanalytical Laboratory, New York. Melting points (Table 1) were obtained in capillaries and are uncorrected. Infrared spectra (Table 2) were taken in KBr pellets and recorded on a Perkin-Elmer 225 grating spectrometer. Each spectrum was calibrated using the 1601 or 1944 cm^{-1} band of polystyrene film. Proton NMR spectra (Table 2) were run in acetone- d_6 solution with TMS as an internal standard on a Jeol JNM-MH-100 spectrometer.

Nitrogen atmosphere was routinely provided for the following operations: (i) carrying out reactions, (ii) admitting evacuated vessels and (iii) handling filtered solutions of organometallic compounds.

The reagents $\text{RC}_5\text{H}_4\text{Mn}(\text{CO})_2\text{CS}$ ($\text{R} = \text{H}, \text{CH}_3$) were prepared by known procedures [2]. Nitrosonium ($\text{NO}^+\text{SbF}_6^-$) and nitronium ($\text{NO}_2^+\text{PF}_6^-$) salts were purchased from PCR Inc., Gainesville, Fla.

Preparation of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{CS})(\text{NO})]^+\text{SbF}_6^-$. A solution of 2.0 g (9.1 mmol) of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{CS}$ in 50 ml of acetonitrile at 0° was treated dropwise over a 30 min interval with a solution containing 3.0 g (11.3 mmol) of $\text{NO}^+\text{SbF}_6^-$ in 100 ml of the same solvent. The reaction mixture was allowed to warm up to ambient temperature and then was stirred for an additional 30 min. The solvent was removed on a rotary evaporator at $30^\circ/20$ torr and the solid product

TABLE 1

INFRARED (CARBONYL AND THIOCARBONYL REGIONS) AND PROTON NMR SPECTRA OF SOME CYCLOPENTADIENYLMANGANESE THIOCARBONYL DERIVATIVES

Complex	Infrared ^a (cm^{-1})			Proton NMR ^b (τ)		
	$\nu(\text{CS})$	$\nu(\text{NO})$	$\nu(\text{CO})$	RC_5H_4	C_6H_5	CH_3
$[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{CS})(\text{NO})]^+\text{SbF}_6^-$ (II, $\text{R} = \text{H}$, $\text{X} = \text{SbF}_6^-$)	1339	1847	2089	3.54 s		
$[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})(\text{CS})(\text{NO})]^+\text{SbF}_6^-$ (II, $\text{R} = \text{CH}_3$, $\text{X} = \text{SbF}_6^-$)	1339	1840	2090	3.33 s 7.63 s		
$[\text{C}_5\text{H}_5\text{Mn}(\text{CS})(\text{NO})(\text{Ph}_3\text{P})]^+\text{SbF}_6^-$ (IV, $\text{L} = \text{Ph}_3\text{P}$)	1310	1795		4.03 d ^c	1.98 m	
$[\text{C}_5\text{H}_5\text{Mn}(\text{CS})(\text{NO})(\text{Ph}_3\text{As})]^+\text{SbF}_6^-$ (IV, $\text{L} = \text{Ph}_3\text{As}$)	1310	1794		3.91 s	1.98 m	
$[\text{C}_5\text{H}_5\text{Mn}(\text{CS})(\text{NO})(\text{Ph}_3\text{Sb})]^+\text{SbF}_6^-$ (IV, $\text{L} = \text{Ph}_3\text{Sb}$)	1308	1793		3.79 s	1.99 m	

^a Infrared data are quoted within $\pm 2.0 \text{ cm}^{-1}$ accuracy. ^b Proton NMR data are given within ± 0.02 ppm accuracy. ^c $J(\text{PH}) \approx 2.0$ Hz.

TABLE 2
SOME CYCLOPENTADIENYLMANGANESE THIOCARBONYL DERIVATIVES

Complex	Color	Mp (°C)	Yield (%)	Elemental analyses found (calcd.) (%)			
				C	H	S	Mn
$[C_5H_5Mn(CO)(CS)(NO)]^+SbF_6^-$ (II, R = H, X = SbF_6^-)	orange	>185 (dec.)	84	18.41 (18.36)	1.08 (1.10)	6.78 (7.00)	12.18 (11.99)
$[CH_3C_5H_4Mn(CO)(CS)(NO)]^+SbF_6^-$ (II, R = CH_3 , X = SbF_6^-)	orange	>170 (dec.)	64	20.07 (20.34)	1.58 (1.60)	6.53 (6.79)	11.88 (11.63)
$[C_5H_5Mn(CS)(NO)(Ph_3P)]^+SbF_6^-$ (IV, L = Ph_3P)	red	174-176	85	41.86 (41.65)	3.09 (2.91)	4.10 (4.63)	7.54 (7.94)
$[C_5H_5Mn(CS)(NO)(Ph_3As)]^+SbF_6^-$ (IV, L = Ph_3As)	red	172-174	70	38.93 (39.16)	2.55 (2.74)	4.27 (4.36)	7.35 (7.46)
$[C_5H_5Mn(CS)(NO)(Ph_3Sb)]^+SbF_6^-$ (IV, L = Ph_3Sb)	brown	134-135	50	36.86 (36.82)	2.43 (2.57)	4.93 (4.09)	7.59 (7.02)

obtained, $[C_5H_5Mn(CO)(CS)(NO)]^+SbF_6^-$, was washed with Et_2O until the washings were colorless. The analytically pure sample of the complex was obtained by recrystallizations from acetonitrile—toluene mixtures.

The methyl analog $[CH_3C_5H_4Mn(CO)(CS)(NO)]^+SbF_6^-$ was prepared by essentially the same procedure.

Preparation of $[C_5H_5Mn(CS)(NO)(PPh_3)]^+SbF_6^-$. A solution of 0.7 g (1.53 mmol) of $[C_5H_5Mn(CO)(CS)(NO)]^+SbF_6^-$ and 1.0 g (3.83 mmol) of Ph_3P in 100 ml of CH_2Cl_2 was stirred and refluxed for a period of 15 h. The solvent was then stripped to dryness on a rotary evaporator at 25°/20 torr and the solid product obtained, $[C_5H_5Mn(CS)(NO)(PPh_3)]^+SbF_6^-$, was washed carefully with benzene to remove the excess of the phosphine ligand. A sample of the complex for elemental analysis was purified by recrystallizations from methylene chloride—toluene mixtures.

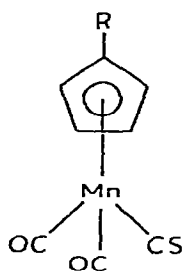
The arsine and stibine derivatives $[C_5H_5Mn(CS)(NO)L]^+SbF_6^-$ (L = Ph_3As and Ph_3Sb) were prepared, isolated and purified by essentially the same procedure described above for the phosphine analog with reaction periods being 48 and 60 h, respectively.

The above procedure was also used to prepare the methylcyclopentadienyl derivatives $[CH_3C_5H_4Mn(CS)(NO)L]^+SbF_6^-$; L = Ph_3P , Ph_3As and Ph_3Sb . Unfortunately, attempts to purify these complexes were unsuccessful. Consequently, their study was abandoned.

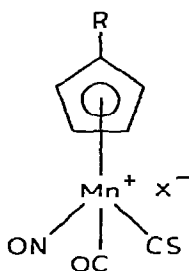
Results and discussion

The air-stable orange manganese thiocarbonyl complexes $[RC_5H_4Mn(CO)(CS)(NO)]^+X^-$ (II; R = H, CH_3 ; X = SbF_6^- , PF_6^-) were prepared by the reaction of $RC_5H_4Mn(CO)CS$ (I: R = H, CH_3) with either $NO^+SbF_6^-$ (64-84%) or $NO^+PF_6^-$ (40%) in acetonitrile solution at 0° temperature. A second product in these reactions are the known [9] cationic manganese dicarbonyl nitrosyl complexes $[RC_5H_4Mn(CO)_2(NO)]^+X^-$ (III; R = H, CH_3 ; X = SbF_6^- , PF_6^-) formed in trace amounts with $NO^+SbF_6^-$ and in almost equal yield to the thiocarbonyl complexes with $NO^+PF_6^-$. The products of each reaction were separated by recrystallizations from acetonitrile—toluene mixtures. The manganese thiocarbonyl complex II;

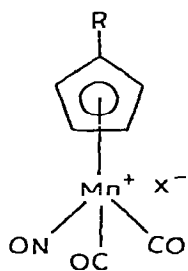
R = H; X = SbF₆ undergoes a facile carbonyl substitution reaction with various Lewis bases (L) under mild conditions, acetonitrile at 25° or boiling methylene chloride, to afford products of the type [C₅H₅Mn(CS)(NO)L]⁺SbF₆⁻ (IV; L = Ph₃P, Ph₃As, Ph₃Sb) in moderate to good yields (50-85%).



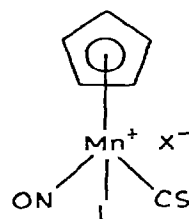
(I)

R = H, CH₃

(II)

R = H, CH₃X = SbF₆, PF₆

(III)

R = H, CH₃X = SbF₆, PF₆

(IV)

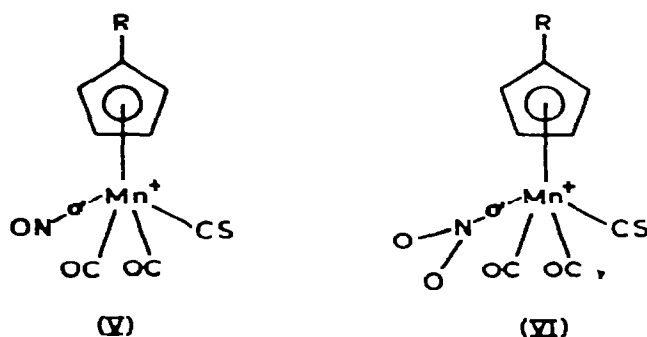
L = Ph₃P, Ph₃As, Ph₃Sb

The structures assigned to the new complexes are in full accord with the spectroscopic properties summarized in Table 2. The infrared spectra in the 2200-1600 cm⁻¹ region confirm the presence of terminal carbonyl and/or nitrosyl groups and the strong bands at 1339 (II; R = H, CH₃; X = SbF₆), 1310 (IV; L = Ph₃P, Ph₃As) and 1308 cm⁻¹ (IV; L = Ph₃Sb) are in the upper 1381-1193 cm⁻¹ region [1] as expected for the stretching frequencies of coordinated thiocarbonyls in cationic metal complexes. A strong band in the 660-654 cm⁻¹ region, characteristic of the hexafluoroantimonate anion, supports the ionic nature of the new complexes.

The proton NMR spectra of II; R = H; X = SbF₆, IV; L = Ph₃As and IV; L = Ph₃Sb exhibit a sharp singlet at τ 3.54, 3.91 and 3.79, respectively, due to the equivalent protons of the cyclopentadienyl ring. In the case of the phosphine analog IV; L = Ph₃P the cyclopentadienyl protons give rise to a doublet at τ 4.03 with $J(\text{PH}) \approx 2\text{Hz}$. The cyclopentadienyl ring protons in II; R = CH₃; X = SbF₆ exhibit a sharp singlet at τ 3.33. The chemical shifts of the phenyl protons in IV and the methyl protons in II; R = CH₃; X = SbF₆ are found in their normal region and the integration ratio of the different type of protons in the spectra of these complexes are in agreement with the proposed structures.

The difference in behavior of the nitrosylating agents NO⁺ and NO₂⁺ may be explained in mechanistic terms. The high electrophilic character of the nitrogen atom in NO⁺ and NO₂⁺ suggests that these reagents oxidatively-add to the neutral manganese complex I to afford the electronically and coordinatively saturated cationic intermediates V and VI respectively, which then dissociate to the products. The σ -nitrosylmanganese intermediate V is envisaged to dissociate by two different pathways, to give II and CO or III and CS, with yields being determined by the relative metal-to-ligand (CO,CS) bond strength in V, which is likely to be similar to that in I. The selective formation of II in the reaction with nitrosonium suggests the presence of a stronger Mn-CS than

Mn—CO bond in V as well as in I. Previously, a similar conclusion concerning the relative metal-to-ligand (CO,CS) bond strength in I; R = H has been reached by considering its mass spectrum (fragmentation modes and ion intensities) [1,10]. The nitrosylation reaction with NO_2^+ is somewhat more complex than that with NO^+ since it also involves a process of oxygen transfer. In this case,



the postulated σ -nitromanganese intermediate VI is believed to undergo an intramolecular oxygen transfer from the nitro to either CO or CS which then is followed by CO_2 and COS dissociation to afford the final products II and III, respectively. The intramolecular oxygen transfer process via an electronically and coordinatively saturated intermediate of the type VI is likely to be favoured over an alternative intermolecular oxygen transfer process between NO_2^+ and I since the former process is expected to afford a lower energy pathway to the products. A random oxygen transfer should afford a mixture of II and III with relative yields of 33 and 66%, respectively. Since the products in the reaction with nitronium are formed in about equal yield, it may appear that compared with thiocarbonyl the carbonyl ligand in I is somewhat more susceptible to the oxygen transfer process. This higher reactivity of the carbonyl ligand may be the result of a weaker Mn—CO than Mn—CS bond in VI.

The related manganese complexes II-IV and $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})\text{L}]^+ \text{PF}_6^-$ (VII; L = Ph_3P , Ph_3As , Ph_3Sb) provide an excellent model system to study the relationship between the ligands CS, CO and NO, whose bonding interaction with the metal atom can be followed by their stretching frequencies. Complex III; R = H [9] shows higher $\nu(\text{NO})$ and $\nu(\text{CO})_{\text{max}}$ than those of the thiocarbonyl complex II; R = H and this may imply stronger Mn—NO and Mn—CO bonds in the thiocarbonyl complex. Conversely, comparison between the $\nu(\text{NO})$ of the respective manganese complexes IV and VII reveals slightly higher frequencies ($3\text{-}8 \text{ cm}^{-1}$) for the former series and thus suggests about equal or somewhat weaker Mn—NO bonds in the thiocarbonyl series. Evidently, these findings represent a dilemma in attempting to assign the relative π -acidity order of these ligands. Obviously, conclusive assignment of the relative π -acidity character of the CS ligand with respect to CO and NO should wait until further relevant information on thiocarbonyl complexes becomes available.

Further studies on the chemical and physical properties of the new cyclopentadienylmanganese thiocarbonyl nitrosyl complexes are currently in progress and will be reported in due course.

Acknowledgement

This work was supported in part by the School of Chemistry and the Research Council of Rutgers University, New Brunswick, New Jersey.

References

- 1 I.S. Butler and A.E. Fenster, *J. Organometal. Chem.*, 66 (1974) 161.
- 2 A.E. Fenster and I.S. Butler, *Inorg. Chem.*, 13 (1974) 915.
- 3 N.J. Coville and I.S. Butler, *J. Organometal. Chem.*, 64 (1974) 101.
- 4 L. Busetto and R.J. Angelici, *J. Amer. Chem. Soc.*, 90 (1968) 3283.
- 5 M.J. Mays and F.P. Stefanini, *J. Chem. Soc. A.*, (1971) 2747.
- 6 A. Efraty, R. Bystrek, J.A. Geaman, S.S. Sandhu Jr., M.H.A. Huang and R.H. Herber, *Inorg. Chem.*, 13 (1974) 1269.
- 7 D.E. Ball and N.G. Connelly, *J. Organometal. Chem.*, 55 (1973) C24.
- 8 N.G. Connelly and L.F. Dahl, *Chem. Commun.*, (1970) 880.
- 9 R.B. King and M.B. Bismette, *Inorg. Chem.*, 3 (1964) 791.
- 10 A.E. Fenster, Ph. D. Thesis, McGill University, Montreal, Quebec, Canada, 1972.
- 11 R.B. King and A. Efraty, *Inorg. Chem.*, 8 (1969) 2374.