

REACTIVITY OF CARBONYL COMPLEXES WITH Mo–Hg BOND. INTERACTION OF TRICARBONYL COMPLEXES OF MOLYBDENUM(0) WITH THIOUREA AND MERCURY CHLORIDE

A. LOPEZ, M. PANIZO and M. CANO

*Facultad de Ciencias Químicas, Departamento de Química Inorgánica, Universidad Complutense,
28003-Madrid (Spain)*

(Received February 25th, 1986)

Summary

Addition of thiourea to (chloromercuri)molybdenum carbonyl complexes of the type $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ ($\text{NN} = 2,2'$ -bipyridine (bipy); 1,10-phenanthroline (phen); 2,9-dimethyl-1,10-phenanthroline (dmp)), gives novel compounds in which the Mo–Hg bond is retained.

The inverse reaction, involving oxidative addition of HgCl_2 to the $\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ complexes, yield the same products only when the reactions are carried out in a molar ratio of 1/1. If an excess of HgCl_2 is employed the reactions proceed via oxidative elimination producing the neutral seven-coordinate complex $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$. In all cases mercuric halide-thiourea complexes of the type $\text{HgCl}_2[(\text{NH}_2)_2\text{CS}]$ are formed.

Introduction

We have previously shown that the mixed carbonyl complexes $\text{NNMo}(\text{CO})_3\text{L}$ ($\text{NN} = \text{bipy}$, phen; $\text{L} = \text{CO}$, PR_3 , py) undergo oxidative addition reactions when treated with mercuric derivatives [1–3]. In all cases the $\text{NNMo}(\text{CO})_3$ moiety is conserved, and the ease of displacement of the L ligand depends on the nature of the acceptor.

Oxidative elimination reactions of basic carbonyl derivatives of Group VI transition metals involving mercuric derivatives as Lewis acids have received considerable attention as preparative methods for a wide range of heteronuclear complexes with Mo–Hg bonds. However, there have been few studies of the reactions of this type of compound. Owing to biological interest in the interaction with mercury in systems containing molybdenum–sulphur bonds we decided to study the reactions of the complexes $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ with ligand S-donors. The thiourea ligand was employed since the carbonyl complexes of type $\text{M}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]_3$ are more stable than analogous complexes containing other S-donor ligands [4].

TABLE 1
ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES FOR THE COMPLEXES $\text{NNM}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$

Compound ^a	Colour	Analyses (Found (calcd.)(%))		M.p. ^b (°C)	Conductivity ^c (ohm ⁻¹ cm ² mol ⁻¹)	$\nu(\text{CO})$ ^d (cm ⁻¹)	λ_{max} ^e (nm)	log ϵ	Assignment
		C	H N						
$\text{bipyM}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$	dark purple	39.81 (40.70)	2.65 (2.91)	13.25 (13.59)	22.40	1895vs	460	3.09	CT M \rightarrow L _{NN}
						1875vs	372	3.18	CT M \rightarrow $\Pi^*(\text{CO}) + d \rightarrow d$
						1730vs	280	3.84	CT M \rightarrow $\Pi^*(\text{CO})$
$\text{phenM}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$	red-brown	43.98 (44.04)	2.80 ^e (2.75)	12.37 (12.84)	12.50	1900vs	522	3.12	CT M \rightarrow L _{NN}
						1870vs	330	3.53	CT M \rightarrow $\Pi^*(\text{CO}) + d \rightarrow d$
						1760sh	280	3.90	CT M \rightarrow $\Pi^*(\text{CO})$
						1720vs			
$\text{dmpM}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$	dark purple	46.32 (46.56)	3.06 (3.45)	11.88 (12.07)	19.66	1890vs	492	3.26	CT M \rightarrow L _{NN}
						1780vs	340	3.40	CT M \rightarrow $\Pi^*(\text{CO}) + d \rightarrow d$
						1725vs	290	3.66	CT M \rightarrow $\Pi^*(\text{CO})$

^a All the complexes are diamagnetic. ^b Decomposition temperature. ^c In DMFA solution and concentration ca. 10^{-4} mol l⁻¹. ^d In KBr. ^e Analytical data reported by Houck and Dobson C, 44.28; H, 2.93% [5].

A parallel study of the behaviour of $\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ complexes towards HgCl_2 was also carried out.

Results and discussion

The $\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ complexes

Thiourea reacted with a molar equivalent $\text{NNMo}(\text{CO})_4$ (NN = bipy, dmp) in xylene under nitrogen, to give dark purple crystalline solids $[\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]]$. (This result parallels that obtained with the corresponding phen derivatives [5].) The products are insoluble in aliphatic and aromatic hydrocarbons and in most common solvents, but soluble in DMFA and DMSO, but the colour of the solution in these solvent changes shortly after they are made up. Although the products are fairly stable as solids, their suspensions decompose when exposed to air. The analytical data (Table 1) are consistent with the proposed formulations, and conductance measurements confirm the neutral character of the complexes.

The IR spectra of the complexes indicate that the thiourea ligand is attached to the molybdenum atom via sulphur [6]. Three bands in the stretching carbonyl region (Table 1, Scheme 1) can be assigned to the $2A' + A''$ modes [7] of a C_s local symmetry and to a *fac*-configuration.

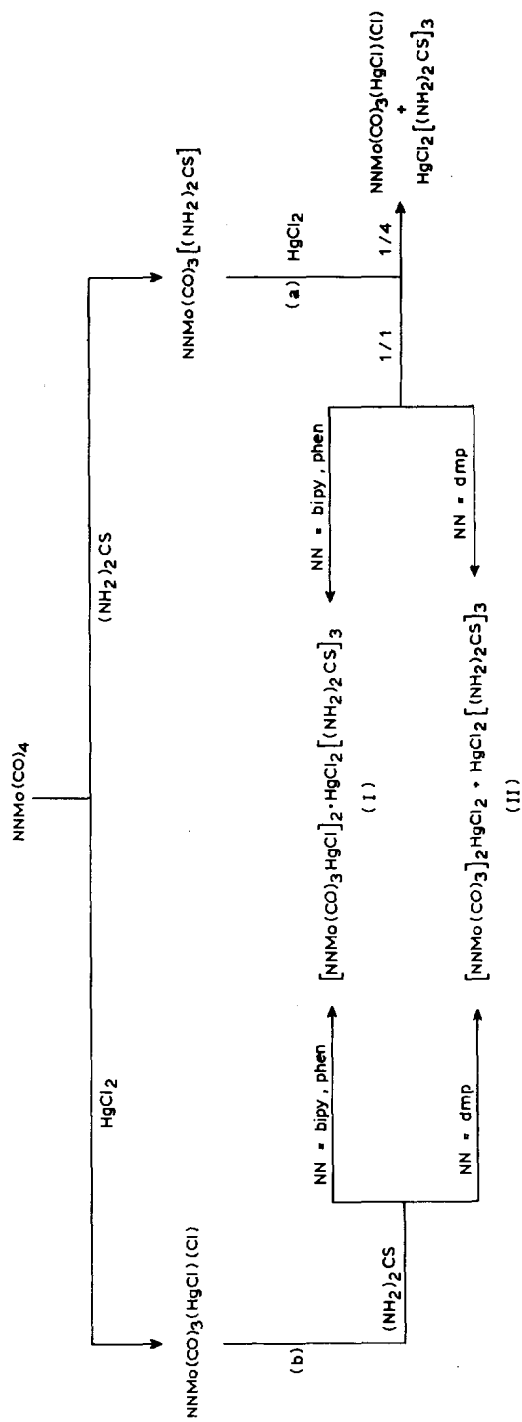
The UV-VIS spectra of the complexes were recorded in freshly made up DMFA solution in the 200–600 nm range, and the maximum absorption (λ_{max}) intensities and tentative assignments are listed in Table 1. In all cases three bands are observed, and these have been assigned in accordance with published data [8–10].

Reactions of $\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ with HgCl_2 (a)

The carbonyl thiourea complexes $\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ (NN = bipy, phen, dmp) react with HgCl_2 in acetone or dichloromethane at room temperature under nitrogen. The colour of the solution changes and various types of products are obtained depending on the proportion of HgCl_2 employed and the nature of NN donor ligand.

When a 1/1 molar ratio of basic-metal/mercuric chloride is employed, the products isolated (Scheme 1) are of the lattice type: $\text{NNMo}(\text{CO})_3\text{HgCl}$ (I) (NN = bipy, phen) or $[\text{dmpMo}(\text{CO})_3]_2\text{HgCl}_2$ (II). In all cases these compounds are precipitated along with $\text{HgCl}_2[(\text{NH}_2)_2\text{CS}]_n$ complexes [11,12]. The two products could be separated only for NN = dmp.

The compounds of type I (Scheme 1) are insoluble in organic solvents. The IR spectra of the solids in the carbonyl stretching region show three bands, clearly split and shifted towards the higher frequencies with respect to those of the tricarbonyl starting materials (Fig. 1). These shifts are consistent with an increase in the formal oxidation state of the transition metal. The IR spectrum of the bipy derivative in this region was identical with that of a sample $\text{bipyMo}(\text{CO})_3\text{HgCl}$ [1], which had been prepared from $\text{bipyMo}(\text{CO})_3(\text{py})$ and HgCl_2 . The compounds of type I show the typical absorptions of NN and thiourea ligand bands in the 1600–400 cm^{-1} region [13,14]. In addition there is a new band, at ca. 700 cm^{-1} , characteristic of S-thiourea coordination to mercury in the $\text{HgCl}_2[(\text{NH}_2)_2\text{CS}]_n$ complexes [11]. From the IR spectra it appears that the thiourea ligand is substituted and coordinated to additional HgCl_2 . The analytical data of the compounds are consistent with a formulation of the type $\text{NNMo}(\text{CO})_3\text{HgCl} \cdot 0.5\text{HgCl}_2[(\text{NH}_2)_2\text{CS}]_3$ (NN = bipy,



SCHEME 1. Outline of observed reactions; (a) Reactions of molybdenum thiourea compounds with HgCl_2 in 1/1 and 1/4 molar ratios. (b) Reactions of molybdenum-mercury compounds with thiourea.

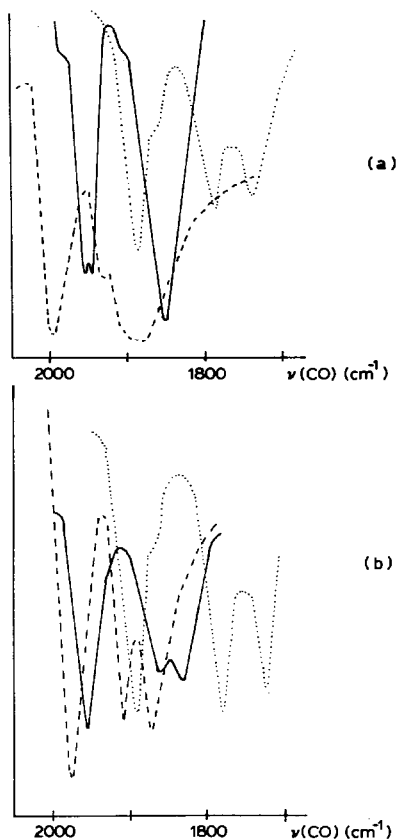


Fig. 1. Carbonyl stretching bands in the solid state (a) — — — $\text{bipyMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$; ····· $\text{bipyMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ — — — $[\text{bipyMo}(\text{CO})_3]_2\text{HgCl}_2[(\text{NH}_2)_2\text{CS}]_3$; (b) — — — $\text{dmpMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$; ····· $\text{dmpMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ — — — $[\text{dmpMo}(\text{CO})_3]_2\text{HgCl}_2$.

phen). The pattern and the splitting of the carbonyl bands are not significantly different from those of the complexes $[\text{Mo}(\text{CO})_3\text{Cp}]_2$ [15]. Thus, a dimeric formulation is tentatively suggested for the compounds of type I.

Compound II (Scheme 1), $[\text{dmpMo}(\text{CO})_3]_2\text{HgCl}_2$ is soluble in THF and CH_2Cl_2 from which it is recrystallized. The analytical data are consistent with the formulation proposed.

No common features were found in the IR spectra of $[\text{CpMo}(\text{CO})_3]_2\text{Hg}$ and $[\text{dmpMo}(\text{CO})_3]_2\text{HgCl}_2$ (II) compounds. The first of these complexes exhibits five carbonyl stretching bands, and this splitting has been explained in terms of a skew configuration with a linear Mo–Hg–Mo arrangement. The second compound, shows only three bands (Fig. 1), and a centrosymmetrical (*trans*-) structure is possible; these bands are shifted to frequencies higher than those of the parent compounds. It appears that the steric and electronic characteristics of the dmp ligand may prevent the formation of the relevant skew configuration.

When the reaction is carried out with an excess of mercuric chloride, the products of oxidative addition, $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ (NN = bipy, phen, dmp) [3,16,17], are always obtained, together with mercuric halide thiourea complexes.

From all the reactions of type (a) we also isolated some of the carbonyl complexes $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$.

Reactions of $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ with thiourea (b)

The stoichiometric reactions of thiourea with the heteronuclear complexes $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ (NN = bipy, phen, dmp) containing a Mo–Hg bond, yield the same products as were obtained from the 1/1 reactions of $\text{NNMo}(\text{CO})_3\text{--}[(\text{NH}_2)_2\text{CS}]$ with HgCl_2 (Scheme 1). An excess of thiourea ligand causes decomposition. The products were characterized by analytical and spectroscopic data, but solubility problems prevent further studies.

The IR spectra in the carbonyl stretching region, show three bands shifted to frequencies lower than those of the parent compounds (Fig. 1), which is consistent with a reduction of the formal oxidation state of molybdenum. In addition, the bands attributed to $\nu(\text{Hg--Cl})$ vibrations which appear at ca. $260\text{--}280\text{ cm}^{-1}$ for the starting compounds are absent from the products obtained with thiourea. Only very weak absorptions shifted to lower frequencies are observed in this region (Table 2). This could be attributed to the existence of $\text{Hg--X}\cdots\text{Hg}$ interactions in the solids [18].

The results are consistent with a change in coordination of the initial compounds. The crystal structure of $\text{bipyMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ [19] shows seven-coordination at molybdenum and the presence of Mo–HgCl and Mo–Cl bonds, similar environments are attributed to analogous phen and dmp derivatives. However, in the compounds isolated from the reactions here, $\text{NNMo}(\text{CO})_3\text{HgCl}$ (NN = bipy, phen) and $[\text{dmpMo}(\text{CO})_3]_2\text{HgCl}_2$, hexacoordination of molybdenum is possible.

The complex $\text{dmpMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ shows unusual behaviour in its reaction with thiourea. When precipitate which separates from the THF solution is extracted with dichloromethane $[\text{NNMo}(\text{CO})_3]_2\text{HgCl}_2$ can be isolated from the extract in low

TABLE 2

VALUES OF $\nu(\text{CO})$ AND $\nu(\text{HgCl})$ FOR THE PRODUCTS FROM THE REACTIONS OF $\text{NNMo}(\text{CO})_3[(\text{NH}_2)_2\text{CS}]$ WITH HgCl_2

NN	1/1 Molar ratio		1/4 Molar ratio	
	$\nu(\text{CO})$	$\nu(\text{HgCl})$	$\nu(\text{CO})$	$\nu(\text{HgCl})$
bipy	1980sh	–	1990vs	285s
	1945vs	260vw	1925sh	
	1935vs	245vw	1880vs	
	1890sh			
	1830vs			
phen	1980sh	–	1990vs	285sh
	1940vs	–	1900vs	270s
	1890sh	240vw	1870vs	
	1850sh			
	1825vs			
dmp	1955vs	280vw	1980vs	280s
	1860vs		1895vs	
	1830vs		1870vs	

yield. The tetracarbonyl complex dmpMo(CO)_4 was isolated from the THF solution. It appears that an unstable carbonyl compound formed during the reaction decomposes with loss of carbon monoxide. This provides a source for further carbonylations leading to the formation of a stable tetracarbonyl complex.

Experimental

All reactions were carried out under nitrogen using standard Schlenk tube techniques and freshly distilled, dried, and degassed solvents.

The NNMo(CO)_4 and $\text{NNMo(CO)}_3(\text{HgCl})(\text{Cl})$ (NN = bipy, phen, dmp) and $\text{phenMo(CO)}_3[(\text{NH}_2)_2\text{CS}]$ compounds were prepared by published methods [5,16].

Analyses. C, H, N analyses were carried out by the Elemental Microanalyses Ltd. Laboratories; Amberley, Beaworth (Devon), United Kingdom.

Physical measurements. Infrared spectra in the $4000\text{--}200\text{ cm}^{-1}$ region were recorded on a Perkin-Elmer 1300 spectrophotometer, the samples were in KBr pellets or Nujol mulls.

Conductance measurements were performed in DMFA solution at room temperature with a Radiometer Copenhagen CDM 2e conductivity bridge and a cell with a constant of a 1 cm^{-1} .

Electronic spectra in the $600\text{--}200\text{ nm}$ region were recorded in DMFA solution with a Kontron Uvikon 280 spectrophotometer.

Preparation of $\text{NNMo(CO)}_3[(\text{NH}_2)_2\text{CS}]$ (NN = bipy, dmp)

NNMo(CO)_4 (1.45 g) and thiourea (0.46 g) were stirred and refluxed in xylene under nitrogen for 1 h. The initial red solution became dark violet. The mixture was cooled to room temperature and the violet precipitate formed, was filtered off, washed with petroleum ether, and dried in vacuum.

Reaction of $\text{NNMo(CO)}_3[(\text{NH}_2)_2\text{CS}]$ complexes with HgCl_2 (NN = bipy, phen, dmp)

Mercuric chloride (0.11 g) was added to a solution of $\text{NNMo(CO)}_3[(\text{NH}_2)_2\text{CS}]$ (0.15 g) in acetone (30 ml). The violet solution turned brown within a few minutes. When NN = bipy or phen the precipitate formed was filtered off and dried in vacuum. The solids isolated were identified as $[\text{NNMo(CO)}_3\text{HgCl} \cdot 0.5\text{HgCl}_2[(\text{NH}_2)_2\text{CS}]_3]$ (Yield 65%) (Found: C, 21.96; H, 2.02; N, 8.81. $\text{C}_{29}\text{H}_{28}\text{Cl}_4\text{Hg}_3\text{Mo}_2\text{N}_{10}\text{O}_6\text{S}_3$ calcd.: C, 21.18; H, 1.70; N, 8.51% for NN = bipy. Found: C, 23.95; H, 1.82; N, 8.98. $\text{C}_{33}\text{H}_{28}\text{Cl}_4\text{Hg}_3\text{Mo}_2\text{N}_{10}\text{O}_6\text{S}_3$ calcd.: C, 23.42; H, 1.65; N, 8.27% for NN = phen).

When NN = dmp, the solid was dissolved in CH_2Cl_2 (20 ml), and the solution was concentrated then diluted with petroleum ether to give a precipitate. This was identified as $[\text{dmpMo(CO)}_3]_2\text{HgCl}_2$. (Found: C, 40.98; H, 2.93; N, 6.15. $\text{C}_{34}\text{H}_{24}\text{Cl}_2\text{HgMo}_2\text{O}_6$ calcd.: C, 38.97; H, 2.29; N, 5.34%).

To provide a molar ratio of 1/4, mercuric chloride (0.26 g) was added to a solution of $\text{NNMo(CO)}_3[(\text{NH}_2)_2\text{CS}]$ (0.11 g), in acetone (30 ml) and the solution was stirred under nitrogen for 2 h, the violet colour turning to brown. When NN = bipy the compound was isolated from the solution by addition of petroleum ether. When NN = phen or dmp the precipitated formed was filtered off and dissolved in CH_2Cl_2 , and the solution was concentrated then diluted with petroleum ether. In both cases the isolated products were identified as $\text{NNMo(CO)}_3(\text{HgCl})(\text{Cl})$.

Reaction of $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ with thiourea

Thiourea (0.02 g) was added to a solution of $\text{NNMo}(\text{CO})_3(\text{HgCl})(\text{Cl})$ (0.17 g) in THF (30 ml). The initially orange solution turned brown immediately. The mixture was stirred under nitrogen for 90 min, then the precipitate was filtered off, washed with acetone and CH_2Cl_2 , and dried in vacuum.

When $\text{NN} = \text{dmp}$ the brown precipitate was extracted with CH_2Cl_2 . The extracts were filtered then concentrated, and petroleum ether was added to yield an orange solid. The THF solution was concentrated and petroleum ether was added to give a red solid, which was identified as $\text{dmpMo}(\text{CO})_4$.

References

- 1 M. Pardo and M. Cano, *J. Organomet. Chem.*, 270 (1984) 311.
- 2 M. Panizo and M. Cano, *J. Organomet. Chem.*, (1984) 247.
- 3 M. Pardo and M. Cano, *J. Organomet. Chem.*, 260 (1984) 81.
- 4 F.A. Cotton and F. Zingales, *Inorg. Chem.*, 1,1 (1962) 145.
- 5 L.W. Houck and G.R. Dobson, *Inorg. Chem.*, 5, 12 (1966) 2119.
- 6 S.C. Tripathi, S.C. Srivastava and R.D. Pandey, *J. Inorg. Nucl. Chem.*, 35 (1973) 457.
- 7 L.W. Houck and G.R. Dobson, *J. Chem. Soc. A.*, (1966) 317.
- 8 H. Saito, J. Fujita and K. Saito, *Bull. Chem. Soc. Japan*, 41 (1968) 359.
- 9 M.S. Wrighton, D.L. Morse, H.B. Gray and D.K. Ottesen, *J. Am. Chem. Soc.*, (1976) 98.
- 10 G.L. Geoffroy and M.S. Wrighton, *Organomet. Photochem.*, Academic Press, New York, (1979) 45.
- 11 A. Korczynski and J. Ziolkowski, *Zesz. Nauk. Politech. Lodz. Chem.*, 19 (1969) 85.
- 12 A. Korczynski, M. Mardelli and M.A. Pellinghelli, *Rocz. Chem. Ann. Soc. Chim. Pol.*, 47 (1973) 905.
- 13 A.A. Schilt and R.C. Taylor, *J. Inorg. Nucl. Chem.*, 9 (1959) 211.
- 14 A. Yamaguchi, R.B. Penland, S. Mizushima, T.J. Lane, C. Currand and J.V. Quagliano, *Inorg. Chem.*, 80 (1958) 537.
- 15 R.D. Fischer and K. Noack, *J. Organomet. Chem.*, 16 (1969) 125.
- 16 R. Edgar, B.F.G. Johnson, J. Lewis and S.B. Wild, *J. Chem. Soc. (A)* (1968) 2855.
- 17 T.R. Jernigan and G.R. Dobson, *Inorg. Chem.*, 11,1 (1972) 81.
- 18 M.M. Kubicki, R. Kergoat, J.E. Guerschais, C. Bois and P. L'Haridon, *Inorg. Chim. Acta*, 43 (1980) 17.
- 19 P.D. Brotherson, J.M. Epstein, A.H. White and S.B. Wild, *Aust. J. Chem.*, 27 (1974) 2667.