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REACTIONS OF METAL CARBONYL COMPLEXES

IV*. SUBSTITUTION REACTIONS OF π-CYCLOPENTADIENYLDICARBONYL(THIOCARBONYL)MANGANESE(I) WITH GROUP VA LIGANDS

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Summary

Photochemical reactions of π-cyclopentadienyldicarbonyl(thiocarbonyl)manganese(I), $C_5H_5Mn(CO)_2(CS)$, with Group VA donor ligands afford the products, $C_5H_5Mn(CO)(CS)L$ [L = PPh_3, $AsPh_3$, $SbPh_3$, $P(C_6H_{11})_3$, PMe_2Ph and $P(OR)_3$ where R = Me, Et, CH_2CH_2Cl, Ph] and $C_5H_5Mn(CS)L_2$ [L = PPh_3 and $P(OR)_3$ where R = Me, Et, CH_2CH_2Cl, Ph]. The new products have been characterized by elemental analyses and by IR, NMR and mass spectrometry. The reactions proceed by successive substitution of the CO groups in $C_5H_5Mn(CO)_2(CS)$.

Introduction

Metal thiocarbonyl complexes have been known since 1966 [2]. The CS ligand in these complexes is thought to be analogous to the CO group in the manner in which it bonds to transition metals. Confirmation of this is provided by crystal structure determinations of the two metal thiocarbonyl complexes $Rh(CS)(PPh_3)_2Cl$ [3], and $[Ir(CO)_2(CS)(PPh_3)_2]PF_6 \cdot Me_2CO$ [4]. In both cases, bonding occurs through the C atom and the metal—C—S linkage is linear. Moreover, the metal—C(S) bond itself is shorter than the metal—C(O) bond in the related metal carbonyl complexes implying a greater bond strength in the former. These data are in line with molecular orbital calculations [5] which predicted that CS should be a better σ donor and a better π acceptor than CO. Richards [5] went on to propose that thiocarbonyl complexes should be more stable than the carbonyl analogues. Surprisingly, however, fewer than forty thiocarbonyl complexes have been detected (even fewer have been isolated) [6], whereas literally thousands of metal carbonyl derivatives are now known. Moreover, chemical evidence on the greater stability of the metal—C(S) bond

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relative to the metal—C(O) bond with respect to substitution has not been forthcoming.

Many substitution reactions of $C_5H_5Mn(CO)_3$ with Group VA donor ligands have been reported and the physical properties (IR, NMR, mass spectra etc.) of the products are well documented [7]. The related thiocarbonyl complex, $C_5H_5Mn(CO)_2(CS)$, was prepared recently in this laboratory [8]. Therefore, it was felt worthwhile studying the substitution reactions of the complex with Group VA donors in order to ascertain whether CO or CS was preferentially substituted. It was hoped that this study would give us an indication of the relative metal—C(S) and metal—C(O) bond strengths within the same manganese thiocarbonyl complex.

Experimental

$C_5H_5Mn(CO)_2(CS)$ was prepared as reported previously [8]. All ligands were used as purchased (Aldrich Chemical Co. or Strem Chemical Inc.). The reactions were performed routinely under a nitrogen atmosphere.

IR and NMR spectra were recorded on a Perkin - Elmer 337 spectrophotometer and a Varian Associates T-60 spectrometer, respectively, as described previously [9]. The mass spectra were recorded in the temperature range 80 - 165° on an AEI model MS902 spectrometer at 70 eV.

Photochemical reactions were carried out in a pyrex vessel ($\approx$ 150 ml capacity) fitted with a water-cooled Pyrex finger[*]. The UV source (Hanovia 100 W high-pressure mercury lamp) was placed inside this finger.

Preparation of $C_5H_5Mn(CO)(CS)L$ complexes [L = PPh_3, $AsPh_3$, $SbPh_3$, $P(C_6H_{11})_3$, PMe_2Ph, and $P(OR)_3$ where R = Me, Et, CH_2CH_2Cl and Ph]

$C_5H_5Mn(CO)_2(CS)$ (1 mmol) was dissolved in freshly distilled tetrahydrofuran (THF) (100 ml) and the irradiation vessel was immersed in an ice-bath. The solution was then irradiated until no further reaction took place, as evidenced by the constancy of the IR spectrum [ν(CO) region]. Extensive decomposition occurred during the irradiation process. Next, the ligand (1 - 2 mmol) was added to the THF solution and the solution was stirred at 35 - 40° for 12 h[**]. After filtration of the decomposition products, the solvent was removed from the filtrate under reduced pressure. The crude product was then eluted on thin layer plates (silica gel); the various eluant systems used are given in Table 1. The solid products were crystallized from CH_2Cl_2/n-hexane mixtures. All the products (including any oils) were dried in vacuo (25°/0.001 mmHg) for 24 h (30 - 60% yields).

Preparation of $C_5H_5Mn(CS)L_2$ complexes [L = PPh_3 and $P(OR)_3$ where R = Me, Et, CH_2CH_2Cl and Ph].

$C_5H_5Mn(CO)_2(CS)$ (1 mmol) and excess of the appropriate ligand (2 - 5 mmol) were dissolved in freshly distilled benzene (100 ml) and the solution was irradiated until its IR spectrum [ν(CO) region] remained unchanged (2 - 4 h).

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[*] An illustration of a similar apparatus is given in ref. 10.

[**] An alternative method of preparation involved irradiation of a solution of $C_5H_5Mn(CO)_2(CS)$ (1 mmol) and L (L = PPh_3, $AsPh_3$, $SbPh_3$) (1 mmol) in benzene (100 ml) for 3 h.

The solution was then filtered and the solvent was removed under reduced pressure. Elution of the material on thin layer plates (silica gel) afforded three complexes: $C_5H_5Mn(CO)_2(CS)$ (< 5%), $C_5H_5Mn(CO)(CS)L$ (5-10%) and $C_5H_5Mn(CS)L_2$ (> 80%). These could readily be separated. The eluant systems are given in Table 1. The solid products were crystallized from CH_2Cl_2/n-hexane mixtures. The oil, $C_5H_5Mn(CS)[P(OEt)_3]_2$, was sublimed at 80°/0.001 mmHg. All the products were dried in vacuo (25°/0.001 mmHg) for 24 h (30 - 60% yields).

Preparation of $C_5H_5Mn(CO)[P(OMe)_3]_2$

$C_5H_5Mn(CO)_3$ (1 mmol) and $P(OMe)_3$ (5 - 10 mmol) were irradiated for 2 h in benzene (100 ml). Minimal decomposition occurred. The solution was filtered and the solvent was removed under reduced pressure. Elution of the crude materials on silica gel thin layer plates with a 2/3 benzene/n-hexane mixture afforded the desired yellow product as the major component. This was crystallized from CH_2Cl_2/n-hexane solution and then dried in vacuo (25°/0.001 mmHg) for 24 h (yield 60%).

Results and discussion

Irradiation of $C_5H_5Mn(CO)_2(CS)$ in THF yields a red solution containing an unstable complex, presumably $C_5H_5Mn(CO)(CS)THF$ [ν(CO), 1912 cm^{-1}]. Extensive decomposition occurs during this irradiation process, as evidenced by the formation of a light-brown precipitate. Addition of ligands (L) to the irradiated solution results in displacement of THF to give almost exclusively products of composition $C_5H_5Mn(CO)(CS)L$. Small amounts of $C_5H_5Mn(CO)_2L$ complexes are also detected spectroscopically (IR and mass spectra).

Since the starting material contains no $C_5H_5Mn(CO)_3$, there are two possible explanations for the formation of $C_5H_5Mn(CO)_2L$. Either small amounts of CS must be substituted in the irradiation process yielding $C_5H_5Mn(CO)_2THF$, which then reacts with L to give $C_5H_5Mn(CO)_2L$, or some unspecified photochemical decomposition reaction of the $C_5H_5Mn(CO)(CS)L$ derivatives must take place. In any event, it is apparent that the chief reaction of $C_5H_5Mn(CO)_2(CS)$ with L is the photochemical formation of the $C_5H_5Mn(CO)(CS)L$ products via rupture of an Mn—C(O) bond.

The thiocarbonyl complex, $C_5H_5Mn(CO)(CS)PPh_3$, has been prepared previously by the thermal reaction of $C_5H_5Mn(CO)(CS)C_8H_{14}$ with PPh_3 [11]. This indirect method of preparation gives a lower yield of product [$\approx$ 15% based on $C_5H_5Mn(CO)_2(CS)$] than that described here ($\approx$ 50%).

Irradiation of $C_5H_5Mn(CO)_2(CS)$ and excess ligand (L) in benzene readily affords the disubstituted products $C_5H_5Mn(CS)L_2$ in good yield. IR and mass spectral data indicate that minute amounts of $C_5H_5Mn(CO)L_2$ are also present as side-products in the reactions.

It should be mentioned that there is only one previous report in the literature (a patent) dealing with the synthesis of $C_5H_5Mn(CO)L_2$ (L = phosphite) complexes [12] and little detail of the physical properties of the complexes was included in this report. Moreover, few $C_5H_5Mn(CO)L_2$ complexes are known, even for L = phosphine. For comparative spectral purposes, it was

TABLE 1
ANALYTICAL DATA FOR THE NEW COMPLEXES

Complex	Eluant mixture[a]		Colour	Decomp. (°C)	Analysis found (calcd.) (%)				Molecular weight[b]
					C	H	P	S	
$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$[c]	5/1	h/a	Yellow	≈ 180	64.1 (63.5)	8.4 (8.1)			472
$C_5H_5Mn(CO)(CS)(PMe_2Ph)$[c]	1/1	h/b	Yellow	Oil	53.6 (54.6)	4.5 (4.9)			330
$C_5H_5Mn(CO)(CS)(PPh_3)$	4/1	h/a	Orange	≈ 110	66.0 (66.1)	4.5 (4.4)		6.3 (7.0)	
$C_5H_5Mn(CO)(CS)(AsPh_3)$	4/1	h/a	Yellow	175—180	59.8 (60.3)	3.9 (4.1)		7.5 (6.4)	
$C_5H_5Mn(CO)(CS)(SbPh_3)$[d]	2/1	h/a	Orange	140—145	55.3 (55.1)	3.9 (3.7)		6.1 (5.9)	544
$C_5H_5Mn(CO)(CS)[P(OEt)_3]$[c]	3/1	h/a	Yellow	Oil	44.2 (43.6)	5.9 (5.6)			
$C_5H_5Mn(CO)(CS)[P(OMe)_3]$[c]	3/1	h/a	Yellow	Oil	38.5 (38.0)	4.4 (4.5)			
$C_5H_5Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$[c]	3/2	h/b	Yellow	Oil	34.0 (33.8)	4.0 (3.7)			460
$C_5H_5Mn(CO)(CS)[P(OPh)_3]$[c]	3/1	h/a	Yellow	100—106	60.1 (59.8)	4.1 (4.0)			502
$C_5H_5Mn(CS)(PPh_3)_2$	10/3	h/a	Red	≈ 135	72.6 (73.2)	5.5 (5.1)			
$C_5H_5Mn(CS)[P(OEt)_3]_2$[c]			Yellow	Oil	42.9 (43.6)	7.3 (7.1)			496
$C_5H_5Mn(CS)[P(OMe)_3]_2$	4/1	h/a	Yellow	≈ 180	35.1 (35.0)	5.6 (5.6)	14.6 (15.0)	8.3 (7.8)	
$C_5H_5Mn(CS)[P(OCH_2CH_2Cl)_3]_2$[e]	2/1	h/a	Yellow	70—75	31.0 (30.8)	4.3 (4.6)	8.7 (8.8)		460
$C_5H_5Mn(CS)[P(OPh)_3]_2$		h	Yellow	108—112	64.9 (64.3)	4.7 (4.5)	7.8 (7.9)	3.9 (4.1)	
$C_5H_5Mn(CO)[P(OMe)_3]_2$	3/2	h/b	Yellow	100—103	36.6 (36.4)	6.0 (5.9)	16.0 (15.6)		396

[a] Abbreviations used: h = n-hexane, b = benzene, a = acetone. [b] These values were determined from the mass spectra. Values quoted are for the ^{121}Sb, ^{32}S and ^{35}Cl isotopes. All values agree with the theoretical values. [c] The C and H analyses for these complexes were performed in our laboratory on a Hewlett—Packard Model 185 CHN analyser. [d] Sb (%): Found (calcd.) 21.6 (22.3). [e] Cl (%): Found (calcd.) 30.4 (30.3).

found necessary to attempt the synthesis of two derivatives of the type $C_5H_5Mn(CO)L_2$ viz., $C_5H_5Mn(CO)[P(OMe)_3]_2$ and $C_5H_5Mn(CO)[P(OPh)_3]_2$. Benzene solutions of the tricarbonyl starting material, together with a five - ten-fold excess of the appropriate ligand were irradiated with UV light. Whereas the desired $P(OMe)_3$ complex could readily be obtained, and is air-stable, the $P(OPh)_3$ complex is air-sensitive and only its IR spectrum was recorded. Since the corresponding thiocarbonyl complex $C_5H_5Mn(CS)[P(OPh)_3]_2$ is air-stable, it seems probable that electronic and not steric factors must be responsible for the instability of the carbonyl analogue.

IR spectra

The IR spectra of the new thiocarbonyl complexes in the CO and CS stretching regions are presented in Table 2. As expected, one ν(CO) absorption (1955 - 1920 cm^{-1}) and one ν(CS) absorption (1255 - 1220 cm^{-1}) are observed for the $C_5H_5Mn(CO)(CS)L$ complexes. A comparison with data for the related $C_5H_5Mn(CO)_2L$ complexes shows that the high frequency (A_1) mode in the dicarbonyls follows the same trend with change of L as the CO stretching mode for the thiocarbonyl complexes.

The IR spectra of the $C_5H_5Mn(CS)L_2$ complexes were also recorded in the ν(CS) region (1225 - 1190 cm^{-1}), one band being observed in each case.

TABLE 2
IR SPECTRA OF THE NEW COMPLEXES[a]

Complex	CS_2 solution (cm^{-1})			n-Hexane solution (cm^{-1})	
	ν(CS)	ν(CO)	ν(CO)[b]	ν(CS)	ν(CO)
$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$	1222	1914	1925[c]	1230	1923
$C_5H_5Mn(CO)(CS)(PMe_2Ph)$	1228	1920	1932[d]	1234	1928
$C_5H_5Mn(CO)(CS)(PPh_3)$[e]	1231	1925	1940[f] 1937[c]	1236	1938, 1929
$C_5H_5Mn(CO)(CS)(AsPh_3)$	1231	1926	1936[c]		1937, 1930
$C_5H_5Mn(CO)(CS)(SbPh_3)$	1230	1925	1935[c]	1237	1932
$C_5H_5Mn(CO)(CS)[P(OEt)_3]$	1236	1933	1945[f]	1243	1950 (sh), 1939
$C_5H_5Mn(CO)(CS)[P(OMe)_3]$	1239	1936	1949[f]	1245	1952, 1943
$C_5H_5Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$	1240	1939	1952[f]	1247	1946, 1940 (sh)
$C_5H_5Mn(CO)(CS)[P(OPh)_3]$	1254	1951	1965[f] 1963[c]		1961, 1954
$C_5H_5Mn(CS)[PMe_2Ph]_2$[g]	1195				
$C_5H_5Mn(CS)[PPh_3]_2$	1193				
$C_5H_5Mn(CS)[P(OEt)_3]_2$	1214				
$C_5H_5Mn(CS)[P(OMe)_3]_2$	1218				
$C_5H_5Mn(CS)[P(OCH_2CH_2Cl)_3]2$	1223				
$C_5H_5Mn(CS)[P(OPh)_3]_2$	1219				
$C_5H_5Mn(CO)[P(OMe)_3]_2$		1865			
$C_5H_5Mn(CO)[P(OPh)_3]_2$		1892			

[a] All bands are strong. [b] This column lists the $A_1\nu$(CO) stretching mode for the corresponding $C_5H_5Mn(CO)_2(L)$ complexes. [c] Ref. 21. [d] Ref. 15. [e] Ref. 11. [f] Ref. 22. [g] No attempt was made to isolate this complex.

These complexes absorb at lower frequencies in this region than do the $C_5H_5Mn(CO)(CS)L$ complexes. The lower CS stretching frequencies for the former can be taken to imply that the C—S bond has become weaker with concomitant strengthening of the Mn—C(S) bond. The difference between the two series of thiocarbonyls, $C_5H_5Mn(CO)(CS)L$ and $C_5H_5Mn(CS)L_2$, is replacement of a CO group by L. A similar bond weakening/bond strengthening effect for C—O/Mn—C(O) bonds has been found on replacement of CO by L in the analogous $C_5H_5Mn(CO)_2L$ complexes [13].

An obvious drawback to the above discussion is that whereas the CO stretching region is well removed from the other bending and stretching modes within the molecules, this is not true for the CS stretching modes. Consequently, the CS band positions are almost certainly affected by coupling with other low frequency modes.

n-Hexane solution spectra of the $C_5H_5Mn(CO)(CS)L$ complexes were also recorded. As noted previously [11], $C_5H_5Mn(CO)(CS)PPh_3$ exhibits two CO absorptions in this solvent. In the present study, a similar effect is observed for the monothiocarbonyl complexes when L = $AsPh_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OCH_2CH_2Cl)_3$ and $P(OPh)_3$ but not for L = $P(C_6H_{11})_3$, PMe_2Ph and $SbPh_3$. A possible reason for this effect is the existence of different conformers in solution [14]. Steric effects are not thought to be important because CO absorption splitting is detected for complexes containing both bulky (e.g. PPh_3) and small ligands [e.g. $P(OMe)_3$]. No splitting of the CS stretching modes is exhibited in n-hexane solution.

NMR spectra

The NMR spectra of all the complexes in CS_2 solution were recorded (Table 3). The splitting of the C_5H_5 resonance, due to coupling with the ^{31}P atoms [15], was used as a diagnostic tool for determining the nature of the new products. The monosubstituted products, $C_5H_5Mn(CO)(CS)L$ (L = phosphine or phosphite) display approximately 1/1 doublets while the disubstituted products exhibit approximately 1/2/1 triplets for the C_5H_5 resonance.

It has been noted previously that for moieties of the type "$C_5H_5M(CO)$", k_{CO} decreases as $\tau(C_5H_5)$ increases [16]. This is also the case for both the CO and CS frequencies in the present work*.

The ligand resonances for the complexed ligands are complicated, and in general, could not be analysed. This complexity arises from the coupling of the protons to the ^{31}P atoms and also from proton—proton coupling within the ligands themselves.

The methoxy resonances in $C_5H_5Mn(CS)[P(OMe)_3]_2$ and $C_5H_5Mn(CO)[P(OMe)_3]_2$ appear as "triplet-like" resonances. At first glance, this would seem to be a case of the protons being coupled equally to both P atoms. However, comparison of the apparent $J(P—H)$ values ($\approx$5.5 Hz) with tne $J(P—H)$ value for the monosubstituted complex, $C_5H_5Mn(CO)(CS)[P(OMe)_3]_2$ [$J(P—H)$ 11.5 Hz] would imply that the coupling constant has been halved in the disubstituted complexes. Also, it is apparent from the

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* k_{CO} and k_{CS} can be calculated from the equation, $\lambda = \mu \cdot k$ (ref. 16) and may be obtained from the authors.

TABLE 3
NMR SPECTRA OF THE NEW COMPLEXES [a]

Complex	C_5H_5	Other
$C_5H_5Mn(CO)(CS)[P(C_6H_{11})_3]$	5.49 doublet (1.2)	Complex at ≈ 8.5, C_6H_{11}
$C_5H_5Mn(CO)(CS)(PMe_2Ph)$	5.73 doublet (1.6)	2.70 complex, Ph; 8.21, 8.30, doublets (9.0), (CH_3)
$C_5H_5Mn(CO)(CS)(PPh_3)$	5.75 doublet (1.6)	2.73 complex, Ph
$C_5H_5Mn(CO)(CS)(AsPh_3)$	5.65	2.70 complex, Ph
$C_5H_5Mn(CO)(CS)(SbPh_3)$	5.50	2.68 complex, Ph
$C_5H_5Mn(CO)(CS)[P(OEt)_3]$	5.53 doublet (1.7)	6.08 multiplet, CH_2; 8.97 triplet (6.9), CH_3
$C_5H_5Mn(CO)(CS)[P(OMe)_3]$	5.48 doublet (1.8)	6.40 doublet (11.5), CH_3
$C_5H_5Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$	5.40 doublet (1.6)	5.79 quartet, OCH_2; 6.40, triplet (5.6), CH_2Cl
$C_5H_5Mn(CO)(CS)[P(OPh)_3]$	6.09 doublet (1.7)	2.80 complex, Ph
$C_5H_5Mn(CS)[PPh_3]_2$	6.23 triplet (1.8)	2.62, 2.88 complex, Ph
$C_5H_5Mn(CS)[P(OEt)_3]_2$	5.81 triplet (1.9)	6.10 multiplet, CH_2; 8.81, triplet (7.0), CH_3
$C_5H_5Mn(CS)[P(OMe)_3]_2$	5.63 triplet (1.7)	6.45 triplet (11.2) [b], CH_3
$C_5H_5Mn(CS)[P(OCH_2CH_2Cl)_3]_2$	5.55 triplet (1.8)	5.80 multiplet OCH_2; 6.36, triplet (5.4), CH_2Cl
$C_5H_5Mn(CS)[P(OPh)_3]_2$	6.41 triplet (1.9)	2.92 complex Ph
$C_5H_5Mn(CO)[P(OMe)_3]_2$	5.97 triplet (1.8)	6.60 triplet (11.2) [b], CH_3

[a] τ values listed, with coupling constant [J(P—H) Hz] given in brackets following the multiplicity. The spectra were recorded for ≈ 0.5M solutions in CS_2. [b] Value in brackets is the separation for the outer two peaks in the apparent triplet.

spectra that the resonances are not true 1/2/1 triplets because of broadening of the central resonance.

Recently, X-ray structure determinations of $C_5H_5Mn(CO)_2PPh_3$ and $C_5H_5Mn(CO)(PPh_3)_2$ have been reported [17]. The results suggest that for the complexes $C_5H_5Mn(L)[P(OMe)_3]_2$ (L = CO, CS), the $P(OMe)_3$ groups can be regarded as being *cis* to each other in an octahedral environment. Therefore, the most likely explanation for the NMR spectra is that they must be analysed as a special case of the $X_9AA'X'_9$ system in which J(P—P) is large [18]. Then J(P—H) is approximately equal to the separation between the outer two peaks (≈ 11 Hz) in the "triplet" and so is similar to the coupling constant for the monosubstituted complex. It can be inferred from this analysis that a large value is anticipated for the *cis* phosphites in these complexes. J(P—P) values for *fac*-$Mn(CO)_3[P(OMe)_3]_2Br$ and $C_5H_5Mn(CO)[P(OCH_2)_3CMe]_2$ have now been reported and are as large as the J(P—P) value found for *mer*-$Mn(CO)_3[P(OMe)_3]_2I$ [23].

The methyl resonance for the PMe_2Ph ligand in $C_5H_5Mn(CO)(CS)PMe_2Ph$ appears as two doublets (apparently 1/1/1/1). This situation has been described before [19], and arises from the *gem*-methyl groups of the ligand becoming magnetically non-equivalent when bonded to an optically active metal centre. In this work, the two doublets are assigned tentatively as arising from the first and third and the second and fourth peaks in the 1/1/1/1 "quartet". This assignment is based on the similarity of J(P—H) for the methyl resonance in $C_5H_5Mn(CO)_2PMe_2Ph$ (8.4 Hz) [15] and J(P—H) found for the thiocarbonyl complex (9.0 Hz). The alternative choice of peaks gives J(P—H) 5.8 Hz.

Mass spectra

The mass spectra of several of the new thiocarbonyl complexes were recorded. The parent ion for each complex is in effect reported in Table 1 (molecular weight). The spectra of the $C_5H_5Mn(CO)(CS)L$ derivatives are very similar to those of the $C_5H_5Mn(CO)_2L$ complexes [20]. However, in the case of the thiocarbonyls, more fragments containing the Mn—C(S) rather than the Mn—C(O) group are observed. A complete analysis of the mass spectra will be reported later.

Conclusion

Under the photochemical conditions employed in this study the substitution reactions of $C_5H_5Mn(CO)_2(CS)$ with Group VA donor ligands take place by successive substitution of the CO groups. These results are in line with Richards' predictions [5] vis-a-vis the strength of the Mn—C(S) bond compared to the Mn—C(O) bond in similar organometallic complexes. Consequently, it appears that the present lack of thiocarbonyl complexes is related to problems with experimental technique (the generation of the CS ligand) rather than the inherent instability of these complexes.

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