

Synthesis by Reflux and U V Irradiation and Characterization of Arylthiosemicarbazide Derivatives of Tungsten Carbonyl

A. NATH¹ AND R.V.PRASAD²

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

² Department of Chemistry A.N.D.Kisan P.G.College Babhnan Gonda. U.P.

Corresponding Author: vishunram72@gmail.com

Abstract

Reactions of five arylthiosemicarbazides (L), viz, phenylthiosemicarbazide (ptsc), o-tolylthiosemicarbazide (ottsc), p-tolylthiosemicarbazide (pttsc), o-anisylthiosemicarbazide (oatsc) and p-anisylthiosemicarbazide (patsc) with $W(CO)_6$ have been performed both by reflux and ultra-violet irradiation methods in which only monosubstituted product $[(L)W(CO)_5]$ are obtained several mixed ligand tungstencarbonyl derivatives, viz, $[(o\text{-phen or } 2,2'\text{-bipy})(L)W(CO)_3]$ and $[(Ph_3P \text{ or } Ph_3As)(L)W(CO)_4]$ have also been synthesized. Halogenations of $[(L)W(CO)_5]$ yielded heptacoordinate $[(L)W(CO)_4 X_2]$ ($X = Br \text{ or } I$). The complexes have been characterized by micro analytical data, conductivity and IR measurement. The CO-CO stretch-stretch interaction constant of $[(L)W(CO)_5]$ derivatives have also been evaluated from IR data.

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

Introduction

There have been considerably study of the ligand behavior of sulphur donors like dialkyl or diarylsulphide¹, dialkyl or diarylthioalkanes², 2-thiouracil³, thioaldehydes⁴, dialkylthiosulphides⁵, thiophosphine⁶, dialkylthiocarbamates^{7,30}, thioethers⁸, thiourea⁹⁻¹⁰, dithiolenes¹¹, Schiff bases^{12,31-32} etc, in the displacement of CO in metallocarbonyls, 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 synthesized¹³. Metal complexes of arylthiosemicarbazides are also synthesized¹⁴⁻¹⁶.

In continuation of our recent publications¹⁷⁻¹⁸ diarylthiourea 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 tungsten hexacarbonyl employing both reflux and ultra-violet irradiation methods. Reactions of these donor atoms with $[(o\text{-phen or } 2,2'\text{-bipy})W(CO)_4]$, $[(Ph_3P \text{ or } Ph_3As)W(CO)_5]$ and halogen oxidation of $[(L)W(CO)_5]$ have also been investigated.

Bonding properties of these arylthiosemicarbazides have been interpreted by measurement of IR spectra of synthesized substituted tungsten 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 or *in vacuo*. The arylthiosemicarbazide ligands, $[(2,2'\text{-bipy})W(CO)_4]$ and $[(Ph_3P \text{ or } Ph_3As)W(CO)_5]$ have been prepared by

standard procedures given in literature^{19-20,22}. The purity of these compound checked by TLC and m.p. determination. All chemicals were of AR grade. Tungsten 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⁻¹. Halogen contents were estimated gravimatically by preparation of silver salts. Details of the preparation and data of representative compounds are given below.

Preparation of pentacarbonylphenylthiosemicarbazid tungsten(0) Reflux method

Hexacarbonyl tungsten(0) (0.70g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were refluxed in toluene (25cm³) 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 (40-60⁰c). The product was recrystallized from benzene. It was characterized as pentacarbonyl phenyl thiosemicarbazid tungsten(0). [PhNHCSNHNH₂(CO)₅] (yield: 0.84g, 81.5%) C₁₂H₉N₃O₅SW (491.13g mol⁻¹) calcd. C 29.4; H 1.9; N 8.6; S 6.5; Found C 29.5; H 1.8; N 8.4; S 6.6.

UV irradiation method

Hexacarbonyl tungsten(0) (0.70g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were irradiated by UV light in tetrahydrofuran (30cm³) 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'-bipyridinetetracarbonylphenylthiosemicarbazid tungsten(0)

A mixture of 2,2'-bipyridinetetracarbonyl tungsten(0) (1.06g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were refluxed in xylene (40cm³) 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 (40-60⁰c) and 2-3 time with benzene to remove unreacted reactants. It was dried *in vacuo*. It was characterized as 2, 2'-bipyridinetetracarbonylphenylthiosemicarbazide- tungsten (0) [(PhNHCSNHNH₂) (C₁₀H₈N₂)W(CO)₃] (yield:1.08g, 77.7%) C₂₀H₁₇N₅O₃S-W (591.3g mol⁻¹) calcd. C 40.7; H 2.9; N 11.8; S 5.4; found C 40.6; H 3.1; N 11.6; S 5.5.

Preparation of tetracarbonylphenylthiosemicarbazidetriphenylphosphinetungsten(0)

Pentacarbonyltriphenylphosphinetungsten(0) (1.17g, 2mmol) and phenylthiosemicarbazide (0.33g, 2mmol) were refluxed in xylene (25cm³) 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 - phosphinetungsten(0). [(PhNHCSNHNH₂)(Ph₃P)W(CO)₄] (yield: 1.04g, 69%) C₂₉H₂₄N₃O₄PSW (725.42g mol⁻¹) calcd. C 48.0; H 3.3; N 5.8; S 4.4; found C48.1; H 3.1; N 5.9; S 4.2.

Preparation of tetracarbonylphenylthiosemicarbazidediiodotungsten(II)

A hexane solution of iodine (0.10g, in 30cm³) was added drop wise to a solution of pentacarbonylphenylthiosemicarbazidetungsten(0) (0.90g, in 10cm³ 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 cm³) and reprecipitated by adding hexane (40 cm³). The precipitate was dried in *vacuo* and was characterized as tetracarbonylphenylthiosemicarbazidediiodotungsten(II)

[(PhNHCSNHNH₂)W(CO)₄I₂] (yield: 0.42g, 68%) C₁₁H₉N₃O₄SI₂W (716.93 gmol⁻¹) calcd. C 18.4; H 1.3; N 5.9; S 4.5; I 35.4; found C 18.6; H 1.4; N 5.7; S 4.3; I 35.2.

Result and Discussion

Five arylthiosemicarbazides (L) were found to react with tungsten hexacarbonyl to give the corresponding penta carbonyl derivatives [(L)W(CO)₅] (yield: 76.2-81.5%). 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 tungsten via the sulphur atom. A strong of absorption of the parent arylthiosemicarbazide ~1060 cm⁻¹ 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⁻¹ observed for the bond near ~830 cm⁻¹ 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 410-415 cm⁻¹ which are assignable to ν(M-S) vibrations.

Table1. CO stretching frequencies with modes and force constants of [(L)W(CO)₅] complexes.

Complex	ν(co)(cm ⁻¹)	Force constant (mdynes/Å)		
		k ₁	k ₂	k _i
[(ptsc)W(CO) ₅]	2072(A ₁) 1976(B ₁) 1920(E) 1894(A ₁)	14.49	15.76	0.44
[(ottsc)W(CO) ₅]	2070(A ₁) 1973(B ₁) 1919(E) 1895(A ₁)	14.50	15.72	0.45
[(pttsc)W(CO) ₅]	2069(A ₁) 1970(B ₁) 1920(E) 1894(A ₁)	14.49	15.67	0.39
[(oatsc)W(CO) ₅]	2065(A ₁) 1972(B ₁) 1921(E) 1895(A ₁)	14.50	15.70	0.40
[(patsc)W(CO) ₅]	2060(A ₁) 1974(B ₁) 1924(E) 1895(A ₁)	14.48	15.73	0.39

Complexes of type [(L)W(CO)₅] must have local C_{4v} symmetry due to which there should be three IR active C-O stretching bands assigned to 2A₁+E modes, but the IR spectra of the complexes exhibited four stretching bands in the ranges 2060-2072, 1972-1976, 1919-1924 and 1894-1895 cm⁻¹

(Table 1). Bands in range $2060\text{-}2072\text{cm}^{-1}$ arises from the A_1 mode of the trans pair of the carbonyl groups and bands in the range $1919\text{-}1924\text{ cm}^{-1}$ may be due to E mode whereas bands of range $1894\text{-}1895\text{ cm}^{-1}$ can be assigned as the A_1 mode of *cis*-carbonyls. Bands due to B_1 mode ($1970\text{-}1976\text{ cm}^{-1}$) 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 Orgel²³, Cotton and Kraihanzel²⁴.

Table 2. CO stretching frequencies of mixed Ligand derivatives.

Complex	$\nu(\text{co})$ (cm^{-1})
$[(\text{ptsc})(\text{Ph}_3\text{P})\text{W}(\text{CO})_4]$	1958w 1905s 1818s 1790m
$[(\text{ottsc})(\text{Ph}_3\text{P})\text{W}(\text{CO})_4]$	1960w 1908s 1830s 1792m
$[(\text{pttsc})(\text{Ph}_3\text{P})\text{W}(\text{CO})_4]$	1968w 1910s 1825s 1793m
$[(\text{oatsc})(\text{Ph}_3\text{P})\text{W}(\text{CO})_4]$	1970w 1912s 1822s 1790m
$[(\text{patsc})(\text{Ph}_3\text{P})\text{W}(\text{CO})_4]$	1965w 1908s 1820s 1800m
$[(\text{ptsc})(\text{Ph}_3\text{As})\text{W}(\text{CO})_4]$	1958w 1900s 1818s 1788m
$[(\text{ottsc})(\text{Ph}_3\text{As})\text{W}(\text{CO})_4]$	1955w 1902s 1820s 1795m
$[(\text{pttsc})(\text{Ph}_3\text{As})\text{W}(\text{CO})_4]$	1958w 1900s 1822s 1785m
$[(\text{oatsc})(\text{Ph}_3\text{As})\text{W}(\text{CO})_4]$	1960w 1904s 1818s 1792m
$[(\text{patsc})(\text{Ph}_3\text{As})\text{W}(\text{CO})_4]$	1958w 1902s 1820s 1790m
$[(\text{ptsc})(2,2'\text{-bipy})\text{W}(\text{CO})_3]$	1890w 1780s 1747s
$[(\text{ottsc})(2,2'\text{-bipy})\text{W}(\text{CO})_3]$	1888w 1776s 1745s
$[(\text{pttsc})(2,2'\text{-bipy})\text{W}(\text{CO})_3]$	1886w 1790s 1746s
$[(\text{oatsc})(2,2'\text{-bipy})\text{W}(\text{CO})_3]$	1889w 1780s 1742s
$[(\text{patsc})(2,2'\text{-bipy})\text{W}(\text{CO})_3]$	1900w 1775s 1750s
$[(\text{ptsc})(\text{o-phen})\text{W}(\text{CO})_3]$	1890w 1785s 1744s
$[(\text{ottsc})(\text{o-phen})\text{W}(\text{CO})_3]$	1898w 1790s 1742s
$[(\text{pttsc})(\text{o-phen})\text{W}(\text{CO})_3]$	1895w 1802s 1755s
$[(\text{oatsc})(\text{o-phen})\text{W}(\text{CO})_3]$	1892w 1798s 1756s
$[(\text{patsc})(\text{o-phen})\text{W}(\text{CO})_3]$	1900w 1796s 1753s

Table 3. CO stretching frequencies of halogenated derivatives.

Complex	$\nu(\text{co})(\text{cm}^{-1})$
$[(\text{ptsc})\text{W}(\text{CO})_4\text{I}_2]$	2068m 2012s 1974sh 1924s
$[(\text{ottsc})\text{W}(\text{CO})_4\text{I}_2]$	2066m 2010s 1976sh 1922s
$[(\text{pttsc})\text{W}(\text{CO})_4\text{I}_2]$	2065m 2010s 1972sh 1925s
$[(\text{oatsc})\text{W}(\text{CO})_4\text{I}_2]$	2066m 2014s 1975sh 1923s
$[(\text{patsc})\text{W}(\text{CO})_4\text{I}_2]$	2065m 2012s 1976sh 1935s
$[(\text{ptsc})\text{W}(\text{CO})_4\text{Br}_2]$	2080m 2017s 1977sh 1930s
$[(\text{ottsc})\text{W}(\text{CO})_4\text{Br}_2]$	2078m 2018s 1978sh 1928s
$[(\text{pttsc})\text{W}(\text{CO})_4\text{Br}_2]$	2076m 2015s 1976sh 1929s
$[(\text{oatsc})\text{W}(\text{CO})_4\text{Br}_2]$	2075m 2018s 1977sh 1928s
$[(\text{pttsc})\text{W}(\text{CO})_4\text{Br}_2]$	2078m 2016s 1978sh 1930s

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_i , the CO-CO interaction constants have been calculated by Cotton and Kraihanzel's secular equations²⁴. The values of k_1 , k_2 and k_i for these derivatives have been found in the ranges 14.48-14.50, 15.67-15.76 and 0.39-0.45 mdyne/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 ligands²⁵⁻²⁶ and lower than other derivatives containing alkyl or aryl sulphides as ligands^{5, 27}. These data clearly indicate that the sulphur atom in the arylthiosemicarbazides functions as a significant π -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)W(CO)₃] (L-L=0-phen or 2,2'-bipy, L= arylthiosemicarbazides) were obtained by refluxing equimolar mixtures of [(L-L)W(CO)₄] 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 in donor behaviour of this ligand was further exhibited when *o*-phen or 2,2'-bipy displaced it from [(L)W(CO)₅] and ultimately [(*o*-phen or 2,2'-bipy)W(CO)₄] 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_s symmetry. The C-O stretching frequencies fall in the ranges 1890-1900, 1775-1790 and 1742-1750 cm⁻¹ for 2,2'-bipy derivatives, and 1890-1900, 1785-1802 and 1742-1756 cm⁻¹ 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 refluxed with [(Ph₃P or Ph₃As)W(CO)₅] and led to the formation of *cis*-[(Ph₃P or Ph₃PAs)(L)W(CO)₄]. 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 1955-1970, 1900-1912, 1818-1830 and 1785-1800 cm⁻¹ which have been assigned²⁴ due to A₁, A₂, B₁ and B₂ modes, respectively (Table 2) as expected for C_{2v} symmetry.

Halogenation of arylthiosemicarbazide tungsten pentacarbonyls in benzene yielded products of stoichiometry [(arylthiosemicarbazide)W(CO)₄X₂] (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 1922-1930 cm⁻¹) along with one medium to shoulder band (1972-1978 cm⁻¹) in the C-O region when measured in KBr discs. The spectra resembled closely to those of the reported²⁸⁻²⁹ heptacoordinated [(amine)M(CO)₄X₂] (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.

Acknowledgements

The authors are thankful to the Principal B.R.D.P.G College Deoria for providing necessary laboratory facilities, Analytical services from the RSIC, CDRI, Lucknow are gratefully acknowledged.

References

- [1] M.H.B.Stiddard, J. Chem. Soc. 1963; 756.
- [2] L.W.Houk, G.R. Dobson, J.Chem.Soc. 1966; A(3), 317 Inorg. Chem. 1966; 5,2119 .
- [3] W.Beck, N. Kottmair, Chem. Ber.1976; 109, 970.
- [4] G.J. Kruger, L.Linford, H.G. Raubenheimer, J. Chem. Soc. Dalton Trans. 1984; 2337.
- [5] F.W. Abel, S.K. Bhargava, P.K. Mittal, K.G. Orrell, V. Sik, J. Chem. Soc. Dalton Trans. 1985; 561.
- [6] G. Barrado, M.M. Hricko, D. Miguel, V. Riera, H. Wally, S.G. Granda, Organometallics 1998; 17, 820 .
- [7] G. Ujaque, F. Maseras, A. Lledos, L. Contreras, A.Pizzano, D. Rodewald, L. Sanchez, E. Carmona, A. Momge, C.Ruiz, Organometallics 1999; 18, 3294.
- [8] D. Morals, J. Perez, L. Riera, V.Riera, D.Miguel, Organometallics 2001; 20, 4517.
- [9] F.A. Cotton, F. Zingales, Chem. Ind. 1960; 1219.
- [10] A.O. Baghalf, M. Ishaq, A.S. Daifullah, Polyhedron 1984; 3, 235.
- [11] D.V. Fomitchev, B.S. Lim, R.H. Holm, Inorg.Chem. 2001; 40, 645.
- [12] Amar Srivastava, A.K. Srimal, Indian J. Chem. 2002; 41(A), 785.
- [13] M.A. Reynolds, I.A. Guzei, B.C. Logsdon, L.M. Thomas, R.A. Jacobson, R.J. Angelici, Organometallics 1999; 18, 4075.
- [14] T.V. Kaksharova, I.V. Stoyanova, Russian J. of Coordination Chemistry, 2006; 32 No1, 21- 22.
- [15] Rakesh Jada, Naimi;h Chavda, Manish K. Shah, J.Chem. Pharm. Res. 2011; 3(2), 290-297 .
- [16] I.O. Adeoye, O.O. Adelowo, O.O.E. Onawumi, J. Chem. Pharm. Res 2012; 4(1), 1-5.
- [17] Amar Srivastava, A.K. Srimal, Amar Nath, Z. Natureforsch 2004; 58b, 1-5.
- [18] Amar Srivastava, A.K. Srimal, Amar Nath, Indian J. Chem. 2004; 43A, 511-515.
- [19] R.P. Rao, Record of Chemical Progress, 1968; 29, 103.
- [20] E. Lieber, C.N. Pillai, R.D. Hites, Con. J. Chem. 1957; 35, 832-842.
- [21] C.N. Mtthews, T.A. Magee, J.H. Wotiz, J. Am. Chem. Soc. 1959; 81, 2273.
- [22] W. Strohmeier, F.J. Mueller, Chem. Ber. 1969; 102, 3608.
- [23] L.E. Oegel, Inorg. Chem, 1962; 1, 25.
- [24] F.A. Cotton, C.S. Kraihanzel, J.Am. Chem. Soc. 1962; 84, 4432.
- [25] S.C. Tripathi, S.C.Srivastava, G. Prasad, R.P. Mani, J. Organomet. Chem. 1975; 86, 229.
- [26] F.A. Cotton, C.S. Kraihanzel, Inorg. Chem, 1963; 2, 533.
- [27] F.A. Cotton, F. Zingales, J.Am. Chem. Soc. 1961; 83, 351.
- [28] S.C. Tripathi, S.C. Srivastava, R.P. Mani, J. Organomet. Chem. 1976; 105, 239.
- [29] S.C. Tripathi, S.C. Srivastava, A.K. Srimal, Inorganica Chim. Acta, 1976; 18, 231.
- [30] L.Zhao,C.Zhao et al Inorganica Chem.Acta. 2016: 450, 12-22.
- [31] Z.Selbhi, A.Jibri, M.Hayfa et al. Inorganic Chem. Acta. 2016; 450. 50-56.
- [32] D.Bandhopadhyay, M.Layek et al. Inorganic Chem. Acta. 2017; 461,174-182