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REACTIONS OF ARYL- AND DIARYL-THIOUREAS WITH SOME MOLYBDENUM CARBONYL DERIVATIVES

S.C. TRIPATHI *, S.C. SRIVASTAVA, R.D. PANDEY and R.P. MANI
Department of Chemistry, University of Gorakhpur, U.P. (India)

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Summary

Cycloheptatrienemolybdenum tricarbonyl reacted with ligands (L) (L = phenyl-, *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, α-naphthyl-, β-naphthyl-, *sym*-diphenyl-, *sym*-di-*o*-tolyl-, *sym*-di-*p*-tolyl- or *sym*-di-α-naphthyl-thiourea) to give $Mo(CO)_5L$ derivatives although the expected products were *cis*-$Mo(CO)_3L_3$. Evidence has been obtained for the formation of *trans*-$Mo(CO)_4L_2$ derivatives when L = *sym*-diphenyl- and *sym*-di-*o*-tolyl-thiourea. These donors on reaction with $Mo(CO)_4B$ (B = *o*-phenanthroline or 2,2′-bipyridine) yielded mixed ligand derivatives of the type $Mo(CO)_3BL$. The appearance of three C—O stretching bands is in agreement with the C_s symmetry of mixed-ligand molybdenum carbonyls.

Introduction

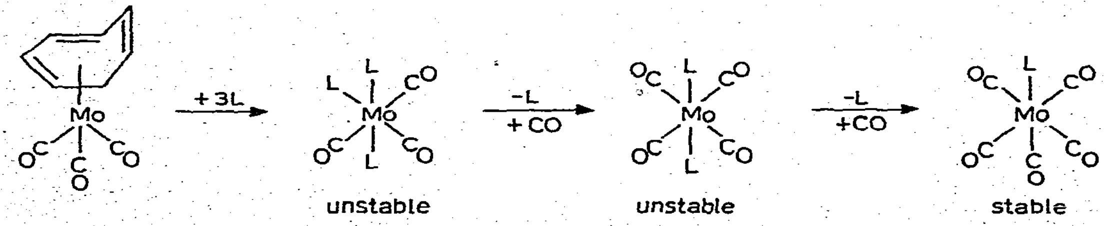
Until recently [1], the displacement of CO by aryl- and diaryl-thioureas in metal carbonyls had not been attempted. We first reported [1] the preparation of some aryl- and diaryl-thioureamolybdenum pentacarbonyls by straightforward thermal reactions. It was noted that the bonding of two or more ligand molecules to a single metal atom was not possible by direct reaction. Aiming to achieve higher substitution, we employed cycloheptatrienemolybdenum tricarbonyl in place of molybdenum hexacarbonyl in this work. The former is a very good starting material for the preparation of various trisubstituted molybdenum carbonyl derivatives, as it generates three free coordination sites on the metal atom, which makes the attachment of three ligand molecules to a single metal atom easier. In these reactions also only monosubstituted derivatives, $Mo(CO)_5L$ (L = phenyl-, *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, α-naphthyl-, β-naphthyl-, *sym*-diphenyl-, *sym*-di-*o*-tolyl-, *sym*-di-*p*-tolyl- or *sym*-di-α-naphthyl-thiourea) were obtained instead of the expected trisubstituted, $Mo(CO)_3L_3$, derivatives. Although IR evidence was obtained for the formation of *trans*-disubstituted derivatives in a few cases, these were converted into monosubstituted compounds during isolation.

The reactions of donor molecules with $Mo(CO)_4B$ (B = *o*-phenanthroline or 2,2′-bipyridine) have also been studied. In these reactions mixed trisubstituted derivatives, $Mo(CO)_3BL$ (L = phenyl, *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, α-naphthyl-, β-naphthyl-, *sym*-diphenyl-, *sym*-di-*o*-tolyl-, *sym*-di-*p*-tolyl- or *sym*-di-α-naphthyl-thiourea), were obtained.

Results and dissussion

Phenyl-, *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, α-naphthyl-, β-naphthyl-, *sym*-diphenyl-, *sym*-di-*o*-tolyl-, *sym*-di-*p*-tolyl or *sym*-di-α-naphthyl-thiourea reacted immediately with cycloheptatrienemolybdenum tricarbonyl in a 1 : 1 mixture of benzene and dichloromethane at −5 to +30°C to give $Mo(CO)_5L$ derivatives. The red colour of the cycloheptatrienemolybdenum tricarbonyl solution rapidly changed to yellowish brown on mixing the solutions of the two reactants at −5°C or room temperature (30°C). In the IR spectra of the reaction mixtures the C—O bands of cycloheptatrienemolybdenum tricarbonyl disappeared and new bands around 2060, 1980, 1960 and 1900 cm^{-1} gradually appeared. These new bands closely resembled the bands of $Mo(CO)_5L$ derivatives reported earlier [1]. On isolation and purification of the products only $Mo(CO)_5L$ derivatives were obtained, along with a brownish black insoluble substance, instead of the expected $Mo(CO)_3L_3$ derivatives. The IR spectrum of this brownish black substance showed no C—O bands. It appears that some unstable carbonyl compounds are formed during the reactions, which decompose and generate carbon monoxide leaving a brownish black intractable substance. The carbon monoxide formed acts as a good source for further carbonylation resulting in the formation of monosubstitution complexes. We propose a mechanism (Scheme 1), similar to that proposed by King and Korenowski [2], for the formation of monosubstituted derivatives in these reactions:

SCHEME 1



Infrared evidence for the formation of *trans*-disubstituted derivatives, which are intermediates in this proposed mechanism, has been obtained for the reactions of *sym*-diphenylthiourea and *sym*-di-*o*-tolylthiourea. Only one very strong C—O absorption (ν(CO): 1920 cm^{-1}) along with one weaker satellite (ν(CO): 1960 cm^{-1}) in the higher frequency region appeared in the IR spectra of the reaction mixtures of cycloheptatrienemolybdenum tricarbonyl and these ligands. However, during isolation they were converted into monosubstituted derivatives.

NH_2CSNH_2 was reacted with cycloheptatrienemolybdenum tricarbonyl (already reported by Cotton et al. [3] using identical conditions) and the formation of $Mo(CO)_3(NH_2CSNH_2)_3$ [ν(CO): 1900, 1754 cm^{-1} (reported); 1898, 1765 cm^{-1} (observed)] was noted. This suggests that steric factors possibly prevent the formation of trisubstituted derivatives in the case of aryl- and diaryl-thioureas which contain more bulky groups.

Thioureas reacted with $Mo(CO)_4B$ in a 1 : 1 mixture of dichloromethane and toluene under nitrogen to give $Mo(CO)_3BL$ (L = phenyl-, *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, α-naphthyl-, β-naphthyl-, *sym*-diphenyl-, *sym*-di-*o*-tolyl-, *sym*-di-*p*-tolyl- or *sym*-di-α-naphthyl-thiourea). They were black crystalline solids insoluble in aliphatic or aromatic hydrocarbons and light petroleum (all fractions), but dissolved in methanol, acetone, chloroform, and dichloromethane. Although they were fairly stable as solids, they decomposed when their solutions were exposed to air. The IR spectra of these complexes indicated the attachment of aryl- or diaryl-thiourea molecules to the molybdenum atom via sulphur, as reported earlier [1].

Since the molecular geometry of these derivatives is consistent with C_s symmetry, three C—O bands due to $2A' + A''$ modes are expected. In fact, three strong C—O stretching bands were observed (Table 1) in the IR spectra of these complexes. The frequencies of these bands were very low, contrary to expectation for the sulphur donor ligands. Such lowering may be attributed to the enhanced basicity of the sulphur atom due to the partial delocalisation of the lone pair of electrons on the nitrogen atoms of aryl- and diaryl-thioureas. The splitting of the E mode into A' and A'' modes in these complexes is slightly greater than for *cis*-$Mo(CO)_3(C_{12}H_8N_2)(NH_2)_2CS$ [4] or $Mo(CO)_3(C_{12}H_8N_2)(CH_3CSNH_2)$ [4], which indicates a somewhat greater acceptor capability of aryl- or diaryl-thiourea molecules compared with NH_2CSNH_2 or CH_3CSNH_2.

Experimental

General

Cycloheptatrienemolybdenum tricarbonyl was purchased from Strem Chemicals, Inc., U.S.A. *o*-Phenanthrolinemolybdenum tetracarbonyl and 2,2′-bipyridinemolybdenum tetracarbonyl were prepared by literature methods [5,6]. All reactions were performed under dry nitrogen. Infrared spectra were measured on a Perkin—Elmer spectrophotometer model 137.

The reaction of phenylthiourea with cycloheptatrienemolybdenum tricarbonyl

A solution of cycloheptatrienemolybdenum tricarbonyl (0.27 g) in benzene (25 ml) was mixed with a solution of phenylthiourea (0.50 g) in dichloromethane (25 ml) at −5°C under an atmosphere of nitrogen. The red colour of cycloheptatrienemolybdenum tricarbonyl immediately disappeared and the reaction mixture turned yellow. After half an hour the solvents were evaporated in vacuo. Unreacted phenylthiourea was removed by several washings with ethanol. The grey coloured solid thus obtained was extracted with acetone. A small quantity of brownish black product which remained undissolved was removed by filtration under nitrogen. On concentrating the acetone solution, a blackish grey product was obtained. It was identified as $Mo(CO)_5(C_6H_5NHCSNH_2)$ (0.16 g; 35%), reported earlier [1]. (Found: C, 37.0; H, 2.2; N, 6.9. calcd.: C, 37.1; H, 2.0; N, 7.2%.) ν(CO): 2058, 1981, 1962, 1897 cm^{-1}.

TABLE 1. REFLUX TIME, YIELD, C—O STRETCHING BANDS, MODES OF VIBRATION AND ANALYTICAL DATA OF *cis*-$Mo(CO)_3BL$ DERIVATIVES

Complex	Reflux time (h)	Yield (%)	C—O stretching bands (cm^{-1})^{a}/modes			Analysis found (calcd.) (%)		
			A'	A'	A''	C	H	N
$Mo(CO)_3(C_{10}H_8N_2)$(*o*-$CH_3C_6H_4NHCSNH_2$)	1½	75.3	1888	1782	1745	49.3 (50.1)	2.3 (2.5)	11.1 (11.1)
$Mo(CO)_3(C_{10}H_8N_2)$(*m*-$CH_3C_6H_4NHCSNH_2$)	2½	78.6	1898	1787	1745	49.8 (50.1)	2.4 (2.5)	11.1 (11.1)
$Mo(CO)_3(C_{10}H_8N_2)$(*p*-$CH_3C_6H_4NHCSNH_2$)	2½	66.6	1888	1779	1742	49.4 (50.1)	2.3 (2.5)	10.9 (11.1)
$Mo(CO)_3(C_{10}H_8N_2)$(α-$C_{10}H_7NHCSNH_2$)	2	62.3	1898	1782	1745	52.8 (53.5)	3.2 (3.3)	10.4 (10.4)
$Mo(CO)_3(C_{10}H_8N_2)$(β-$C_{10}H_7NHCSNH_2$)	2	64.9	1888	1782	1745	54.6 (53.5)	2.8 (3.3)	9.9 (10.4)
$Mo(CO)_3(C_{10}H_8N_2)$(*sym*-$C_6H_5NHCSNHC_6H_5$)	2	59.8	1898	1800	1760	54.8 (55.3)	3.6 (3.5)	9.8 (9.9)
$Mo(CO)_3(C_{10}H_8N_2)$(*sym*-*o*-$CH_3C_6H_4NHCSNHC_6H_4CH_3$)	2½	67.8	1888	1782	1745	56.9 (56.7)	4.2 (4.0)	9.3 (9.4)
$Mo(CO)_3(C_{10}H_8N_2)$(*sym*-*p*-$CH_3C_6H_4NHCSNHC_6H_4CH_3$)	2	60.3	1898	1800	1753	56.9 (56.7)	3.8 (4.0)	9.6 (9.4)
$Mo(CO)_3(C_{10}H_8N_2)$(*sym*-α-$C_{10}H_7NHCSNHC_{10}H_7$)	2½	58.4	1888	1779	1742	62.6 (61.4)	3.8 (3.6)	8.7 (8.4)
$Mo(CO)_3(C_{12}H_8N_2)(C_6H_5NHCSNH_2)$	2	72.0	1888	1782	1745	52.3 (51.5)	3.2 (3.1)	10.7 (10.9)
$Mo(CO)_3(C_{12}H_8N_2)$(*o*-$CH_3C_6H_4NHCSNH_2$)	2	75.4	1898	1787	1745	51.8 (52.4)	2.9 (3.4)	10.8 (10.6)
$Mo(CO)_3(C_{12}H_8N_2)$(*m*-$CH_3C_6H_4NHCSNH_2$)	2½	68.0	1898	1787	1745	52.4 (52.4)	3.8 (3.4)	10.8 (10.6)
$Mo(CO)_3(C_{12}H_8N_2)$(*p*-$CH_3C_6H_4NHCSNH_2$)	2	70.1	1888	1782	1745	51.1 (52.4)	3.9 (3.4)	10.6 (10.6)
$Mo(CO)_3(C_{12}H_8N_2)$(α-$C_{10}H_7NHCSNH_2$)	2½	65.5	1888	1782	1745	55.4 (55.4)	3.2 (3.2)	9.9 (9.9)
$Mo(CO)_3(C_{12}H_8N_2)$(β-$C_{10}H_7NHCSNH_2$)	2½	66.6	1888	1782	1745	54.8 (55.4)	2.9 (3.2)	9.7 (9.9)
$Mo(CO)_3(C_{12}H_8N_2)$(*sym*-$C_6H_5NHCSNHC_6H_5$	3	56.4	1888	1787	1739	56.9 (57.1)	3.3 (3.4)	9.3 (9.5)

[a] KBr discs.

On repeating the same experiment at room temperature similar results were obtained.

Similarly *o*-tolyl-, *m*-tolyl-, *p*-tolyl-, α-naphthyl-, β-naphthyl-, *sym*-diphenyl-, *sym*-di-*o*-tolyl-, *sym*-di-*p*-tolyl-, and *sym*-di-α-naphthyl-thiourea reacted with cycloheptatrienemolybdenum tricarbonyl under identical conditions to give the corresponding $Mo(CO)_5L$ derivatives.

Preparation of 2,2'-bipyridinephenylthioureamolybdenum tricarbonyl

2,2'-Bipyridinemolybdenum tetracarbonyl (0.2 g) and phenylthiourea (0.08 g) were refluxed in a 1 : 1 mixture of toluene and dichloromethane under nitrogen for 2 h. The red mixture turned violet, and finally black crystals appeared at the bottom of the flask. The reaction mixture was cooled and the supernatant liquid was decanted. The black product was washed several times with light petroleum (40—60°C) to remove unreacted 2,2'-bipyridinemolybdenum tetracarbonyl. It was recrystallised in a mixture of methanol and acetone (1 : 1) and was dried *in vacuo*. It was identified as $Mo(CO)_3(C_{10}H_8N_2)(C_6H_5NHCSNH_2)$ (0.19 g; 70.8%). (Found: C, 59.0; H, 3.2; N, 11.5. Calcd.: C, 49.1; H, 3.2; N, 11.4%.) It was insoluble in hydrocarbons, carbon tetrachloride, light petroleum and benzene, but dissolved in acetone and dichloromethane. It showed three strong absorptions at 1898, 1787 and 1745 cm^{-1}.

The preparations and IR frequencies of the other products are given in Table 1.

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References

1 S.C. Tripathi, S.C. Srivastava and R.D. Pandey, J. Inorg. Nucl. Chem., 35 (1973) 457.
2 R.B. King and T.F. Korenowski, Inorg. Chem., 10 (1971) 1188.
3 F.A. Cotton and F. Zingales, Chem. Ind. (London), (1960) 1219.
4 L.W. Houk and G.R. Dobson, Inorg. Chem., 5 (1966) 2119.
5 W. Hieber and F. Muhlbauer, Z. Anorg. Allgem. Chem., 221 (1935) 337.
6 E.W. Abel, M.A. Bennette and G. Wilkinson, J. Chem. Soc., (1959) 2323.