Sulphur–Arsenic Ligands. Dimethyl(methylthio)arsine Complexes of Halogenotrimethylplatinum(IV) and Tricarbonylhalogenorhenium(I) *

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Dimethyl(methylthio)arsine, $AsMe_2(SMe)$ (L), is a potentially ambidentate ligand with the possibility of arsine and/or sulphur co-ordination to a transition metal. We have investigated the reaction of the ligand for the scission of the tetrameric trimethylplatinum halides, and that for carbon monoxide displacement from the rhenium pentacarbonyl halides. In both of these reactions organic arsines and sulphides individually are known to be effective, producing well characterised stable products. Ligand L reacts with $[(PtXMe_3)_4]$ (X = Cl, Br, or I) and with $[ReX(CO)_5]$ (X = Cl, Br, or I) to yield respectively *fac*-$[PtXMe_3L_2]$ and *fac*-$[ReX(CO)_3L_2]$ in good yield. Hydrogen-1 and ^{13}C n.m.r. studies demonstrate that in all complexes the ligand behaves in a monodentate manner with exclusively arsenic–metal bonds. In solution the compounds give no indications of any fluxional behaviour in the temperature range −80 to +80 °C. The *fac* structure of all of these complexes gives rise to the interesting observation that all three methyl groups in the co-ordinated ligand $AsMe_2(SMe)$ are non-equivalent.

Dimethyl(methylthio)arsine (L) has lone-pair electrons at both sulphur and arsenic atoms and has potential therefore as an ambidentate ligand. Four of the possible modes of co-ordination for this ligand are illustrated in Figure 1. As part of a programme investigating the transition metal complexes of such multi-electron ligands we report the reaction of L with tetrameric halogenotrimethylplatinum(IV) and pentacarbonylhalogenorhenium(I) compounds. Both systems are known to produce d^6 octahedral complexes with both arsenic[1] and with sulphur[2] ligands. Of particular interest was the possibility that arsenic- and sulphur-bonded species would be of comparable energy, with the consequential likelihood of a fluxionality involving an intramolecular metal 1,2-shift between sulphur and arsenic. In this respect it is of interest that the first report[3] of a metal complex of dimethyl(methylthio)arsine was the action of $AsMe_2Cl$ on $[Cr(CO)_5\{S(Me)SnMe_3\}]$ to produce $[Cr(CO)_5L]$. In this L is co-ordinated to the Cr^0 centre *via* an arsenic atom; this implies that at some stage during the reaction the metal undergoes a 1,2-intramolecular shift from sulphur to arsenic [structure (**1b**) $\longrightarrow$ (**1a**)]. More recently the complexes $[M(CO)_5L]$ (M = Cr, Mo, or W) have been prepared directly from reaction of L with metal carbonyl complexes, and here also the ligand attachment to metal is believed to be through the arsenic atom.[4–6]

We now report the synthesis and spectroscopic properties of several new complexes of dimethyl(methylthio)arsine with Re^I and Pt^{IV}.

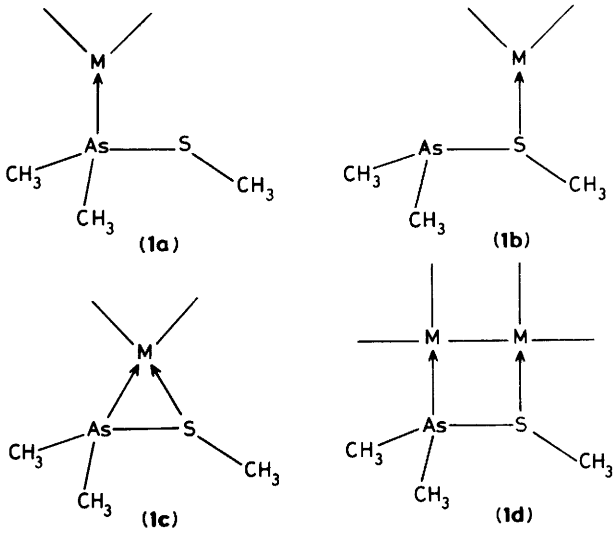

Figure 1. Schematic structures illustrating four of the possible co-ordination modes of dimethyl(methylthio)arsine

Results and Discussion

Dimethyl(methylthio)arsine (L) attacks the tetrameric halogenotrimethylplatinum(IV) compounds to produce high yields of the mononuclear complexes *fac*-$[PtXMe_3L_2]$ (X = Cl, Br, or I), equation (1) (see Table 1). We detect only one type of product

$$[\{PtXMe_3\}_4] + 8L \xrightarrow[\text{CHCl}_3]{\Delta,\ 6\ \text{h}} 4\,fac\text{-}[PtXMe_3L_2] \qquad (1)$$

from these reactions, despite the use of a wide variety of ratios of reactants and reaction conditions. N.m.r. studies (see below) show that these complexes are non-fluxional over the range −80 to +80 °C, and that the co-ordination mode is *via* arsenic as illustrated in Figure 2, structure (**2a**).

Isoelectronic and isostructural complexes of rhenium(I) are also prepared in high yields according to equation (2) (see Table

$$[ReX(CO)_5] + 2L \longrightarrow fac\text{-}[ReX(CO)_3L_2] + 2\,CO \qquad (2)$$

1). In these complexes the ligand is arsenic bound with overall *fac* geometry around the rhenium atom, structure (**2b**).

N.M.R. Spectra of the Complexes $[PtXMe_3L_2]$.—The ^1H and ^{13}C data for these complexes are given in Table 2 and a representative ^1H spectrum for $[PtIMe_3L_2]$ is illustrated in Figure 3. The ^1H spectra of all complexes show five signals (all of which demonstrate coupling to ^{195}Pt), from low to high field of relative intensities 2:2:2:2:1. The two signals at highest field

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* *Non-S.I. unit employed:* mmHg ≈ 133 N m^{-2}.

Table 1. Complexes of dimethyl(methylthio)arsine (L)

Complex[a]	Reaction solvent	Reaction time (h)	Yield (%)	Melting point (°C)	Analysis[b] (%) C	Analysis[b] (%) H
$[PtClMe_3L_2]$	$CHCl_3$	6	50	79—80	18.95 (18.8)	4.65 (4.65)
$[PtBrMe_3L_2]$	$CHCl_3$	6	55	101—103	17.75 (17.45)	4.30 (4.35)
$[PtIMe_3L_2]$	$CHCl_3$	6	60	125—127	16.35 (16.1)	4.00 (4.00)
$[ReCl(CO)_3L_2]$	$CHCl_3$	18	60	51—52	18.0 (18.0)	2.95 (3.00)
$[ReBr(CO)_3L_2]$	thf	24	59	76—78	16.45 (16.5)	2.80 (2.75)
$[ReI(CO)_3L_2]$	thf	72	50	110—112	15.4 (15.5)	2.65 (2.55)

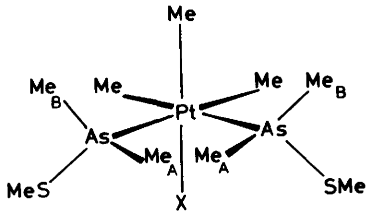
[a] All complexes are white or colourless crystalline solids. [b] Calculated values are in parentheses.

Table 2. N.m.r. parameters[a] for the dimethyl(methylthio)arsine complexes *fac*-$[PtXMe_3L_2]$

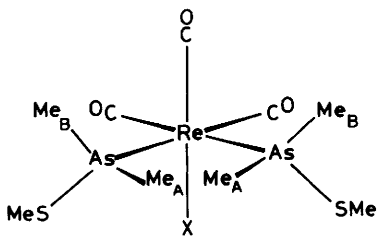
	Pt-CH_3 (*trans* As)				Pt-CH_3 (*trans* X)			
	$\delta(^1H)^b$/ p.p.m.	$\delta(^{13}C)^b$/ p.p.m.	$^1J(^{195}Pt-^{13}C)$/ Hz	$^2J(^{195}Pt-^1H)$/ Hz	$\delta(^1H)^b$/ p.p.m.	$\delta(^{13}C)^b$/ p.p.m.	$^1J(^{195}Pt-^{13}C)$/ Hz	$^2J(^{195}Pt-^1H)$/ Hz
fac-$[PtClMe_3L_2]$	1.22	7.98	576.9	64.5	0.84	−8.79	639.8	73.2
fac-$[PtBrMe_3L_2]$	1.29	6.92	571.7	64.8	0.96	−4.32	632.2	72.6
fac-$[PtIMe_3L_2]$	1.42	4.67	565.7	65.4	1.13	+2.17	611.4	70.3

	$AsMe_2$				SMe			
	$\delta(^1H)^b$/ p.p.m.	$\delta(^{13}C)^b$/ p.p.m.	$^2J(^{195}Pt-^{13}C)$/ Hz	$^3J(^{195}Pt-^1H)$/ Hz	$\delta(^1H)^b$/ p.p.m.	$\delta(^{13}C)^b$/ p.p.m.	$^3J(^{195}Pt-^{13}C)$/ Hz	$^4J(^{195}Pt-^1H)$/ Hz
fac-$[PtClMe_3L_2]$	1.83	10.83	*c*	5.1	2.28	11.06	*ca.* 2.0	*c*
	1.69	7.94	10.5	5.7				
fac-$[PtBrMe_3L_2]$	1.88	11.77	*c*	5.4	2.27	11.10	*ca.* 2.0	*c*
	1.71	8.17	10.5	5.8				
fac-$[PtIMe_3L_2]$	1.99	13.79	*c*	5.7	2.26	11.23	*ca.* 2.2	*ca.* 1.0
	1.77	8.97	10.2	6.1				

[a] Samples recorded at room temperature in $CDCl_3$ solution. [b] Values to high frequency (low field) of $SiMe_4$. [c] Unresolved.



(2a)



(2b)

Figure 2. Structures of *fac*-$[PtXMe_3L_2]$ (**2a**) and *fac*-$[ReX(CO)_3L_2]$ (**2b**) indicating the magnetically non-equivalent arsenic-methyl groups Me_A and Me_B

are assigned to the platinum methyls and the three at lower field are assigned to the ligand methyls. In these *fac* complexes there is no mirror plane through either of the Pt–As bonds [see (**2a**)], and thus in the absence of any fluxionality the two arsenic-methyl groups are magnetically non-equivalent, and give rise to individual resonances. Indeed, the number of signals in the ^1H spectra and their relative intensities are consistent only with arsenic-bonded ligands and a *fac* orientation about the platinum(IV) centre.

The platinum-methyl region shows the expected two signals of relative intensity 2:1, with the signal at highest field assigned to the unique methyl group *trans* to halogen. The magnitude of $^2J(^{195}Pt-^1H)$ is within the range 70.3—73.2 Hz consistent with a methyl group *trans* to halogen in Pt^{IV} complexes.[7,8] The hydrogens of the platinum-methyl groups of relative intensity 2 have $^2J(^{195}Pt-^1H)$ values of *ca.* 65 Hz, which are comparable to magnitudes reported[9,10] for platinum-methyl groups *trans* to arsenic in such complexes as *fac*-$[PtXMe_3(o\text{-}Me_2AsC_6H_4AsMe_2)]$ and *fac*-$[PtXMe_3(AsMe_2Ph)_2]$. These are well outside the range (68.7—71.7 Hz) reported for systems where sulphur is the donor atom *trans* to methyl in platinum(IV) complexes.[8]

Coupling to ^{195}Pt is observable for the ligand hydrogen atoms, where $^3J(^{195}Pt-As-C-^1H)$ is 5.1—6.1 Hz, again comparable[10] to such values in *fac*-$[PtXMe_3(AsMe_2Ph)_2]$. In *fac*-$[PtIMe_3L_2]$ we are able to observe $^4J(^{195}Pt-As-S-C-^1H)$ with a value of *ca.* 1 Hz.

By comparison with the free ligand the hydrogen atoms in the complexed ligand are shifted downfield; in the case of the arsenic methyls by an average of *ca.* 0.5 p.p.m. and for the sulphur methyls by only *ca.* 0.1 p.p.m.

The ^{13}C spectrum of *fac*-$[PtIMe_3L_2]$ is illustrated in Figure 4 and is representative of the series. Five individual ^{13}C

Table 3. Spectroscopic properties of *fac*-$[ReX(CO)_3L_2]$ complexes

		^1H N.m.r.[b]		^{13}C N.m.r.[b]			
Complex	ν(CO)[a]/cm^{-1}	SMe	AsMe$_2$[c]	AsMe$_2$[c]	SMe	CO[d] (*trans* As)	CO[e] (*trans* X)
$[ReCl(CO)_3L_2]$	2 040 (sh), 1 956, 1 913	2.33	1.96 1.88	14.71 12.16	12.30	189.3	187.6
$[ReBr(CO)_3L_2]$	2 032 (sh), 1 954, 1 911	2.32	1.99 1.93	15.12 12.89	12.43	188.6	187.0
$[ReI(CO)_3L_2]$	2 038 (sh), 1 955, 1 916	2.30	2.04 2.02	16.03 14.65	12.69	187.2	185.9

[a] In $CHCl_3$ solution. [b] Values are (δ/p.p.m.) to high frequency of $SiMe_4$ in $CHCl_3$ solution at room temperature. [c] Hydrogen-1 and ^{13}C resonances correlated by ^{13}C-{^1H} experiments. [d] Intensity 2. [e] Intensity 1.

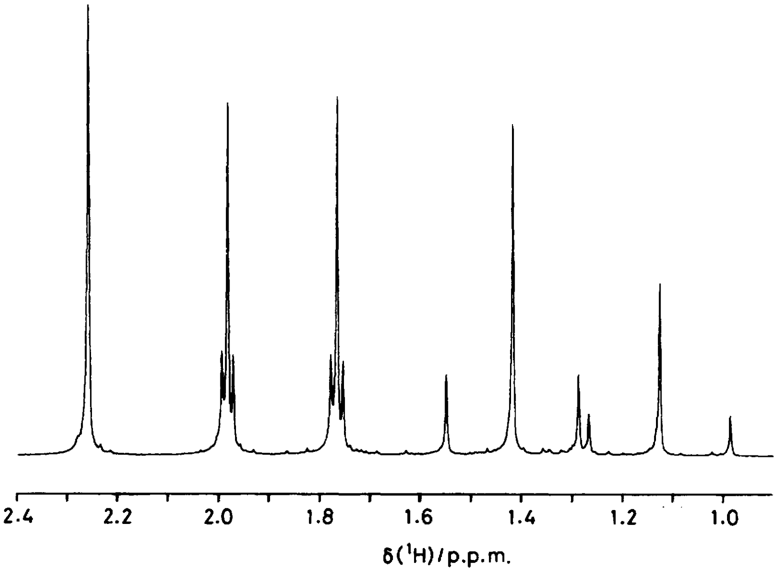


Figure 3. 250-MHz ^1H spectrum of *fac*-$[PtIMe_3L_2]$ recorded at room temperature in $CDCl_3$ solution

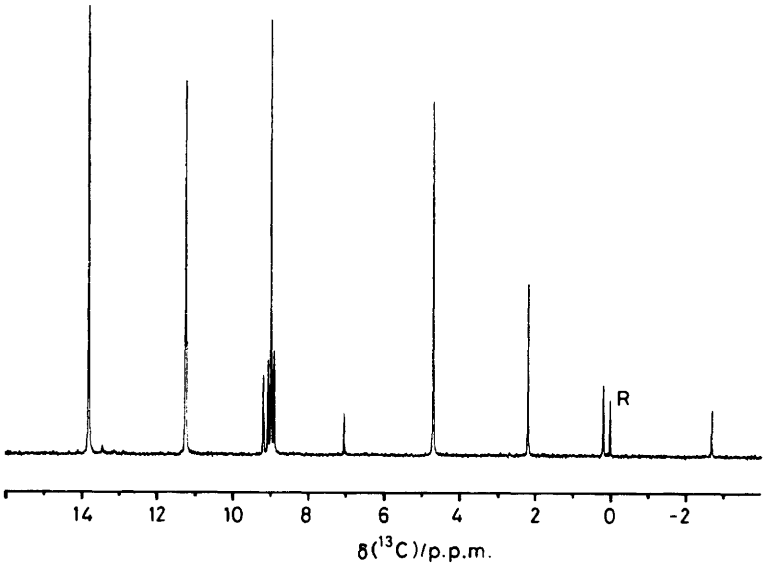


Figure 4. 62.8-MHz ^{13}C-{^1H} spectrum of *fac*-$[PtIMe_3L_2]$ recorded at room temperature in $CDCl_3$. Resonance R is the internal standard $SiMe_4$ (= 0.0 p.p.m.)

resonances are distinguishable, with those at highest and next highest field assigned to platinum-methyl carbon atoms *trans* to halogen and to arsenic respectively, $^1J(^{195}Pt-^{13}C)$ values being comparable[11] to those in *fac*-[$PtXMe_3(AsMe_2Ph)_2$]. The other three ^{13}C signals have been attributed to the three non-equivalent ligand-methyl groups by $^{13}C-\{^1H\}$ experiments (Table 2). The high-field arsenic-methyl carbon shows $^2J(^{195}Pt-As-^{13}C)$ of *ca.* 10.3 Hz and the sulphur-methyl carbon has $^3J(^{195}Pt-As-S-^{13}C)$ at *ca.* 2 Hz, whereas interestingly the low-field arsenic-methyl carbon appears to be uncoupled to platinum.

N.M.R. Spectra of the Complexes [$ReX(CO)_3L_2$].—Hydrogen-1 and ^{13}C data are reported in Table 3, where all three methyls are non-equivalent in each ligand as a result of the *fac* structure (**2b**). The ligand resonances are closely analogous to those already discussed for the [$PtXMe_3L_2$] complexes, and clearly demonstrate the arsenic–rhenium bonded *fac* configuration for these rhenium analogues.

Carbon-13 spectra of the carbonyl groups in these complexes show two broad resonances of approximate relative intensity 2:1 with the more intense signal at lower field assigned to carbonyl groups *trans* to arsenic. These ^{13}C resonances are in the range 185—189 p.p.m. with signals moving to higher field for the series chlorine, bromine, iodine. This halide shift appears to bear equally upon both *cis* and *trans* carbonyl groups indicating a notable *cis* effect.

Experimental

General.—Reactions were carried out using standard Schlenk conditions under nitrogen, and solvents were dried and distilled under nitrogen from an appropriate drying agent [CaH_2 for $CHCl_3$; sodium benzophenone ketyl for thf (tetrahydrofuran) and light petroleum (b.p. 60—80 °C)] before use. Dimethyl(methylthio)arsine was prepared from a modification of a literature[12] method (see below) and halogenotrimethylplatinum(IV) and pentacarbonylhalogenorhenium(I) compounds were prepared by standard procedures.[13–17] The preparations of the dimethyl(methylthio)arsine complexes were very similar, a representative method is given for the synthesis of *fac*-[$PtIMe_3(Me_2AsSMe)_2$] and conditions for other reactions are reported in Table 1.

Preparation of Dimethyl(methylthio)arsine.—A suspension of $Pb(SMe)_2$[18] (35 g, 116 mmol) in dry light petroleum (50 cm^3) was stirred vigorously during the dropwise addition of chlorodimethylarsine[19] (22.6 g, 160 mmol) over a period of 1 h. The subsequent mixture was heated under reflux for a further 1 h, after which all volatiles were removed by vacuum transfer (0.2 mmHg) into a liquid-nitrogen cooled trap. The clear liquid obtained was distilled at atmospheric pressure under nitrogen to remove light petroleum, and the residue was then distilled under reduced pressure to yield the product[20] (16.4 g, 69%), b.p. 35 °C (15 mmHg). ^1H N.m.r. δ 2.18 (s, 3 H, SMe) and 1.32 p.p.m. (s, 6 H, $AsMe_2$).

Preparation of fac-[$PtIMe_3L_2$].—The tetrameric iodotrimethylplatinum (0.110 g, 0.075 mmol) and dimethyl(methylthio)arsine (0.110 g, 0.75 mmol) were heated together under reflux in dry chloroform (5 cm^3) for 6 h. The reaction mixture was reduced in volume to *ca.* 0.5 cm^3, and 5 cm^3 of light petroleum were added to precipitate the crude product. This was recrystallized from light petroleum at −20 °C overnight to yield the product (0.120 g, 60%), see Table 1.

N.M.R. Studies.—Hydrogen-1 and ^{13}C experiments were performed on a Bruker AM250 instrument at 250 and 62.8 MHz respectively. Samples were dissolved in $CDCl_3$ for room-temperature spectra, and variable-temperature ^1H spectra (−80 to +80 °C) were recorded in [$^2H_8$]toluene.

References

1 J. C. Cloyd and C. A. McAuliffe, in 'Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan Press, London, 1973, pp. 207—267.
2 E. W. Abel, K. G. Orrell, and S. K. Bhargava, *Prog. Inorg. Chem.*, 1984, **32**, 1.
3 W. D. Ehrl and H. Vahrenkamp, *Chem. Ber.*, 1970, **103**, 3563.
4 J. Grobe and D. Le Van, *Z. Naturforsch., Teil B*, 1979, **34**, 1653.
5 J. Grobe and D. Le Van, *Z. Naturforsch., Teil B*, 1980, **35**, 694.
6 J. Grobe and D. Le Van, *J. Fluorine Chem.*, 1984, **24**, 25.
7 T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
8 E. W. Abel, K. G. Orrell, and A. W. G. Platt, *J. Chem. Soc., Dalton Trans.*, 1983, 2345.
9 A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 1971, 3545.
10 J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 1969, 2964.
11 B. E. Mann, *Adv. Organomet. Chem.*, 1974, **12**, 135.
12 W. R. Cullen, *Can. J. Chem.*, 1963, **41**, 2424.
13 J. C. Baldwin and W. C. Kaska, *Inorg. Chem.*, 1975, **14**, 2020.
14 D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, 1965, **21**, 357.
15 D. E. Clegg and J. R. Hall, *J. Organomet. Chem.*, 1970, **22**, 491.
16 G. Dolcetti and J. R. Norton, *Inorg. Synth.*, 1976, **16**, 35.
17 W. Heiber, R. Schuh, and H. Fuchs, *Z. Anorg. Allg. Chem.*, 1941, **248**, 243.
18 E. W. Abel, *J. Chem. Soc.*, 1960, 4406.
19 G. P. Vanderkelen, *Bull. Soc. Chim. Belg.*, 1956, **65**, 343; *Chem. Abstr.*, 1956, **51**, 13747d.
20 L. S. Sagan, R. A. Zingaro, and K. J. Irgolic, *J. Organomet. Chem.*, 1972, **39**, 301.

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