

Reactivity of 1-Isothiocyanato Six Membered Silatrane towards Transition Metal Carbonyls

Gurjaspreet Singh

Department of Chemistry, Panjab University, Chandigarh, India.

ABSTRACT: This manuscript deal with the reaction of the 1-isothiocyanato six membered silatrane with different transition metal carbonyls. The adducts **1, 2, 3, 4** and **5** so formed were characterized by elemental analysis, infrared spectroscopy, ^1H , ^{13}C , ^{29}Si NMR spectroscopy. $\eta^1\text{-S}$ bonding pattern was observed amongst the various coordination modes of the isothiocyanato group.

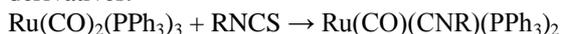
KEYWORDS: 1-Isothiocyanato six membered silatrane, Metal carbonyl, $\eta^1\text{-S}$ bonding

I. INTRODUCTION

Isothiocyanate group has been shown to exhibit ambidentate character with both monodentate and bridging bonding capabilities. In contrast, only a few reports on the behavior of RNCS with metal carbonyl are described [1,2]. Majority of such compounds known so far incorporate isothiocyanate group in a $\eta^2\text{-CS}$ coordination mode. For example, adduct resulting from the reaction of iron tris(triphenylphosphine) dicarbonyl with alkyl/aryl isothiocyanate reveals $\eta^2\text{-CS}$ mode of coordination [3-8]. The reaction may be represented as below:



Besides exhibiting $\eta^2\text{-CS}$ mode of coordination to metal carbonyls, alkyl isothiocyanates can also undergo desulfurization [2]. For example, reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with RNCS (R=Ph, Et, Me) yields dithiocarbamate derivatives.



Whereas incase of Mo, W, Cr carbonyls we found $\eta^1\text{-S}$ bonding pattern of the isothiocyanato group. Prompted by these studies, we are interested in studying the reactions of 1-Isothiocyanato six membered silatrane with different transition metal carbonyls.

II. MATERIALS AND METHODS

All operations were carried out under dry nitrogen atmosphere. Dichloroethane and acetonitrile were freshly distilled under inert atmosphere from phosphorus pentoxide before use. $\text{Mo}(\text{CO})_4(\text{CH}_3\text{CN})_2$, $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_2$, $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$, *Cis*- $\text{W}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$, 1-isothiocyanato six membered ring silatrane were synthesized according to the procedure reported in literature [9,10]. IR spectra were obtained as thin films or nujol mulls on Perkin-Elmer RX-1 FTIR spectrophotometer. ^1H (300.4 MHz), ^{13}C (75.45 MHz), ^{29}Si NMR (59.60 MHz) spectra were obtained on JEOL AL 300 instrument. Chemical shifts were reported with respect to TMS as an external standard.

III. SYNTHESIS

Reaction of 1-Isothiocyanato six membered silatrane with $\text{Mo}(\text{CO})_4(\text{CH}_3\text{CN})_2$ (**1**)

To the pale yellow colored solution of $\text{Mo}(\text{CO})_4(\text{CH}_3\text{CN})_2$ (1.40 g, 4.30 mmol) and 1,2-dichloroethane, taken in two necked round bottomed flask, solution of 1-isothiocyanato six membered silatrane (4.30 g, 8.60 mmol) was added. Contents were heated at 80 °C for 2 h in a constant temperature oil bath. Reaction mixture was allowed to attain room temperature and the solvent was removed under reduced pressure. Light brown mass was left behind was stirred in solvent ether for 15 min, filtered and dried.

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Reaction of 1-Isothiocyanto six membered silatrane with $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$ (2)

$\text{Cis-Mo}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$, (1.60 g, 4.30 mmol) was dissolved in dry 1,2-dichloroethane in two necked round bottomed flask. Solution of 1-isothiocyanto six membered silatrane (4.30 g, 8.60 mmol) was added drop wise with help of hypodermic syringe in to the flask. The reaction mixture was heated at 80 °C in a constant temperature oil bath. The color of reaction mixture turned light brown after one hour of heating. Contents were heated for 5 h. Then, reaction mixture was allowed to attain room temperature. Solvent was removed under reduced pressure. Light brown colored solid was extracted using solvent diethyl ether, which was filtered and dried under vacuum.

Reaction of 1-Isothiocyanto six membered silatrane with $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_2$ (3)

$\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_5)_2$ (1.50 g, 4.30 mmol) was made to react with 1-isothiocyanto six membered silatrane (4.30 g, 8.60 mmol) in 1,2 dichloroethane medium in a manner similar to that described above for the piperidine analogue 2.

Reaction of 1-Isothiocyanto six membered silatrane with $\text{Cis-W}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$ (4)

$\text{Cis-W}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$ (2.00 g, 4.30 mmol) was dissolved in dry dichloroethane in two necked round bottomed flask. Solution of 1-isothiocyanto six membered silatrane (4.30 g, 8.60 mmol) was added to it and reaction mixture was heated to 80 °C. During the course of the reaction, color of reaction mixture was changed to light brown. Contents were allowed to attain room temperature after 8 h of heating. The solvent was removed and solid was extracted using diethyl ether. The light brown solid was filtered and dried under vacuum.

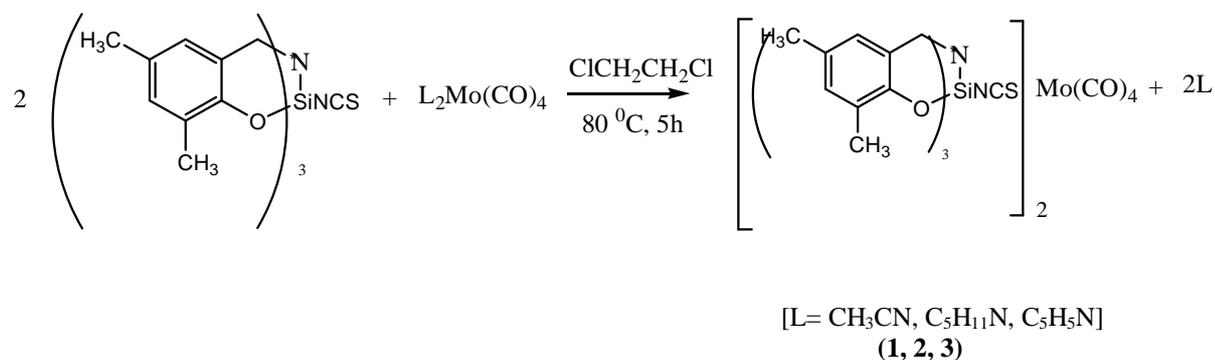
Reaction of 1-Isothiocyanto six membered silatrane with $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (5)

Chromium hexacarbonyl (1.00 g, 4.50 mmol) was taken in a two necked round bottomed flask fitted with reflux condenser. Acetonitrile (20 ml) was added to it and contents were refluxed for 1 h at 85 °C in a constant temperature oil bath. Solution of 1-isothiocyanto six membered silatrane (4.50 g, 9.00 mmol) was added to it and contents were refluxed for five hours. The reaction mixture was allowed to cool down and solvent was removed under reduced pressure. A dirty white solid left behind was extracted using diethyl ether and dried under vacuum.

IV. RESULTS AND DISCUSSION

a) Reaction of 1-Isothiocyanto six membered silatrane and molybdenum(0) carbonyls

The reaction of 1-isothiocyanto six membered ring silatrane with molybdenum hexacarbonyl fails to occur in non-coordinating solvents like decalin and 1,2-dichloroethane even under drastic conditions (80-150 °C, 24 h) and the starting materials are recovered in quantitative yields. Alternatively, substituted molybdenum tetracarbonyls such as $\text{Mo}(\text{CO})_4(\text{CH}_3\text{CN})_2$, $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_2$, $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$ have been found to react with the title silatrane in 1,2-dichloroethane medium at 80 °C in 5 h to yield a dirty white solid. Elemental analysis of the solid obtained in each case corresponds to the composition, $\text{Mo}(\text{CO})_4[\text{NCS}.\text{Si}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}]_2$. The compound thus obtained is quite stable under inert conditions and is soluble in dimethyl sulfoxide. The reaction may be represented as follows (Scheme 1):



Scheme 1. Reaction of 1-isothiocyanto six membered silatrane and molybdenum(0) carbonyls.

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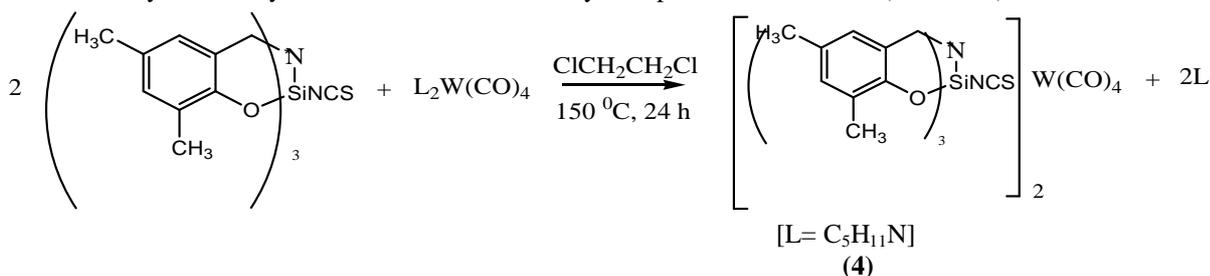
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IR Spectra: The infrared spectrum of complex of 1-isothiocyanato six membered silatrane with molybdenum(0) carbonyls has been obtained either in nujol mull or 4000-400 cm^{-1} range. The most significant region in infrared spectrum of the complex lies between 2200-1700 cm^{-1} . A strong peak (in nujol) at 2092 cm^{-1} has been ascribed to the $\nu_{\text{as}}\text{NCS}$ mode. Thus, a negative spectral shift of 23 cm^{-1} is observed as compared to the parent silatrane ($\nu_{\text{as}}\text{NCS}$:2115 cm^{-1}). Amongst the known coordination complexes of alkyl isothiocyanates in which $\eta^2\text{-CS}$ coordination mode is the most common, a large negative spectral shift of the order of 400-500 cm^{-1} relative to the free ligand is reported [1,6]. In such complexes, the νNCS modes are generally observed at 1600-1700 cm^{-1} . Thus, in the present case a marginal shift of 23 cm^{-1} does not correspond to the $\eta^2\text{-CS}$ coordination. Instead, $\eta^1\text{-sulfur}$ as the donor site may be suggested. The marginal spectral shift may be a consequence of $\sigma\text{-donor}/\pi\text{-acceptor}$ ability of the sulfur atom. Contrary to the four νCO absorption bands (2000, 1930, 1880, 1780 cm^{-1}) found in the $\text{cis-Mo(CO)}_4(\text{C}_5\text{H}_{11}\text{N})_2$, the silatrane adduct shows a single strong absorption at 1920 cm^{-1} . Literature records similar spectral features in the νCO region in many related compounds. These results are analyzed in the light of trans disposition of the bulky incoming donor ligands. Accordingly, similar stereochemistry may be thought to arise in the present compound too, where the sulfur atom of the silatrane adopts a trans structure. These include bands at 2920, 1466, 1370, 1061 and 487 cm^{-1} attributable to νCH_2 (aliphatic), $\delta_{\text{as}}\text{CH}_2$, $\delta_{\text{s}}\text{CH}_2$, $\nu\text{Si-O(C)}$ and νCS respectively. Infrared spectrum of the complex in solution state is also found to be similar to that observed in the nujol mull. The results clearly suggest that the molecule remains non-fluxional in the solution state.

NMR Spectra: ^1H NMR spectrum of the complex in $\text{DMSO-}d_6$ reveals singlets at 2.16 and 2.18 ppm owing to Ar-CH_3 , singlet at 4.24 ppm due to NCH_2 , singlets at 6.72 and 6.75 ppm due to Ar-H respectively. As expected, the signals due to diethyl ether molecule are absent in the adduct. ^{13}C NMR spectrum of the complex reveals a signal at 206.12 ppm attributable to the carbonyl group linked to molybdenum atom. Comparison of this chemical shift value with that of the starting molecule $\text{cis-Mo(CO)}_4(\text{C}_5\text{H}_{11}\text{N})_2$ [$\delta^{13}\text{C}(\text{CO})$: 219.61, 219.86 ppm] reveals an upshift of 13.7 ppm. By analogy with the literature data [7], increased shielding of carbonyl resonance in the complex reflects a significant synergic bond between the transition metal and donor sulfur atom of the 1-Isouthiocyanato six membered silatrane. Besides this peak, ^{13}C NMR spectrum reveals two singlets at 16.21, 20.57 ppm due to Ar-CH_3 , singlets at 56.79 ppm due to NCH_2 , signals at 125.16, 126.91, 127.83, 129.03, 131.11 and 151.09 ppm attributed to aromatic carbons respectively. Isothiocyanato carbon appears as a triplet at 128.90, 129.09 and 129.26 ppm with coupling constant [$^1J(^{13}\text{C-}^{14}\text{N}) = 13.58\text{Hz}$]. In literature [8], a correlation between $\delta^{13}\text{C}(\text{CO})$ and infrared absorption of νCO mode has been reported. It is suggested that an increased shielding of carbonyl carbon results in the positive shift of νCO mode as a consequence of synergic effect. The present complex also shows similar spectral trends. Thus, a $\sigma\text{-donor}/\pi\text{-acceptor}$ ability of the donor sulfur atom is expected in the complex. Similarly, ^{29}Si NMR spectrum appears as a triplet of equal intensities at -144.40, -144.96 and 145.51 ppm with [$^1J(^{29}\text{Si-}^{14}\text{N}) = 33.07\text{ Hz}$].

b) Reaction of 1-Isouthiocyanato six membered silatrane and tungsten carbonyl

The reactions of 1-Isouthiocyanato silatrane with tungsten carbonyls have been attempted. The silatrane fails to react with tungsten hexacarbonyl even under the drastic conditions (150 $^\circ\text{C}$, 24 h) in solvent like decalin. However, the reaction of $\text{cis-W(CO)}_4(\text{C}_5\text{H}_{11}\text{N})_2$ with 1-isouthiocyanato silatrane in refluxing 1,2-dichloroethane results in the formation of a light brown solid. Elemental analysis of a solid correspond to the composition $\text{W(CO)}_4[\text{NCS.Si(OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}]_2$. The compound isolated above is quite stable in nature under inert conditions and is soluble only in dimethyl sulfoxide. The reaction may be represented as follows (Scheme 2):



Scheme 2. Reaction of 1-isouthiocyanato six membered silatrane and tungsten carbonyl.

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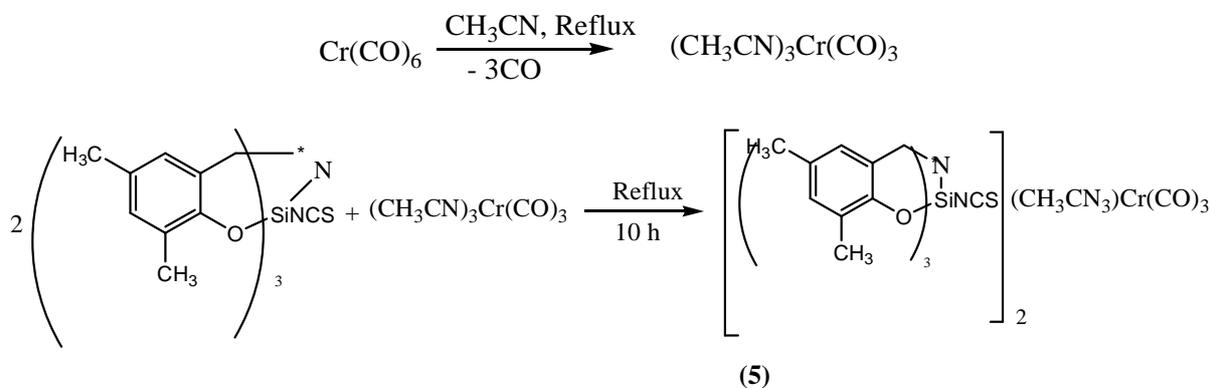
IR Spectra: Infrared spectrum of the complex **4** in nujol mull reveals a strong peak at 2090 cm^{-1} ascribed to the coordinated $\nu_{\text{as}}\text{NCS}$. The negative spectral shift of 25 cm^{-1} as compared to that of parent silatrane ($\nu_{\text{as}}\text{NCS}$: 2115 cm^{-1}) has been attributed to η^1 -S coordination of isothiocyanato group to the tungsten(0) atom. In the νCO region ($2000\text{-}1700\text{ cm}^{-1}$), the spectrum is dominated by a single strong absorption band at 1910 cm^{-1} . By analogy with the literature trends, single absorption of the carbonyl groups may suggest the trans disposition of incoming silatranyl ligands. Similar spectral trends are also observed for **2** described earlier. Other absorption bands at 2927 , 1469 , 1378 , 1065 and 792 cm^{-1} have been attributed to νCH_2 (aliphatic), $\delta_{\text{as}}\text{CH}_2$, $\delta_{\text{s}}\text{CH}_2$, $\nu\text{Si-O(C)}$ and νCS modes.

NMR Spectra: ^1H NMR spectrum of the complex **4** in $\text{DMSO-}d_6$ reveals singlets at 2.17 and 2.20 ppm owing to Ar-CH_3 , singlet at 4.31 ppm due to NCH_2 , singlets at 6.69 and 6.73 ppm due to Ar-H respectively. As expected, the ^1H NMR spectrum reveals the absence of piperidine group. ^{13}C NMR spectrum of the complex in $\text{DMSO-}d_6$ reveals a signal at 201.86 ppm attributable to the carbonyl group attached to the tungsten atom. Significantly, this resonance suffers an upfield shift by $\sim 10\text{ ppm}$ as compared to the starting metal carbonyl complex i.e $\text{cis-W(CO)}_4(\text{C}_5\text{H}_{11}\text{N})_2$ [$\delta^{13}\text{C(CO)}$ 191.57]. The ^{13}C NMR spectrum also reveals signals at 16.71 , 19.47 ppm due to Ar-CH_3 , singlets at 57.39 ppm due to NCH_2 signals at 118.06 , 124.87 , 125.16 , 128.53 , 131.57 and 151.29 ppm are attributed to aromatic carbons respectively. Isothiocyanato carbon appears as a triplet at 127.78 , 127.94 and 128.13 ppm with coupling constant [$^1J(^{13}\text{C-}^{14}\text{N}) = 13.20\text{ Hz}$]. This is similar to that of isothiocyanato group in parent silatrane. The results are in fair agreement with those described for the corresponding molybdenum carbonyl derivative. Thus, a synergic bonding between the transition metal and the silatranyl sulfur atom is suggested in the present compound also.

^{29}Si spectrum of the complex exhibits a triplet of equal intensity at -144.41 , -144.95 and -146.54 ppm with coupling constant [$^1J(^{29}\text{Si-}^{14}\text{N}) = 33.67\text{ Hz}$]. Thus, pentacoordination of silicon atom and linearity of Si-NCS group is retained even in the complex.

c) Reaction of 1-Isothiocyanato six membered silatrane and chromium carbonyl

The reaction of chromium hexacarbonyl with 1-isothiocyanato six membered silatrane fails to occur in a non-coordinating solvent like decalin. However, reaction of 1-isothiocyanato six membered silatrane with chromium hexacarbonyl in refluxing acetonitrile results in the formation of greenish solid. Elemental analysis of the product corresponds to the composition $\text{Cr(CO)}_3(\text{CH}_3\text{CN})[\text{NCS.Si(OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}]_2$. The reaction is supposed to proceed in two steps. In the first step, acetonitrile reacts thermally with chromium hexacarbonyl to form chromium tricarbonyl complex [9]. In the second step, the reactive intermediate, $\text{Cr(CO)}_3(\text{CH}_3\text{CN})_3$, reacts with silatrane to yield the compound, $\text{Cr(CO)}_3(\text{CH}_3\text{CN})[\text{NCS.Si(OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}]_2$. Solid obtained above is hygroscopic in nature and is soluble in dimethyl sulfoxide. Thus, the overall reaction may be represented as follows (Scheme 3):



Scheme 3. Reaction of 1-isothiocyanato six membered silatrane and chromium carbonyl.

IR Spectra: Infrared spectrum of the complex **5** in nujol and HCB shows a strong absorption at 2115 cm^{-1} attributable to νCN of the isothiocyanato group. The typical metal carbonyl absorption region ($2000\text{-}1700\text{ cm}^{-1}$) reveals two

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absorptions at 1935 and 1900 cm^{-1} , while the precursor compound, $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$, exhibits two strong absorptions at 1910 and 1718 cm^{-1} . Thus, a positive shift of νCO mode in the resulting complex may be attributed to the ability of the sulfur atom to form synergic bond with the chromium atom. A weak band at 2280 cm^{-1} has been attributed to the $\nu\text{C}\equiv\text{N}$ of the coordinated acetonitrile and shows a positive shift of $\sim 30 \text{ cm}^{-1}$ as compared to free acetonitrile ($\nu\text{C}\equiv\text{N}$ 2310 cm^{-1}). Other routine absorptions at 2925, 1460, 1370, 1060 cm^{-1} are ascribed to the $\nu\text{CH}_2(\text{aliphatic})$, $\delta_{\text{as}}\text{CH}_2$, $\delta_{\text{s}}\text{CH}_2$, $\nu\text{Si-O}(\text{C})$ respectively.

NMR Spectra: ^1H NMR spectrum of the complex **5** in $\text{DMSO}-d_6$ reveals singlets at 2.19 and 2.21 ppm owing to Ar-CH_3 , singlet at 4.27 ppm due to NCH_2 , singlets at 6.91 and 6.99 ppm due to Ar-H respectively. A singlet observed at 2.01 ppm has been ascribed to CH_3 group of coordinated acetonitrile. Proton integration ratio of various peaks is in agreement with the proposed formulation of the complex.

^{13}C NMR spectrum of the complex reveals signals at 15.71, 20.17 ppm due to Ar-CH_3 , singlets at 59.01 ppm due to NCH_2 , signals at 124.06, 127.81, 128.17, 129.43, 130.57 and 150.22 ppm are attributed to aromatic carbons respectively. Isothiocyanato carbon appears as a triplet at 128.80, 128.97 and 129.14 ppm with coupling constant [$^1J(^{13}\text{C}-^{14}\text{N}) = 12.82\text{Hz}$]. Two singlets at 119.91 and 1.18 ppm are ascribed to the coordinated acetonitrile. The carbonyl groups appear at 212.16 and 213.71 ppm. The upfield shift ($\sim 10\text{ppm}$) as compared to $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ [$\delta^{13}\text{C}(\text{CO}) : 221.34, 223.12 \text{ ppm}$] supports the synergic bond between the silatranyl sulfur and the metal atom^[8].

Table 1 summarizes the results obtained from the present study along with the possible mode of coordination of the title silatrane with transition metal carbonyls.

Table 1. Possible site of coordination of 1-Isothiocyanato silatrane with transition metal carbonyls.

Lewis acid	Composition of adduct	Coordination site
$\text{Mo}(\text{CO})_4(\text{CH}_3\text{CN})_2$	$[\text{Sil}]_2 \cdot \text{Mo}(\text{CO})_4$	$\eta^1\text{-S}$
$\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$	$[\text{Sil}]_2 \cdot \text{Mo}(\text{CO})_4$	$\eta^1\text{-S}$
$\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_2$	$[\text{Sil}]_2 \cdot \text{Mo}(\text{CO})_4$	$\eta^1\text{-S}$
$\text{W}(\text{CO})_4(\text{C}_5\text{H}_{11}\text{N})_2$	$[\text{Sil}]_2 \cdot \text{W}(\text{CO})_4$	$\eta^1\text{-S}$
$\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$	$[\text{Sil}]_2 \cdot \text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})$	$\eta^1\text{-S}$

V. APPLICATIONS

Silatrane is a valuable object for medicinal chemistry [11,12] owing to the broad spectrum of biological activities they possess. They find applications as bactericides [13] and fungicides [14], as anticancer [15] and antitumour [16] agents and are also useful for immobilizations of DNA [17].

VI. CONCLUSIONS

The reactions of 1-isothiocyanato six membered silatrane with $\text{M}(\text{CO})_4\text{L}_2$ ($\text{M}=\text{W},\text{Mo}$; $\text{L}=\text{CH}_3\text{CN}$, $\text{C}_5\text{H}_{11}\text{N}$, $\text{C}_5\text{H}_5\text{N}$) or $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ afford compounds of the composition $[\text{NCS.Si}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}]_2\text{M}(\text{CO})_4$, ($\text{M}=\text{W},\text{Mo}$) or $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})$ $[\text{NCS.Si}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}]_2$ respectively. A detailed spectral data of these compounds reveal that the sulfur atom of silatrane molecule behaves as a two electron donor. The spectral studies also provide evidence in favour of synergic bond between the silatranyl sulfur and transition metal centre. The potential donor site of sulfur is in accord with the unique structure of the silatrane. Although, the conclusive structural features of these complexes are yet

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to be confirmed by X-ray crystal analysis, the solution state spectral data gathered here may provide evidence for the trans silatranyl disposition in these compounds. This may be due to the steric effects of the bulky silatrane molecules acting as donor system.

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