Interaction of Dimethyl(dimethylarsinothio)arsine Sulphide with Group 6 Metal Carbonyls

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The interaction of dimethyl(dimethylarsinothio)arsine sulphide, $Me_2(S)As{\cdot}S{\cdot}AsMe_2$, with u.v.-irradiated tetrahydrofuran solutions of the appropriate metal hexacarbonyls yields the complexes $[M(CO)_5L]$ (M = Cr or W, L = $Me_2As{\cdot}S{\cdot}AsMe_2$) and $[MM'(CO)_{10}L]$ (M = M' = Cr, L = $Me_2As{\cdot}AsMe_2$; M = Cr, M' = W or M = M' = W, L = $Me_2As{\cdot}S{\cdot}AsMe_2$). The binuclear complexes with L = $Me_2As{\cdot}S{\cdot}AsMe_2$ are thermally unstable and lose sulphur. The complex $[Cr(CO)_5L]$ affords $[Cr(S_2AsMe_2)_3]$ on heating.

RECENTLY we reported [1] the results of a study on a series of complexes $[M(CO)_5L]$ (M = Cr or W; L = tertiary phosphine or arsine sulphide). This work has now been extended to include an investigation of the interaction of the related ligand, dimethyl(dimethylarsinothio)arsine sulphide (dmdas) with Group 6 metal carbonyls. Although dmdas has structure (I) in the solid state,[2] n.m.r. and i.r. spectra indicate that in solution an equilibrium is established with another species postulated to be (II).[3] It is not surprising therefore that the reaction of dmdas with metal salts is complicated, and gives a variety of products.[4] These often contain the dimethyldithioarsenate ion $[Me_2AsS_2]^-$, *e.g.* $[Ni(dmdas)_2(S_2AsMe_2)]ClO_4$ or $[SZn_4(S_2AsMe_2)_6]$. In contrast we now find that the complexes isolated initially from the reaction of dmdas with metal carbonyl species contain solely trivalent arsenic, being bis(dimethylarsino)sulphur (dmas) or tetramethyldiarsane (tmda) derivatives such as $[Cr(CO)_5(dmas)]$ and $[Cr_2(CO)_{10}(tmda)]$.

$Me_2(S)As{\cdot}S{\cdot}AsMe_2$ (I) $Me_2As{\cdot}S{\cdot}S{\cdot}AsMe_2$ (II)

RESULTS AND DISCUSSION

The reaction of dmdas in equimolar proportions with the appropriate metal carbonyl complex $[M(CO)_5(thf)]$ (M = Cr or W; thf = tetrahydrofuran) yielded the moderately air stable, yellow, crystalline complexes $[M(CO)_5(dmas)]$. I.r. spectra showed (in the region 2 100—1 800 cm^{-1}) a carbonyl-stretching-frequency pattern typical of $[M(CO)_5L]$ systems (L = unidentate arsenic donor ligand [5]) and that the strong ν(As=S) absorption observed at 480 cm^{-1} in dmdas [3] was no longer present. Furthermore, identical products were isolated from the reaction of dmas itself with the $[M(CO)_5(thf)]$ species [equation (1)]. The loss of sulphur from dmdas

$$[M(CO)_5(thf)] \xrightarrow[M\,=\,Cr\ or\ W]{dmdas\ or\ dmas} [M(CO)_5(dmas)] \qquad (1)$$

during the preparation of these complexes may be contrasted with the behaviour of trimethylarsine sulphide which under similar conditions remains intact, affording $[M(CO)_5(SAsMe_3)]$ (M = Cr or W) complexes.[1] The complex $[Cr(CO)_5(dmas)]$, when heated under reflux in cyclohexane, produced, in low yield, purple crystals of $[Cr(S_2AsMe_2)_3]$, identical to an authentic sample.[6] Under similar conditions the analagous tungsten complex remained unchanged.

Bridged binuclear species have also been isolated. Thus reaction of dmdas with $[Cr(CO)_5(thf)]$ (2 mol) afforded the previously reported tmda complex $[(CO)_5Cr(\mu\text{-tmda})Cr(CO)_5]$. In contrast a similar reaction with $[W(CO)_5(thf)]$ yielded the complex $[(CO)_5W(\mu\text{-dmas})W(CO)_5]$. The direct synthesis of this complex from dmas has been recently reported elsewhere.[7] The mixed species $[(CO)_5Cr(\mu\text{-dmas})W(CO)_5]$ may be prepared by reacting the ' free ' end of dmas in $[W(CO)_5(dmas)]$ with more $[Cr(CO)_5(thf)]$. The i.r. spectrum of this latter complex showed the A_1'' carbonyl modes to be split, confirming the presence of two different metal atoms.

It is not clear why dmas should not form a bridged chromium complex, especially in view of the fact that the corresponding positive ion was detected in a mass spectrometer (see below), but steric factors or a greater weakening of the As–S bond may be important. The isolated bridged dmas complexes do show a tendency to lose the bridgehead sulphur in solution. Thus, although $[(CO)_5W(\mu\text{-dmas})W(CO)_5]$ was reported to be thermally stable,[7] we found that, after warming under reflux in cyclohexane (3 h), the appearance of a peak at τ 8·81 (C_6H_6) in the n.m.r. spectrum was indicative of sulphur loss [8] (*ca.* 75%). In the presence of the sulphur scavenger Ph_3P, the sulphide Ph_3PS was isolated. The behaviour of $[(CO)_5Cr(\mu\text{-dmas})W(CO)_5]$ was more complicated. On standing in $CDCl_3$, peaks at τ 8·06 and 8·21 in the n.m.r. spectrum indicate $[(CO)_5Cr(\mu\text{-tmda})W(CO)_5]$ is formed, but at higher temperatures n.m.r. evidence indicated that other possible species, *e.g.* $[(CO)_5W(\mu\text{-tmda})W(CO)_5]$, are also produced.

^1H N.m.r. spectral data for the dmas complexes are listed in the Table. In $CDCl_3$ solution the unidentate complexes $[M(CO)_5(dmas)]$ exhibited two resonances. The higher-field resonance (*ca.* τ 8·5) is attributable to the

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methyl protons on the non-co-ordinated arsenic and was virtually unchanged from that of free dmas, while the lower-field resonance (*ca.* τ 8·1) can be assigned to the deshielded methyl protons near the co-ordinated end of the molecule. Also given in the Table are values of the aromatic-solvent-induced shift, Δ.[9] As in other systems,[1,10,11] the increase in the Δ value for the methyl protons which occurs on co-ordination may be related to an increase in positive charge on the arsenic atom. However, unlike the τ ($CDCl_3$) values, Δ values for the two different types of methyl protons in the complexes $[M(CO)_5(dmas)]$ were similar. This suggests that in this case other factors, *e.g.* steric, also contribute to the magnitude of Δ. These results may be contrasted to those observed for the complexes $[M(CO)_5(Me_2PCH_2CH_2PMe_2)]$ where the Δ values for the different methyl protons did reflect the expected difference in positive charge on the two phosphorus atoms.[11]

Spectral, analytical, and m.p. data for the complexes

Compound	$\nu(CO)$ [a]/cm^{-1}	^1H N.m.r.[b] (τ)		Analyses [d]/%			M.p., θ_c/°C
		Free CH_3–As ($\Delta\tau$) [c]	Bound CH_3–As ($\Delta\tau$) [c]	C	H	S	
dmas [e]		8·60 (0·22)					
$[Cr(CO)_5(dmas)]$	2 065m, 1 984w, 1 945vs, 1 917 (sh)	8·53 (0·48)	8·16 (0·58)	26·2 (24·9)	3·0 (2·8)	7·4 (7·4)	41—43
$[Mo(CO)_5(dmas)]$ [f]	2 075m, 1 988w, 1 953vs	8·54	8·17				
$[W(CO)_5(dmas)]$	2 075m, 1 985w, 1 945vs, 1 916 (sh)	8·52 (0·47)	8·03 (0·51)	19·8 (19·1)	2·3 (2·1)	5·8 (5·7)	42—44
$[CrW(CO)_{10}(dmas)]$	2 075m, 2 065m, 1 985w, 1 947vs, 1 917 (sh)		7·96 (0·70), 7·81 (0·75)	22·4 (22·2)	1·8 (1·6)	4·4 (4·2)	83—85
$[W_2(CO)_{10}(dmas)]$	2 075m, 1 986w, 1 945vs, 1 917 (sh)		7·81 (0·74)	19·0 (18·9)	1·4 (1·4)	4·4 (3·6)	96—99

[a] In cyclohexane. [b] In $CDCl_3$. [c] $\Delta\tau = \tau(C_6H_6) - \tau(CDCl_3)$. [d] Calculated values are given in parentheses. [e] dmas = Bis(dimethylarsino)sulphur. [f] Not isolated analytically pure.

The mass spectra of the dmas complexes exhibited parent molecular ions as well as peaks due to the sequential loss of carbon monoxide. Peaks corresponding to the loss of sulphur from the co-ordinated dmas ligand were also observed. In contrast, under similar conditions, the complexes $[M(CO)_5L]$ (M = Cr, Mo, or W; L = potentially bidentate ligand such as $Me_2PCH_2CH_2PMe_2$) did not show parent molecular ions but only peaks corresponding to $[M(CO)_4L]^+$ and its subsequent decomposition.[11] For the binuclear complex $[(CO)_5Cr(\mu\text{-}dmas)W(CO)_5]$, $[(CO)_5W(\mu\text{-}dmas)W(CO)_5]^+$, and $[(CO)_5Cr(\mu\text{-}dmas)Cr(CO)_5]^+$ ions as well as the molecular ion occurred in moderate abundance.

EXPERIMENTAL

I.r. spectra were recorded on a Beckman I.R. 20 spectrophotometer, n.m.r. spectra on a JEOL JNM-C-60 HL spectrometer, and mass spectra on an A.E.I. MS9 mass spectrometer at 70 eV.* Microanalyses (Table) were carried out by Professor A. Campbell, University of Otago.

All reactions were carried out under an atmosphere of oxygen-free dinitrogen. Tetrahydrofuran (thf) was sodium dried; other laboratory grade solvents were used as purchased. Dimethyl(dimethylarsinothio)arsine sulphide (dmdas),[3] bis(dimethylarsino)sulphur (dmas),[3] sodium dimethyldithioarsenate,[12] and tris(dimethyldithioarsenato)-chromium(III) [6] were prepared according to literature methods.

The Complexes $[M(CO)_5(dmas)]$ (M = Cr *or* W).—The complex $[M(CO)_6]$ (2 mmol) was dissolved in thf (60 cm^3) and the solution irradiated in an u.v. cell for 1 h. dmdas (2 mmol), dissolved in thf (20 cm^3), was added to the orange solution and the resulting mixture stirred for 15 min. The solvent was removed *in vacuo* and excess of the hexacarbonyl was sublimed from the residue *in vacuo* at room temperature. The resulting oil was dissolved in pentane (25 cm^3), leaving an unidentified brown solid which was removed by filtration through Kieselguhr. After removal of the pentane the remaining oil was allowed to crystallise (0 °C) and then sublimed *in vacuo* (50 °C, 0·1 mmHg) to yield the *product* as yellow crystals, yield 40—60%. The complexes were also prepared as above but using dmas.

The Complex $[W_2(CO)_{10}(dmas)]$.—As in the above method, dmdas (0·27 g, 1 mmol) was added to a u.v.-irradiated solution of $[W(CO)_6]$ (0·76 g, 2 mmol). After stirring and solvent removal, excess of $[W(CO)_6]$ was sublimed from the residue *in vacuo* and the resulting solid dissolved in benzene (25 cm^3) and filtered through Kieselguhr. The yellow filtrate was reduced in volume (10 cm^3) and, on addition of n-hexane, yellow *crystals* formed, yield 40%. An analytical sample was recrystallised from cyclohexane. A similar reaction involving $[Cr(CO)_6]$ (2 mmol) and dmdas (1 mmol) yielded the tetramethyldiarsane complex $[Cr_2(CO)_{10}(tmda)]$, m.p. 109—112 °C (lit.[8,13] 112, 108—110 °C), τ ($CDCl_3$) 8·27.

Thermal Reaction of the Complex $[Cr(CO)_5(dmas)]$.—The complex (0·1 g, 0·25 mmol) was heated under reflux in cyclohexane (25 cm^3) for 30 min. The dark purple solid which formed was filtered from the yellow solution and recrystallised from chloroform, yield 0·02 g. The complex was identified as $[Cr(S_2AsMe_2)_3]$ from a comparison of its i.r. and u.v. spectrum with those of an authentic sample.[6] The addition of sulphur to the reaction mixture did not increase the yield significantly and longer reflux times led to precipitation of an insoluble brown material.

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* 1 eV $\simeq$ 1·60 × 10^{-19} J.

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