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THE FORMATION OF THIOAMIDE COMPLEXES OF MANGANESE, MOLYBDENUM AND RHODIUM FROM ORGANOSILICON AND ORGANOTIN INTERMEDIATES

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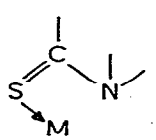
Summary

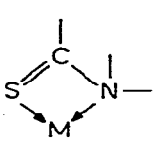
The interaction of *N*-trimethylsilylthioacetanilide and *N*-phenyl-*S*-trimethyltinthioacetimidate, with carbonyl halides of molybdenum, manganese and rhodium afforded a range of *N*-phenylthioacetamido metal carbonyl complexes in which the group behaves as a chelating ligand, and also in two different ways as a bridging group in binuclear products.

Introduction

Transition metal thioamide complexes in which the ligand acts as a formally two electron donor (I) [1—8] have been widely reported, but the chelating mode of bonding as a formally four electron donor (II) or as a formally three electron donor (III) [9—10] are much less common.



(I)



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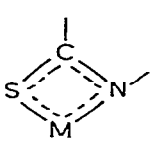
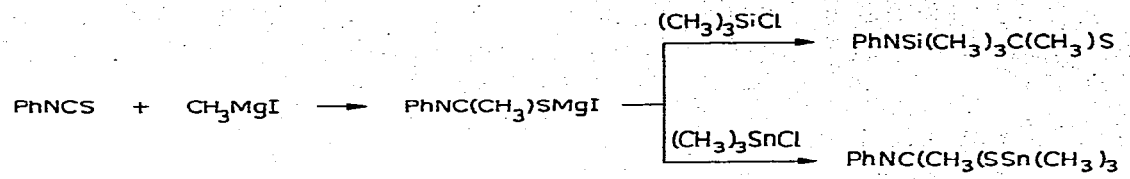


(III)

This has prompted us to prepare trimethylsilyl and trimethylstannyl thioamides, and to examine their role as synthetic intermediates for the formation of transition metal complexes. It is already well established that trimethylsilicon and trimethyltin are excellent leaving groups in a wide range of metathetical reactions yielding novel ligand types [11].

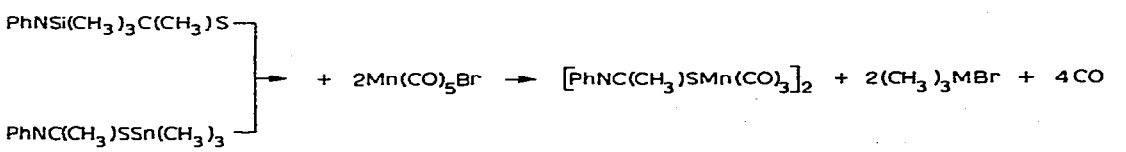
Results and discussion

The trimethylsilyl and trimethyltin reagents were both prepared from phenylisothiocyanate via a Grignard reaction [12].



N-alkyl-*N*-trimethylsilylthioacetamides have been reported to have the thioamide and thioimidate isomers present as equilibrium mixtures, with the appropriate temperature variable NMR spectra [13]. We have observed no variation in the NMR spectrum for the organosilicon derivative formed according to the above scheme. During the course of this work an extensive series of silyl substituted thioamides has been reported, and we agree with the conclusions of Walter et al. [14], based on spectroscopic evidence that our organosilicon reagent exists exclusively in the *N*-trimethylsilylthioacetanilide form as a moisture sensitive solid. In contrast the trimethyltin reagent is not hydrolysed, and on this basis we believe it to have the hydrolytically stable Sn—S bond rather than the very water sensitive Sn—N bond. Thus the organotin reagent is thought to exist in the *N*-phenyl-*S*-trimethyltinthioacetimidate form, though it is possible that the tin is five coordinate as illustrated in III.

Such a difference in the structures of the organosilicon and organotin precursors does not appear to effect either reactivity or overall reaction, thus both *N*-trimethylsilylthioacetanilide and *N*-phenyl-*S*-trimethyltinthioacetimidate undergo reaction with bromopentacarbonylmanganese to give bis(*N*-phenylthioacetamidotricarbonylmanganese).



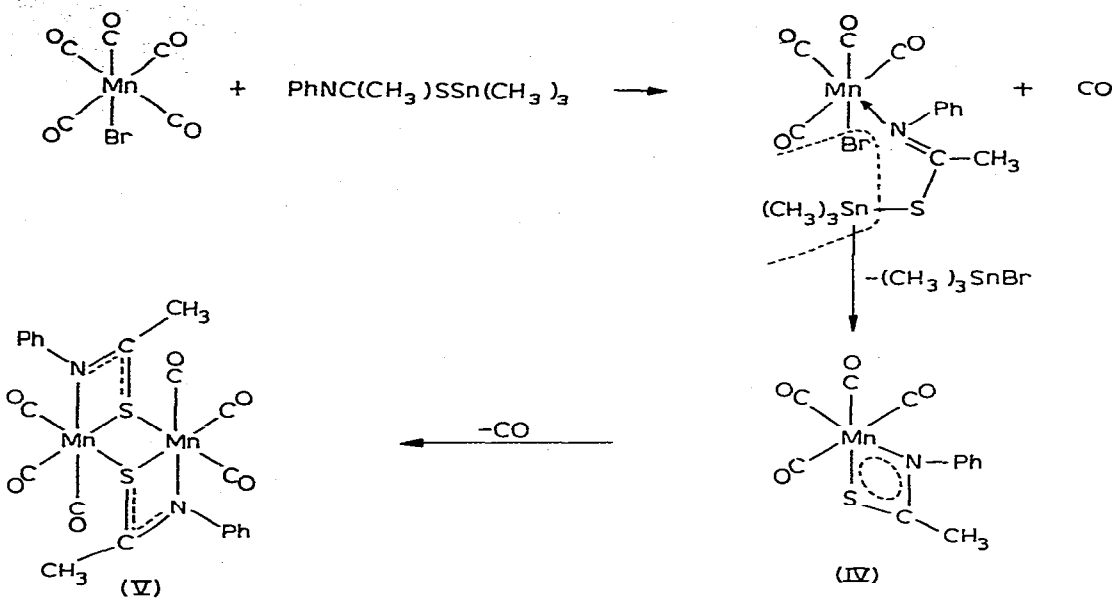
These reactions were carried out at 55°C, and after 4 h the IR spectra of the reaction mixtures in the metal carbonyl region suggested the presence of a *cis*-$L_2Mn(CO)_4$ species (*N*-phenylthioacetamidotetracarbonylmanganese(IV)), but this was never isolated. Further, if before work-up triphenylphosphine was added to the reaction mixture there was formed and isolated triphenylphosphine-*N*-phenylthioacetamidotricarbonylmanganese, with evolution of carbon monoxide, again suggesting the presence of a tetracarbonyl species in the reaction mixture. It is interesting to note that it has been claimed that thiobenzamidotetracarbonyl can be isolated as the monomeric species [15].

A possible route for reaction of the organotin reagent is outlined in Scheme 1, though the initial co-ordination of the reagent to manganese in sulphur is also possible. The corresponding reaction(s) with the organosilicon reagent would involve the elimination of $(CH_3)_3SiBr$ by fission of the Si—N bond.

It is likely that the remaining labile carbon monoxide group in the proposed intermediate (IV) is displaced by intermolecular attack of the sulphur of another molecule to form the sulphur bridged species (V) as the one to be eventually isolated.

The assigned structure and configuration of (V) is based upon the mass spec-

SCHEME 1

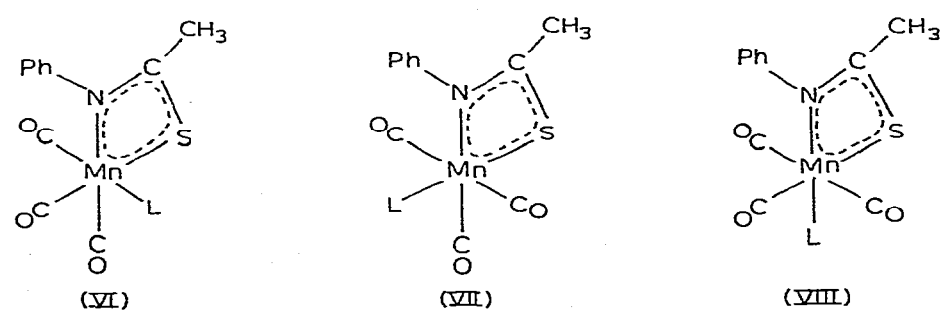


trum, which included the parent ion and the $(MnS)_2^+$ residue, and the IR spectrum which suggests this *trans*-C_{2h} structure as opposed to the less symmetrical *cis*-bridged alternative. Depending upon the exact nature of the bridging ligand both *cis* and *trans* species have been recorded [10,16,17] and a *cis*-structure has been confirmed [18] by X ray diffraction for the related species $[Mn(CO)_3SC(SCH_3)NCH_3]_2$.

It was found possible to break the sulphur bridge in (V) by a variety of donor ligands to produce monomeric complexes in which the thioamide was behaving as a pseudo-allyl ligand, in a mononuclear species.

$[PhNC(CH_3)SMn(CO)_3]_2 + 2L \rightarrow 2PhNC(CH_3)SMn(CO)_3L$
$(L = C_5H_5N, Ph_3P, Ph_2PCH_3, Ph_3As)$

There are three possible structures (VI), (VII) and (VIII) for these complexes. In each of our complexes there are three metal carbonyl stretching modes of approximately equal intensity.

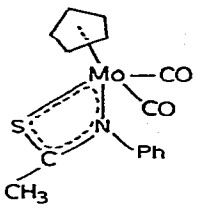


(L = C_5H_5N; Ph_3P; Ph_2PCH_3; Ph_3As)

This would suggest [19] the *fac*-isomer (VI) rather than the two possible *mer*-isomers (VII) and (VIII). Further, in the absence of substantial rearrangement, it is the *fac*-isomer that would arise from the bridge fission of the dimer (V). It is interesting to note that these *fac* complexes have such low symmetry, that each will exist as two diastereoisomers.

The interaction of η^5-cyclopentadienylchlorotricarbonylmolybdenum and *N*-phenyl-*S*-trimethyltinthioacetimidate produced the *N*-phenylthioacetamido-cyclopentadienyldicarbonylmolybdenum (IX).

$$PhNC(CH_3)SSn(CH_3)_3 + \eta^5\text{-}C_5H_5Mo(CO)_3Cl \longrightarrow$$



$$+ (CH_3)_3SnCl$$

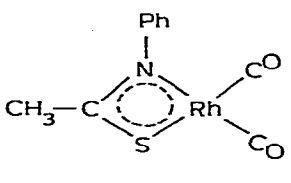
(IX)

Presumably due to the considerable steric requirements of the η^5-cyclopentadienyl group this complex in contrast to the manganese complex showed no tendency to dimerize. In the absence of a plane of symmetry IX exists as two diastereoisomers [20].

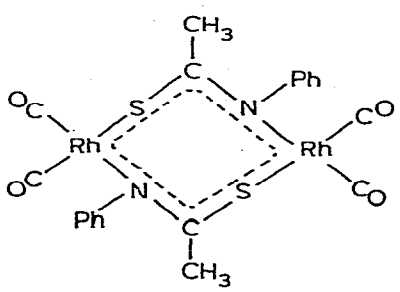
N-Phenyl-*S*-trimethyltinthioacetimidate underwent instantaneous reaction with bis(chlorodicarbonylrhodium) at room temperature in hexane to produce bis(*N*-phenylthioacetamidodicarbonylrhodium) (XI).

$$2PhNC(CH_3)SSn(CH_3)_3 + [Rh(CO)_2Cl]_2 \rightarrow [PhNC(CH_3)SRh(CO)_2]_2 + 2(CH_3)_3SnCl$$

Although the monomeric complex X appears perfectly feasible, the actual product is dimeric. In contrast to the earlier described manganese reaction, however, the dimerization does not involve loss of carbon monoxide.



(X)



(XI)

For the dimer we propose the structure XI closely analogous to that proposed [21] for the corresponding 1,3-diphenyltriazenido complex.

In the IR spectra of the thioamido complexes reported above, we find a band of medium intensity around 1490 cm^{-1}. This lies between the C—N (1250—1350 cm^{-1}) and C=N (1640—1690 cm^{-1}) frequencies of amines and imines and further suggests the S—C—N pseudo-allyl nature of these complexes.

Experimental

All reactions were carried out routinely under an atmosphere of dry nitrogen, and solvents were dried by distillation from potassium benzophenone. IR spectra were recorded in hexane or tetrahydrofuran solution using calcium fluoride 0.1 mm cells on a Perkin—Elmer 257 spectrophotometer; NMR spectra were obtained in carbon tetrachloride or carbon disulphide solution using a Jeol 100 MHz spectrometer. Mass spectra were recorded on a Perkin—Elmer Hitachi RMV-6 spectrometer, and molecular weights were determined on a Mechrolab osmometer.

$Mn(CO)_5Br$ [22] $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ [23] and $[Rh(CO)_2Cl]_2$ [24] were prepared by literature methods.

N-Trimethylsilylthioacetanilide

The reaction was carried out using the advised [12] 50% excess of Grignard reagent. Methyl iodide (39.4 g) was added slowly to magnesium shavings (6.6 g) in diethylether (600 ml). After the reaction was complete, but while the mixture was still warm phenylisothiocyanate (25 g) was added slowly with stirring. The mixture was then stirred vigorously until no further adduct appeared to precipitate. After filtration under nitrogen the remaining solid was washed with dry ether (2 × 100 ml). To the washed solid was then added ether (200 ml) followed by trimethylchlorosilane (20 g) and the mixture stirred (12 h) at room temperature. After filtration, ether was removed from the filtrate by distillation, and the last traces under reduced pressure (25°C/15 mmHg). The remaining brown solid was recrystallized from hexane to yield the product (20 g, 42%). (Found: C, 58.6; H, 7.32; N, 6.38. Calcd.: C, 59.3; H, 7.64; N, 6.29%). ^1H NMR spectrum in CCl_4; τ values 3.04—3.44 (C_6H_5); 7.98 singlet (CH_3); 9.76 singlet ($(CH_3)_3Si$).

N-Phenyl-S-trimethyltinthioacetimidate

This was prepared in an exactly analogous manner to the silicon compound above by adding trimethyltinchloride in place of trimethylchlorosilane. The product was purified by distillation under vacuum (89°C/0.02 mmHg). Yield 60%. (Found: C, 41.7; H, 5.46; N, 4.37. Calcd.: C, 42.1; H, 5.42; N, 4.46%). ^1H NMR spectrum in CCl_4; τ values 2.71—3.50 (C_6H_5); 7.97 singlet (CH_3); 9.58 singlet ($(CH_3)_3Sn$) with satellites $J(^{119}Sn—H)$ 57.3 Hz and $J(^{117}Sn—H)$ 54.7 Hz.

Interaction of N-trimethylsilythioacetanilide and manganese pentacarbonyl bromide

To a stirred suspension of the pentacarbonyl bromide (1 g) in hexane (15 ml) at 55°C was added the thioacetanilide (1.2 g). Solvent was removed (20°C/15 mmHg) after 4 h, and the resultant yellow oil was purified (20°C/0.01 mmHg) for 1 h to remove last traces of trimethylchlorosilane. The residue was recrystallized from hexane to give bis(*N*-phenylthioacetamidotricarbonylmanganese) (0.3 g, 29%) m.p. 135 (dec.) (Table 1). Mass spectrum 578 $[Mn(CO)_3PhNC(CH_3)S]_2^+$ $(M)^+$; 522, $(M - 2CO)^+$; 495, $(M - 3CO)^+$; 466, $(M - 4CO)^+$; 438, $(M - 5CO)^+$; 410, $(M - 6CO)^+$; 395, $(Mn_2PhNC(CH_3)S(PhNCS))^+$; 380, $(Mn_2(PhNCS)_2)^+$; 333, $(Mn_2PhNC(CH_3)S)(NC(CH_3)S))^+$; 205, $(MnPhNC(CH_3)S)^+$; 174,

TABLE 1

THIOAMIDE COMPLEXES OF MANGANESE, MOLYBDENUM AND RHODIUM

Compound	Found (calcd.) (%)			ν(CN) (cm^{-1}) (KBr)	ν(CO) (cm^{-1})	NMR τ values (ppm)
	C	H	N			
$[PhNC(CH_3)SMn(CO)_3]_2$	45.7 (45.7)	2.66 (2.79)	4.82 (4.84)	1489	2037(w), 2017(s), 1935(s), 1917(s) [a]	2.34–2.84(Ph); 7.84(CH_3) [d]
$[PhNC(CH_3)SMn(CO)_3PPh_3]$	63.1 (63.2)	4.44 (4.20)	2.63 (2.54)	1483	2026(s), 1946(s), 1917(s).	2.24–3.50(Ph); 8.20 doublet J = 1 Hz (CH_3) [c]
$[PhNC(CH_3)SMn(CO)_3(CH_3PPh_2)]$	58.9 (58.9)	4.33 (4.33)	2.89 (2.86)	1486	2025(s), 1945(s), 1913(s).	2.30–3.63(Ph); 7.97 doublet J = 1.8 Hz (CH_3PPh); 8.24 doublet J = 1 Hz (CH_3–C) [c]
$[PhNC(CH_3)SMn(CO)_3AsPh_3]$	58.3 (58.5)	3.84 (3.89)	2.40 (2.35)	1485	2019(s), 1939(s) 1914(s).	2.37–3.50(Ph); 8.44(CH_3) [b]
$[PhNC(CH_3)SMn(CO)_3C_5H_5N]$	51.8 (52.2)	3.64 (3.56)	7.29 (7.61)	1487	2021(s), 1933(s), 1913(s).	1.20(C_5H_5N); 2.10–3.10 (C_5H_5N and Ph); 7.95(CH_3) [c]
$[PhNC(CH_3)SMo(CO)_2(\eta^5\text{-}C_5H_5)]$	48.8 49.1)	3.50 (3.57)	3.45 (3.81)	1484	1965(s), 1882(s)	2.60–3.20(Ph); 4.61(η^5-C_5H_5); 8.13(CH_3) [c]
$[PhNC(CH_3)SRh(CO)_2]_2$	38.7 (38.9)	2.54 (2.61)	4.26 (4.53)	1485	2081(s), 2054(s), 2018(s).	2.60–3.60(Ph); 7.94(CH_3) [b]

[a] In tetrahydrofuran, all other IR spectra in hexane. [b] In carbon disulphide. [c] In carbon tetrachloride. [d] In d^6-dimethylsulphoxide.

$(MnS)_2^+$; 150, $(PhNC(CH_3)S)^+$; 135, $(PhNCS)^+$; 118, $(PhNCCH_3)^+$; 91, $(PhN)^+$; 87, $(MnS)^+$; 77, $(Ph)^+$; 55 $(Mn)^+$; 41, $(CH_3CN)^+$.

Following the same procedure *N*-phenyl-*S*-trimethyltinacetimidate gave the same product in essentially the same yield.

N-Phenylthioacetamido(pyridine)tricarbonylmanganese

To a stirred solution of bis(*N*-phenylthioacetamidotricarbonylmanganese) (0.52 g) in tetrahydrofuran (5 ml) was added pyridine (1 ml). After 3 h solvent was removed (25°C/0.01 mmHg) to leave a yellow oil. The oil was recrystallized from hexane to give the yellow crystalline product (0.2 g, 80%) m.p. 84—86°C (Table 1).

N-Phenylthioacetamido(triphenylphosphine)tricarbonylmanganese

To a stirred solution of bis(*N*-phenylthioacetamidotricarbonylmanganese) (0.3 g) in tetrahydrofuran at 65°C was added triphenylphosphine (0.28 g). After 15 min solvent was removed (20°C/0.1 mmHg), and the residue recrystallized from 20 : 80 dichloromethane/hexane to give yellow crystals of the product (0.345 g, 60%) m.p. 159—162°C (Table 1).

This compound was also prepared in situ from the original reaction mixture as outlined below, suggesting the presence of monomeric *N*-phenylthioacetamidotetracarbonylmanganese prior to work up, when dimerization occurred.

N-Phenyl-*S*-trimethyltinthioacetimidate (0.34 g) was added to a stirred suspension of manganese pentacarbonyl bromide (0.3 g) in hexane (5 ml). After stirring for 4 h no further reaction took place but when triphenylphosphine (0.28 g) was added, there was a substantial evolution of carbon monoxide. When effervescence had ceased solvent was removed (20°C/15 mmHg) and the residual yellow solid pumped further (25°C/0.01 mmHg) to remove last traces of trimethyltin bromide. The residue was recrystallized from 20 : 80 dichloromethane/hexane to give the yellow crystalline product (0.48 g, 80%) m.p. 160—162°C, identical to that obtained above (Table 1).

N-Phenylthioacetamido(methyldiphenylphosphine)tricarbonylmanganese

To a stirred solution of bis(*N*-phenylthioacetamidotricarbonylmanganese (0.05 g) in tetrahydrofuran (2 ml) was added methyldiphenylphosphine (0.2 g). After 2 h solvent was removed (20°C/15 mmHg), and the remaining yellow residue pumped (25°C/0.01 mmHg) for 2 h to remove excess phosphine. The residue was recrystallized from 20 : 80 dichloromethane/hexane to yield the yellow crystalline product (0.07 g, 88%) m.p. 128—129°C (Table 1).

N-Phenylthioacetamido(triphenylarsine)tricarbonylmanganese

By the method described above the interaction of triphenylarsine and bis-(*N*-phenylthioacetamidotricarbonylmanganese) gave the product (69%) as orange crystals m.p. 131—132°C (Table 1).

Interaction of (η^5-cyclopentadienyl)molybdenum tricarbonyl chloride and N-phenyl-S-trimethyltinthioacetimidate

To a stirred suspension of the carbonyl chloride (0.5 g) in hexane (15 ml) at 60°C was added the thioacetimidate (0.54 g). After 2 h solvent was removed

(20°C/15 mmHg) and the residual red oil pumped for a further 2 h to remove trimethyltinchloride. Recrystallization of the oil from 10 : 90 dichloromethane/hexane gave deep red crystals of *N*-phenylthioacetamido-η^5-cyclopentadienyldicarbonylmolybdenum (0.36 g, 56%) m.p. 125—127°C (Table 1). Mass spectrum 367, $(PhNC(CH_3)SMo(\eta^5\text{-}C_5H_5)(CO)_2)^+$ (M^+); 339, $(M - CO)^+$; 311, $(M - 2CO)^+$; 161, $((\eta^5\text{-}C_5H_5)Mo)^+$; 135, $(PhNCS)^+$; 118, $(PhNC(CH_3))^+$; 77, Ph^+; 65, $(\eta\text{-}C_5H_5)^+$; 41, $(CH_3CN)^+$.

Interaction of bis(dicarbonylchlororhodium) and N-phenyl-S-trimethyltinthioacetimidate

To a stirred solution of the carbonyl chloride (0.2 g) in hexane (5 ml) at room temperature was added *N*-phenyl-*S*-trimethyltinthioacetimidate (0.32 g). This produced an instantaneous purple colouration, and after 10 min solvent was removed (20°C/15 mmHg), and the resulting solid pumped for a further 1 h to remove trimethyltin chloride. The residue was recrystallized from hexane to give bis(*N*-phenylthioacetamidodicarbonylrhodium) (0.138 g, 44%) m.p. 134°C (dec.) as deep purple crystals. (Table 1). (Mol.wt. osmometrically in benzene 646, calcd. 618).

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