

## Synthesis and Halogenation Oxidation of Arylthiosemicarbazide Derivatives of Molybdenumhexacarbonyl

A.NATH<sup>1</sup>, R.V.PRASAD<sup>2</sup>

<sup>1</sup> Department of Chemistry, B.R.D.P.G. College Deoria- 274001 India.

<sup>2</sup> Department of Chemistry A.N.D.Kisan P.G.College Babhnan Gonda. U.P.

Corresponding Author id:- a.nath76.brdpg@gmail.com

### Abstract

Reactions of five arylthiosemicarbazides (L), viz, phenylthiosemicarbazide (ptsc), o-tolylthiosemi-carbazide (ottsc), p-tolylthiosemicarbazide (pttsc), o-anisylthiosemicarbazide (oatsc) and p-anisyl-thiosemicarbazide (patsc) with Mo(CO)<sub>6</sub> have been performed both by reflux and ultra-violet irradiation methods in which only monosubstituted product [(L)Mo(CO)<sub>5</sub>] are obtained several mixed ligand tungstencarbonyl derivatives, viz, [(o-phen or 2,2'-bipy)(L)Mo(CO)<sub>3</sub>] and [(Ph<sub>3</sub>P or Ph<sub>3</sub>As)-(L)Mo(CO)<sub>4</sub>] have also been synthesized. Halogenations of [(L)Mo(CO)<sub>5</sub>] yielded heptacoordinate [(L)Mo(CO)<sub>4</sub>X<sub>2</sub>] (X= Br or I). The complexes have been characterized by micro analytical data, conductivity and IR measurement. The CO-CO stretch-stretch interaction constant of [(L)Mo(CO)<sub>5</sub>] derivatives have also been evaluated from IR data.

**Key words:** Molybdenum Carbonyl, Arylthiosemicarbazide Ligand, C-O force constant.

### Introduction

There have been considerably study of the ligand behavior of sulphur donors like dialkyl or diarylsulphide<sup>1</sup>, dialkyl or diarylthioalkanes<sup>2</sup>, 2-thiouracil<sup>3</sup>, thioaldehydes<sup>4</sup>, dialkylthiosulphides<sup>5</sup>, thiophosphine<sup>6</sup>, dialkylthiocarbamates<sup>7,30</sup>, thioethers<sup>8</sup>, thiourea<sup>9-10</sup>, dithiolenes<sup>11</sup>, Schiff bases<sup>12,31,32</sup> etc, in the displacement of CO in metalcarbonyls, thiophene, benzo and dibenzothiophene substituted metal carbonyl derivatives found to be useful in the hydrodesulphurization process of the petroleum based feed stocks and important for both environmental and industrial reasons, have also synthesized<sup>13</sup>. Metal complexes of arylthiosemicarbazides are also synthesized<sup>14-16</sup>

In continuation of our recent publications<sup>17-18,33</sup> diarylthiourea and thiosemicarbazide derivatives of tungsten carbonyl and its halogen oxidation. We describe here a study of the ligand behavior of the arylthiosemicarbazide (L) viz, phenylthiosemicarbazide (ptsc), o-tolyl-thiosemicarbazide (ottsc), p-tolylthiosemicarbazide (pttsc), o-anisylthiosemicarbazide (oatsc) and p-anisylthiosemicarbazide (patsc) in the substitution reactions of Molybdenum hexacarbonyl employing both reflux and ultra-violet irradiation methods. Reactions of these donor atoms with [(o-phen or 2,2'-bipy)Mo(CO)<sub>4</sub>], [(Ph<sub>3</sub>P or Ph<sub>3</sub>As)Mo(CO)<sub>5</sub>] and halogen oxidation of [(L)Mo(CO)<sub>5</sub>] have also been investigated.

Bonding properties of these arylthiosemicarbazides have been interpreted by measurement of IR spectra of synthesized substituted molybdenum carbonyls. The C-O stretching force constants and CO-CO stretch-stretch interaction constant have also been evaluated.

### Experimental Section

All reactions and isolation procedures were carried out under argon and *in vacuo*. The arylthiosemicarbazide ligands, [(2,2'-bipy)Mo(CO)<sub>4</sub>] and [(Ph<sub>3</sub>P or Ph<sub>3</sub>As)Mo(CO)<sub>5</sub>] have been prepared

by standard procedures given in literature<sup>19-20,22</sup>. The purity of these compound checked by TLC and m.p. determination. All chemicals were of AR grade. Molybdenum hexacarbonyl (Fluka) was used. The UV lamp (30w) used was made Philips Co. Holland. IR spectra were recorded on Beckman spectrophotometer (Accu lab9), Perkin-Elmer FT-IR spectrophotometer (Model RX1) and FT-IR-8400 in KBr pallet in the 4000-400cm<sup>-1</sup>. Halogen contents were estimated gravimatically by preparation of silver salts. Details of the preparation and data of representative compounds are given below.

### Preparation of pentacarbonylphenylthiosemicarbazidemolybdenum(0) Reflux method

Hexacarbonylmolybdenum(0) (0.526g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were refluxed in toluene (25cm<sup>3</sup>) under the argon for 5 h. A yellowish brown stable solid was obtained by cooling the reaction mixture and evaporating the solvent *in vacuo*. Unreacted reactants were removed by washing the residue with petroleum ether (40-60<sup>o</sup>c). The product was recrystallized from benzene. It was characterized as pentacarbonylphenylthiosemicarbazidemolydenum(0). [C<sub>6</sub>H<sub>5</sub>NHCSNHNH<sub>2</sub>Mo(CO)<sub>5</sub>] (yield: 0.701g, 82%) C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>O<sub>5</sub>SMo (402.95g mol<sup>-1</sup>) calcd. C 35.7; H 2.2; N 10.4; S 7.9; Found C 35.6; H 2.1; N 10.2; S 7.8.

### UV irradiation method

Hexacarbonylmolybdenum(0) (0.526g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were irradiated by UV light in tetrahydrofuran (30cm<sup>3</sup>) for 26 h under argon atmosphere. The colour of the mixture became deep yellow after 10 h. After 15 h the colour of the reaction mixture changed to brown. The mixture was cooled and the solvent was removed *in vacuo*. Work up the isolation of the product was identical to reflux method.

### Preparation of 2,2'-bipyridinetricarbonylphenylthiosemicarbazidemolybdenum(0)

A mixture of 2,2'-bipyridinetetracarbonylmolybdenum(0) (0.73g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were refluxed in xylene (40cm<sup>3</sup>) under argon atmosphere. During the course of the reaction the colour of the reaction mixture deepened to violet red in 1 h but the reaction was refluxed up to 4 h, when a considerable amount of crystals settled down at the bottom of the flask. The solution was cooled to room temperature and filtered. The crystalline solid was washed with petroleum ether (40-60<sup>o</sup>c) and 2-3 times with benzene to remove unreacted reactants. It was dried *in vacuo*. It was characterized as 2, 2'-bipyridine tricarbonyl phenyl thiosemi carbazidemolybdenum(0)[(C<sub>6</sub>H<sub>5</sub>NHCSNHNH<sub>2</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)Mo(CO)<sub>3</sub>] (yield: 82g, 77.7%) C<sub>20</sub>H<sub>17</sub>N<sub>5</sub>O<sub>3</sub>SMo (502.95g mol<sup>-1</sup>) calcd. C 47.7; H 3.4; N 13.9; S 6.4; found C 47.4; H 3.3; N 13.8; S 6.3.

### Preparation of tetracarbonylphenylthiosemicarbazidetriphenylphosphinemolyben-um(0)

Pentacarbonyltriphenylphosphinemolybdenum(0) (1.0g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were refluxed in xylene (25cm<sup>3</sup>) under the inert atmosphere of argon for 5 h. The solution was cooled to room temperature and a yellow brown solid was recovered by evaporating the solvent under *vacuo*. It was characterized as tetracarbonylphenylthiosemicarbazide tri phenyl phosphinemolybdenum(0). [(C<sub>6</sub>H<sub>5</sub>NHCSNHNH<sub>2</sub>)(Ph<sub>3</sub>P)Mo(CO)<sub>4</sub>] (yield:-1.06g,69%) C<sub>29</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>P-SMo (636.95g mol<sup>-1</sup>) calcd. C 54.6; H 3.7; N 6.6; S 5.0; found C54.5; H 3.6; N 6.4; S 49.

### Preparation of tetracarbonylphenylthiosemicarbazidediiodomolybdenum(II)

A hexane solution of iodine (0.10g, in 30cm<sup>3</sup>) was added drop wise to a solution of pentacarbonylphenylthiosemicarbazidemolybdenum(0) (0.80g, in 10cm<sup>3</sup> benzene) under argon atmosphere at room temperature with constant stirring. The colour of the iodine solution disappeared during the addition and an orange precipitate settled down at the bottom of the reaction flask. The supernatant liquid was decanted out and the precipitate was washed well with hexane to removed unreacted iodine. The solid again dissolved in the minimum amount of benzene (5 cm<sup>3</sup>) and reprecipitated by adding hexane (40 cm<sup>3</sup>). The precipitate was dried in *vacuo* and was characterized as tetracarbonylphenylthiosemicarbazidediiodomolybdenum(II) [(C<sub>6</sub>H<sub>5</sub>NHCSNHNH<sub>2</sub>)W(CO)<sub>4</sub>I<sub>2</sub>] (yield: 0.63g, 70.2%) C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>4</sub>SI<sub>2</sub>Mo (629.95 gmol<sup>-1</sup>) calcd. C 21.0; H 1.4; N 6.7; S 5.1; I 40.6; found C 20.9; H 1.3; N 6.6; S 5.0; I 40.5.

### Result and Discussion

Five arylthiosemicarbazides (L) were found to react with molybdenum hexacarbonyl to give the corresponding penta carbonyl derivatives [(L)Mo(CO)<sub>5</sub>] (yield: 76.2-82.0%). Repeated attempts to achieve a second substitution by prolonged refluxing or ultra-violet irradiations were unsuccessful and not more than one CO could be replaced. These derivatives were yellowish- brown solids, insoluble in petroleum ether (all fractions) or hexane and dissolved in benzene, dichloromethane, chloroform, acetone, tetrahydrofuran and dimethylformamide.

The IR spectra of the complexes indicated that the arylthiosemicarbazide molecules are attached to the molybdenum via the sulphur atom. A strong of absorption of the parent arylthiosemi-carbazide ~1060 cm<sup>-1</sup> is very much weaker or even disappears on complex formation. This observation can be explained by the considerable change in the nature of the N-C bond, as well as C=S bond, on coordination of arylthiosemicarbazides through the sulphur atom. A lowering of ~30 cm<sup>-1</sup> observed for the bond near ~830 cm<sup>-1</sup> may be attributed to the reduced double bond character of the C=S bond. These binding of further supported by the appearance of new bond 405-410 cm<sup>-1</sup> which are assignable to ν(M-S) vibrations.

Table1. CO stretching frequencies with modes and force constants of [(L)Mo(CO)<sub>5</sub>] complexes.

Complex	ν(co)(cm <sup>-1</sup> )	Force constant (mdynes/Å)		
		k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>
[(ptsc)Mo(CO) <sub>5</sub> ]	2070(A <sub>1</sub> ) 1975(B <sub>1</sub> ) 1916(E) 1892(A <sub>1</sub> )	14.48	15.75	0.43
[(ottsc)Mo(CO) <sub>5</sub> ]	2071(A <sub>1</sub> ) 1972(B <sub>1</sub> ) 1918(E) 1894(A <sub>1</sub> )	14.49	15.70	0.44
[(pttsc)Mo(CO) <sub>5</sub> ]	2067(A <sub>1</sub> ) 1971(B <sub>1</sub> ) 1919(E) 1893(A <sub>1</sub> )	14.48	15.66	0.39
[(oatsc)Mo(CO) <sub>5</sub> ]	2063(A <sub>1</sub> ) 1970(B <sub>1</sub> ) 1920(E) 1893(A <sub>1</sub> )	14.49	15.69	0.40
[(patsc)Mo(CO) <sub>5</sub> ]	2059(A <sub>1</sub> ) 1972(B <sub>1</sub> ) 1922(E) 1894(A <sub>1</sub> )	14.47	15.72	0.39

Complexes of type [(L)Mo(CO)<sub>5</sub>] must have local C<sub>4v</sub> symmetry due to which there should be three IR active C-O stretching bands assigned to 2A<sub>1</sub>+E modes, but the IR spectra of the complexes exhibited four stretching bands in the ranges 2059-2071, 1970-1975, 1916-1922 and 1892-1894 cm<sup>-1</sup>

(Table 1). Bands in range  $2059-2071\text{cm}^{-1}$  arises from the  $A_1$  mode of the trans pair of the carbonyl groups and bands in the range  $1916-1922\text{cm}^{-1}$  may be due to E mode whereas bands of range  $1892-1894\text{cm}^{-1}$  can be assigned as the  $A_1$  mode of *cis*-carbonyls. Bands due to  $B_1$  mode ( $1970-1975\text{cm}^{-1}$ ) which are Raman active are also visible in IR spectra of all the complexes because the structure of the arylthiosemicarbazide ligands with the perfect  $C_{4v}$  symmetry. Assignments of all these bands have been made on the basis of work done by Orgel<sup>23</sup>, Cotton and Kraihanzel<sup>24</sup>.

**Table 2. CO stretching frequencies of mixed Ligand derivatives.**

Complex	$\nu(\text{co}) (\text{cm}^{-1})$
[(ptsc)(Ph <sub>3</sub> P)Mo(CO) <sub>4</sub> ]	1957w 1904s 1816s 1788m
[(ottsc)(Ph <sub>3</sub> P)Mo(CO) <sub>4</sub> ]	1958w 1907s 1829s 1790m
[(pttsc)(Ph <sub>3</sub> P)Mo(CO) <sub>4</sub> ]	1966w 1908s 1824s 1792m
[(oatsc)(Ph <sub>3</sub> P)Mo(CO) <sub>4</sub> ]	1969w 1910s 1820s 1790m
[(patsc)(Ph <sub>3</sub> P)Mo(CO) <sub>4</sub> ]	1964w 1907s 1819s 1798m
[(ptsc)(Ph <sub>3</sub> As)Mo(CO) <sub>4</sub> ]	1956w 1895s 1816s 1786m
[(ottsc)(Ph <sub>3</sub> As)Mo(CO) <sub>4</sub> ]	1954w 1901s 1819s 1793m
[(pttsc)(Ph <sub>3</sub> As)Mo(CO) <sub>4</sub> ]	1957w 1998s 1820s 1784m
[(oatsc)(Ph <sub>3</sub> As)Mo(CO) <sub>4</sub> ]	1959w 1903s 1817s 1790m
[(patsc)(Ph <sub>3</sub> As)Mo(CO) <sub>4</sub> ]	1957w 1901s 1818s 1788m
[(ptsc)(2,2'-bipy)Mo(CO) <sub>3</sub> ]	1888w 1778s 1745s
[(ottsc)(2,2'-bipy)Mo(CO) <sub>3</sub> ]	1887w 1776s 1743s
[(pttsc)(2,2'-bipy)Mo(CO) <sub>3</sub> ]	1885w 1790s 1742s
[(oatsc)(2,2'-bipy)Mo(CO) <sub>3</sub> ]	1889w 1778s 1740s
[(patsc)(2,2'-bipy)Mo(CO) <sub>3</sub> ]	1900w 1774s 1748s
[(ptsc)(o-phen)Mo(CO) <sub>3</sub> ]	1892w 1783s 1742s
[(ottsc)(o-phen)Mo(CO) <sub>3</sub> ]	1896w 1790s 1740s
[(pttsc)(o-phen)Mo(CO) <sub>3</sub> ]	1893w 1801s 1754s
[(oatsc)(o-phen)Mo(CO) <sub>3</sub> ]	1890w 1797s 1755s
[(patsc)(o-phen)Mo(CO) <sub>3</sub> ]	1900w 1795s 1752s

**Table 3. CO stretching frequencies of halogenated derivatives.**

Complex	$\nu(\text{co})(\text{cm}^{-1})$
[(ptsc)Mo(CO) <sub>4</sub> I <sub>2</sub> ]	2066m 2010s 1975sh 1923s
[(ottsc)Mo(CO) <sub>4</sub> I <sub>2</sub> ]	2064m 2018s 1976sh 1922s
[(pttsc)Mo(CO) <sub>4</sub> I <sub>2</sub> ]	2064m 2019s 1970sh 1924s
[(oatsc)Mo(CO) <sub>4</sub> I <sub>2</sub> ]	2062m 2012s 1974sh 1921s
[(patsc)Mo(CO) <sub>4</sub> I <sub>2</sub> ]	2062m 2010s 1976sh 1932s
[(ptsc)Mo(CO) <sub>4</sub> Br <sub>2</sub> ]	2079m 2015s 1977sh 1928s
[(ottsc)Mo(CO) <sub>4</sub> Br <sub>2</sub> ]	2077m 2016s 1976sh 1927s
[(pttsc)Mo(CO) <sub>4</sub> Br <sub>2</sub> ]	2075m 2015s 1975sh 1928s
[(oatsc)Mo(CO) <sub>4</sub> Br <sub>2</sub> ]	2075m 2016s 1976sh 1927s
[(pttsc)Mo(CO) <sub>4</sub> Br <sub>2</sub> ]	2077m 2014s 1978sh 1928s

The C-O stretching force constants  $k_1$  and  $k_2$  i.e., force constants of the CO groups *cis* and *trans* to the arylthiosemicarbazide substituent, respectively, and  $k_3$ , the CO-CO interaction constants have been

calculated by Cotton and Kraihanzel's secular equations<sup>24</sup>. The values of  $k_1$ ,  $k_2$  and  $k_i$  for these derivatives have been found in the ranges 14.47-14.49, 15.66-15.75 and 0.39-0.44 mdynes/Å, respectively. These values confirm the validity of the vibrational mode assignments, and the results are in excellent agreement with Cotton and Kraihanzel's analysis. The C-O stretching frequencies and C-O force constants in these complexes are slightly higher as compared to metal pentacarbonyls with nitrogen donor ligands<sup>25-26</sup> and lower than other derivatives containing alkyl or aryl sulphides as ligands<sup>5,27</sup>. These data clearly indicate that the sulphur atom in the arylthiosemicarbazides functions as a significant  $\pi$ -acceptor, but substantially less than the sulphur atom in other ligands such as alkyl or arylsulphides.

Mixed ligand derivatives of the type *cis*-[(L-L)(L)Mo(CO)<sub>3</sub>] (L-L=0-phen or 2,2'-bipy, L= arylthiosemicarbazides) were obtained by refluxing equimolar mixtures of [(L-L)Mo(CO)<sub>4</sub>] and arylthiosemicarbazides in xylene for ~ 4 h. Not more than one CO group could be displaced even by employing a large excess of arylthiosemicarbazide. The decrease donor behaviour of this ligand was further exhibited when *o*-phen or 2,2'-bipy displaced it from [(L)Mo(CO)<sub>5</sub>] and ultimately [(*o*-phen or 2,2'-bipy)Mo(CO)<sub>4</sub>] took place. All the mixed ligand tricarbonyl derivatives were brown-black solids which decomposed on heating. They are insoluble in petroleum ether (all fractions), diethylether and carbon tetrachloride but dissolved in aromatic hydrocarbons, alcohols, acetone, dichloromethane, dioxane and dimethylformamide.

The IR spectra of the complexes exhibited three strong bands in the carbonyl region according to C<sub>s</sub> symmetry. The C-O stretching frequencies fall in the ranges 1885-1889, 1775-1790 and 1740-1748 cm<sup>-1</sup> for 2,2'-bipy derivatives, and 1890-1900, 1783-1801 and 1740-1754 cm<sup>-1</sup> when *o*-phen was present. These bands are assigned to A, A', A'' modes, respectively (Table 2). The frequencies of these bands are very low contrary to expectations for sulphur donor ligands. Such lowering may be attributed to the enhanced basicity of the sulphur atom due to partial delocalization of the lone pair of electrons on the nitrogen atoms of arylthiosemicarbazides.

Arylthiosemicarbazides displaced one CO group when refluxing with [(Ph<sub>3</sub>P or Ph<sub>3</sub>As)Mo(CO)<sub>5</sub>] and lead to the formation of *cis*-[(Ph<sub>3</sub>P or Ph<sub>3</sub>As)(L)Mo(CO)<sub>4</sub>]. All complexes were yellow-brown solids, insoluble in aliphatic hydrocarbons, diethylether, alcohols and acetone. The IR spectra exhibited four C-O stretching bands in the ranges 1954-1969, 1901-1910, 1816-1829 and 1786-1798 cm<sup>-1</sup> which have been assigned<sup>24</sup> due to A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub> and B<sub>2</sub> modes, respectively (Table 2) as expected for C<sub>2v</sub> symmetry.

Halogenation of arylthiosemicarbazidemolybdenum pentacarbonyls in benzene yielded products of stoichiometry [(arylthiosemicarbazide)Mo(CO)<sub>4</sub>X<sub>2</sub>] (X= Br, I) when treated with one equivalent of bromine or iodine in hexane solution at ambient temperature. On using an excess of bromine or iodine, unidentified sticky products were obtained. Similar reaction with chlorine seemed to take place but the products were too unstable to be isolated. The iodine complexes were more stable than their bromo analogues. All the complexes were brown or orange in colour. They were insoluble in aliphatic hydrocarbons and light petroleum (40-60°C) but soluble in aromatic hydrocarbons, tetrahydrofuran, dichloromethane, acetone etc. In oxygenated solvents decomposition occurred and simultaneous evolution of carbon monoxide took place. Their dilute solutions in benzene showed no electrical conductivity. IR spectra (Table 3) exhibited three strong bands (ranges 2065-2080, 2010-2018 and 1922-1928 cm<sup>-1</sup>) along with one medium to shoulder band (1970-1978 cm<sup>-1</sup>) in the C-O region when measured in KBr discs. The spectra resembled closely to those of the reported<sup>28-29</sup> heptacoordinated [(amine)M(CO)<sub>4</sub>X<sub>2</sub>] (M=Mo, W) derivatives, with distorted pentagonal bipyramidal structure, in the frequencies and intensities of bands. The C-O

frequencies of bromo complexes are in considerably higher region in comparison to their iodo analogues which clearly indicate the better electron acceptor capability of bromine than iodine.

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