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Organometallic Heterocyclic Chemistry I. Some Group VI Transition Metal Complexes Containing Thiazole, Isothiazole, and Related Ligands

K. H. PANNELL, C. CHING-YU LEE, C. PÁRKÁNYI and RICHARD REDFEARN (né SNOW)
Department of Chemistry, University of Texas at El Paso, El Paso, Texas, U.S.A.

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The heterocycles thiazole, isothiazole, and 4(5) methyl-isothiazole have been used as ligands in reaction with the group VI metal hexacarbonyls. The resulting pentacarbonyl derivatives are coordinated to the metal via the nitrogen atom exclusively; however, it is clear from mass spectral data that migration of the metal from nitrogen to sulfur is an important process in the fragmentation of the complexes as well as formation of pi-bonded species. The electronic effects of the ligands are very similar and related to those of pyridine.

Introduction

There has been some recent interest in the use of heterocycles containing two or more heteroatoms as potential ligands. Thus, thiazolidine-2-thione has been shown to coordinate to the group VI metals via the sulfur atom in some pentacarbonyl derivatives while both thiazole and isothiazole have been shown to coordinate to group VIII and II metal halides via the nitrogen atom.[1,2,3] In this paper the ligand properties of thiazole, isothiazole, and 4(5)methyl-isothiazole toward the group VI metal hexacarbonyls are reported.

Experimental

The heterocyclic ligands were obtained from Raylo Chemicals Limited, Edmonton, Alberta, Canada and used without further treatment. All solvents used were dry and essentially oxygen free while all reactions and manipulations were performed under an inert atmosphere. Infrared spectra were recorded on a Perkin–Elmer 421 infrared spectrometer and pmr spectra on a Perkin–Elmer R12 spectrometer. Mass spectra were recorded on a DuPont 492 double focussing instrument, source temperature 120°C, ionizing potential 73 eV. Analyses were performed by Heterocyclic Chemical Corporation and Elek Microanalytical Laboratories.

Preparation of $LM(CO)_5$

Typically a 50% excess of thiazole and 1 g (4.5 10^{-3} m) of chromium hexacarbonyl was irradiated in 200 ml of THF for 45 h. After this period the infrared spectrum of the reaction mixture indicated an absence of hexacarbonyl. The solvent was removed under reduced pressure to leave a yellow solid. This crude product was purified by column chromatography on an alumina column as a single band eluting with hexane. Recrystallization from hexane produced 1.07 g (4.32

TABLE I. New Complexes $LM(CO)_5$.[a]

Complexes	mp(°C)	Analyses					
		Calcd			Found		
		%C	%H	%N	%C	%H	%N
$TCr(CO)_5$	75–6	34.7	1.09	5.05	34.7	1.17	
$ITCr(CO)_5$	85	–	–	–	34.5	1.21	4.94
$4(Me)ITCr(CO)_5$	62–3	37.1	1.73	4.81	36.9	2.24	4.07
$5(Me)ITCr(CO)_5$	44	–	–	–	36.9	2.21	4.76
$TW(CO)_5$	81–82	23.5	0.74	3.43	25.7	1.20	3.45
$ITW(CO)_5$	95	–	–	–	24.1	1.02	3.38
$4(Me)ITW(CO)_5$	84–5	25.6	1.19	3.31	25.6	1.23	3.23
$5(Me)ITW(CO)_5$	60–1	–	–	–	25.4	1.41	3.41

[a] T = Thiazole; IT = Isothiazole; 4(Me)IT = 4-methyl-isothiazole; 5(Me)IT = 5-methyl-isothiazole.

10^{-3} m, 85%) of the complex $(C_3H_3NS)Cr(CO)_5$, mp 75–6°C. The following complexes were also prepared using the same procedure in yields ranging from 40–90% (Table I).

Results and Discussion

Ultraviolet irradiation of a mixture of the heterocycle and group VI hexacarbonyl in tetrahydrofuran (THF) leads to good yields of the appropriate yellow diamagnetic pentacarbonyl derivative. Prolonged irradiation with excess ligand results in disubstituted products.

$$M(CO)_6 + L \xrightarrow[THF]{h\nu} LM(CO)_5 \xrightarrow{L} L_2M(CO)_4$$

M = Cr, Mo, W; L = Thiazole (T), Isothiazole (IT), 4(5)methyl-isothiazole (4(5)MIT).

Infrared Spectral Data

The infrared data of the terminal carbonyl region for the pentacarbonyl complexes are recorded in Table II. It is observed that each complex exhibits those bands associated with a gross C_{4v} symmetry, $2A_1$, B_1, E.[4] There is very little variation in the stretching frequencies of all the complexes, indicating that the electronic effects of the ligands are essentially similar and further that they coordinate via the same heteroatom. Indeed, the proximity of the carbonyl stretching frequencies of the new complexes to those of the related pyridine complexes suggest that coordination occurs via the nitrogen donor atom. It has been observed before that pyridine does not participate in any significant retrodative π-bonding with the group VI metals in the pentacarbonyl complexes although it does possess empty (antibonding) π-molecular orbitals of the correct symmetry.[5] The same situation clearly applies to the thiazole and isothiazole ligands. Both HMO and LCI–SCF–MO (PPP) treatments of the ligands indicate very little energy difference between the lowest unoccupied MO's in the thiazole, isothiazole, pyridine, and thiophene molecules. It is therefore not surprising that the π-accepting potential of the ligands appears almost identical, as gauged by the infrared data.

TABLE II. Infrared Spectral Data, $(L)M(CO)_5$, $\nu(C{\equiv}O)$, cm^{-1}, Cyclohexane.

M	L	A_1(w)	B_1(w)	E(s)	A_1(m–w)
Cr	T	2070	1983	1940	1918
	IT	2075	1988	1944	1922
	4MIT	2070		1938	1920
	5MIT	2067		1940	1917
Mo	T	2078	1986	1940	1918
	IT	2075	1991	1945	1926
W	T	2071	1981	1932	1921
	IT	2084	1984	1939	1924
	4MIT	2071		1934	1919
	5MIT	2073		1934	1918
W	Py	2073		1934	1921

Pmr Spectral Data

The pmr data for the new complexes are recorded in Table III. Overall the spectral data are in accord with those expected for the proposed structures based upon coordination of the ligand to the metal via the nitrogen atom. Thus the resonances associated with the H-3 protons of the isothiazole complexes are considerably sharper and often possess fine structure in

TABLE III. Pmr Data, $(L)M(CO)_5$, $\tau(CDCl_3)$.

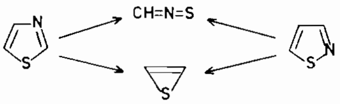
$H_2(3)$	H_4	H_5	$J_{2(3)/4}$	$J_{2(3)/5}$	$J_{4/5}$	
T Cr	1.36 (d)	2.32 (q)	2.62 (d)	1.0	2.0	4.8
Mo	1.22 (d)	2.21 (q)	2.59 (q)	0.8	2.1	3.0
W	1.10 (d)	2.12 (q)	2.62 (q)	1.0	2.0	3.0
IT Cr	1.69 (d)	2.86 (q)	1.49 (d)	1.5	–	6.6
Mo[a]	1.45 (d)	2.79 (m)	1.38 (d)			
W	1.39 (d)	2.86 (q)	1.31 (d)	1.7	–	5.4
	H_3	$H_4(5)$	CH_3			
5-MIT Cr[a]	2.42	3.73	8.07			
W	2.24	3.77	7.90	2.0	$J_{4/CH_3} = 1.0$	
4-MIT Cr[a]	2.43	2.43	8.27			
W[a]	2.27	2.41	8.22			

[a] Resolution insufficient for determination of J values.

contrast to the broad featureless resonances of the free ligands. This is entirely expected since removal of electron density from nitrogen upon coordination will reduce the ^{14}N quadrupolar coupling constant.[6] For the chromium complexes the H-3 resonance appears at higher field than the free ligand, while for molybdenum and tungsten it is at lower field, the more so for tungsten. However, apart from this regular variation, the remainder of the data yields no pattern of varying chemical shift and coupling constants upon coordination of the ligands.

Mass Spectral Data

The mass spectral fragmentation patterns of the new complexes are of particular significance since they illustrate the effect of coordination upon the properties of the ligands. The data are recorded in Table IV. The free ligands thiazole and isothiazole fragment upon electron impact by two major routes outlined below involving loss of neutral acetylene or hydrogen cyanide.[7,8]



All of the new complexes reported exhibit parent ions, $LM(CO)_5$ and the expected ions associated with the stepwise loss of carbonyl groups. For all cases, barring $5(MIT)W(CO)_5$, the carbonyl free metal ligand ion LM is the base peak in the spectrum and it is the fragmentation of this ion that is of interest.

TABLE IV. Mass Spectral Data.

ITCr(CO)$_5$ (25), ITCr(CO)$_4$ (5), ITCr(CO)$_3$ (4), ITCr(CO)$_2$ (5), ITCr(CO) (44), ITCr (100), (CHSN)Cr (16), $(C_2H_2S)Cr$ (8), CrS(7)
TCr(CO)$_5$ (62), TCr(CO)$_4$ (9), TCr(CO)$_3$ (6), TCr(CO)$_2$ (5), TCr(CO) (60), TCr (100), (CHSN)Cr (4·5), $(C_2H_2S)Cr$ (4·5), CrS (5)
4-MITCr(CO)$_5$ (40), 4MITCr(CO)$_4$ (10), 4MITCr(CO)$_3$ (6), 4MITCr(CO)$_2$ (9), 4MITCr(CO) (60), 4MITCr (100), $(C_3H_2NS)Cr$ (6), (CHSN)Cr (1·4), $(CH_3C_2H)Cr$ (1·2)
5-MITCr(CO)$_5$ (24), 5MITCr(CO)$_4$ (6), 5MITCr(CO)$_3$ (3), 5MITCr(CO)$_2$ (5), 5MITCr(CO) (33), 5MITCr (100), $(C_3H_2NS)Cr$ (10), (CHSN)Cr (17), $(CH_3C_2H)Cr$ (17)
ITW(CO)$_5$ (61), ITW(CO)$_4$ (11), ITW(CO)$_3$ (35), ITW(CO)$_2$ (55), ITW(CO) (67), ITW (100), $(C_2H_2S)W$ (64), WS (14)
TW(CO)$_5$ (75), TW(CO)$_4$ (25), TW(CO)$_3$ (36), TW(CO)$_2$ (96), TW(CO) (75), TW (100), $(C_2H_2S)W$ (97), WS (45)
4-MITW(CO)$_5$ (61), 4MITW(CO)$_4$ (13), 4MITW(CO)$_3$ (28), 4MITW(CO)$_2$ (39), 4MITW(CO) (56), 4MITW (100), $(CH_3C_2HS)W$ (39), $(CH_3C_2H)W$ (22)
5-MITW(CO)$_5$ (68), 5MITW(CO)$_4$ (12), 5MITW(CO)$_3$ (28), 5MITW(CO)$_2$ (37), 5MITW(CO) (52), 5MITW (100), $(CH_3C_2HS)W$ (40), $(CH_3C_2H)W$ (120)

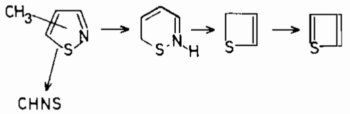
$LM(CO)_5$, L = IT, T; M = Cr, W

The fragmentation of these base ions for the chromium complexes also exhibits the two main routes illustrated above for the free ligands. The loss of hydrogen cyanide with retention of the metal ligand interaction implies a migration of the metal from the nitrogen atom to the sulfur atom. The structure of the C_2H_2S ion is thought to contain a π-system, thus it is possible that coordination may occur via this group, however, the presence of diatomic ions $[CrS]^+$ suggests the more probable coordination via the sulfur atom. Furthermore, the ratios of HCN:CH≡CH elimination for the thiazole and isothiazole chromium complexes are 1:1 and 1:2 respectively. This compares to ratios of 16:1 and 4:1 respectively for the free ligands, under comparable conditions. It is clear that there is a large decrease in the ability of the hydrogen cyanide elimination in both cases as would be expected since the process for the coordinated ligand involves the metal migration. The reduction in HCN elimination is greatest for the thiazole complex where the N–S migration is a 1,3 process as opposed to a 1,2 process for the isothiazole system. If the π system was coordinated to the metal in the ion $C_2H_2S(Cr)$ then the reverse situation might be anticipated since the π system is further removed from the metal in the isothiazole metal ion.

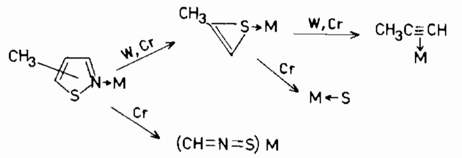
The related tungsten complexes differ from the above description in one important aspect, namely there are no detectable ions present in the spectrum resulting from the elimination of acetylene from the base ion L(W). The exclusive migration of tungsten to sulfur under these conditions as compared to chromium may be explained on the basis of the relative hardness and softness of the metals and the nitrogen and sulfur donor atoms. The larger tungsten atom being softer would form thermodynamically more stable bonds to sulfur relative to nitrogen than chromium. It is also noteworthy that the binuclear species WS is observed in greater relative abundance than the related species CrS for the chromium complexes.

$LM(CO)_5$, L = 4(5)MIT; M = Cr, W

The methyl substituted thiazole and isothiazole complexes also exhibit parent ions and those fragments associated with the stepwise loss of carbonyl groups. Based upon the above analysis of the unsubstituted ligand metal complexes we might expect the methyl derivatives to exhibit two main fragmentation pathways involving loss of hydrogen cyanide or methyl acetylene. The fragmentations of the free ligands have been published and evidence produced that a major fragmentation route involves ring expansion via incorporation of the methyl carbon atom into the hetero ring. This is followed by loss of hydrogen cyanide and hydrogen to produce an ion m/e 71, which is the major fragmentation ion in the spectra. The methyl acetylene expulsion pathway was also observed.



In the present study we find only the fragmentation pathways proceeding via direct elimination of the neutral molecules, and no evidence for ring expansion processes occurring. For the chromium complexes of 4- and 5-methyl-isothiazole the extent of hydrogen cyanide to methylacetylene elimination is equal in both complexes. A significant competing pathway for both base ions MIT(Cr) is loss of methyl group; however, no further fragmentation of the resulting ion is observed. There are no ions associated with the major free ligand fragment m/e 71 C_3H_3S being coordinated to the transition metal. The tungsten complexes exhibit significantly different spectral properties. Loss of hydrogen cyanide is the only observable fragmentation route observed from the base ion MIT(W). This again can be attributed to the more favorable soft–soft tungsten–sulfur interaction. However, in the case of the resulting methyl substituted ions CH_3CCHS–W a further interesting fragmentation occurs with loss of sulfur to form an acetylene metal ion, CH_3CCH(W) m/e 226. This ion is very abundant and it is noteworthy that in these spectra no ions associated with the diatomic WS species are observed. Clearly the addition of an electron releasing methyl group to the heterocyclic ligand alters the nature of its interaction with the metal. The methylacetylene being more electron rich than the parent acetylene is more readily formed and decomposition of the species LM is dramatically changed. A general scheme is outlined below.



It is thus clear that although all the new complexes reported in this paper are formed by coordination of the nitrogen atom to the transition metal, many other interactions are possible in energetically excited states, involving coordination via the sulfur atom and the carbon π system. Furthermore, the nature of the metal as well as the substituents on the heterocyclic ligand are important in determining the exact nature of these ligand metal interactions.

The similarity of thiazole and isothiazole to both thiophene and pyridine prompted comparison of the chemical properties with respect to metal carbonyl substitution. It is clear from the results presented above that the new ligands resemble pyridine more closely than thiophene, an observation in accord with many other reported aspects of the chemistry of these two sulfur–nitrogen heterocycles.[9,10]

Thiophene[11] like benzene[12] has been shown to form π-complexes of chromium carbonyl while the N-methylpyridinium ion which forms a related cationic π-complex of chromium tricarbonyl,[13] is the only substituted pyridine molecule reported to form a π-complex. We have attempted to synthesize thiazole and isothiazole π-complexes of chromium using the reaction outlined below.

$$(CH_3CN)_3Cr(CO)_3 + L \rightarrow (L)Cr(CO)_3$$

These attempts have thus far been without success, as might be inferred from the mass spectral data of the pentacarbonyl complexes, where no extra stability was observed for the $(L)Cr(CO)_3$ ion as might be expected if a $\sigma \rightarrow \pi$ rearrangement took place. The product formed from the reaction scheme illustrated above was a red, insoluble, oxidatively and thermally unstable complex formed in good yields. It has not been completely characterized; however, the infrared spectrum (nujol mull) exhibits bands expected for a tris-substituted chromium tricarbonyl, $(IT)_3Cr(CO)_3$, *i.e.*, $\nu(C{\equiv}O)\,cm^{-1}$, 1895 (s), 1745 (s. bd.).

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