Fluxional Pentacarbonyltungsten(0) Complexes of the Thioaldehyde and Thioketone Valence Isomers of 1,6,6aλ^4-Trithiapentalenes

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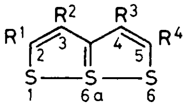
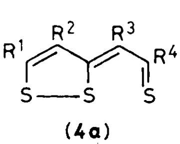
The reaction of silver nitrate with tetraethylammonium pentacarbonyliodotungstate(0) in the presence of 1,6,6aλ^4-trithiapentalenes gives pentacarbonyltungsten(0) complexes of the thioaldehyde and thioketone valence isomers of 1,6,6aλ^4-trithiapentalenes; the symmetrically substituted complexes are fluxional.

1,6,6aλ^4-Trithiapentalenes are bicyclic compounds, *e.g.*, (**1**)—(**3**), which employ four-electron three-centre bonding in the S–S–S sequence. Their thioaldehyde or thioketone valence isomers (**4a**) or (**4b**) have never been detected, although the system (**4a**) $\rightleftharpoons$ (**4b**) of rapidly interconverting isomers has been proposed[1] as an alternative formulation to the bicyclic structure. We now report the preparation of pentacarbonyltungsten(0) complexes of the thiocarbonyl compounds (**4**), starting from the corresponding 1,6,6aλ^4-trithiapentalenes.

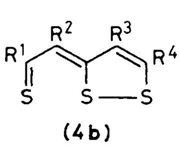
It has been shown[2] that a variety of two-electron ligands (L) react with tetra-alkylammonium pentacarbonylhalogenometallate(0) salts $\{R_4N^+[M(CO)_5X]^-\}$ (M = Cr, Mo, W; X = Cl, Br, I) in the presence of Lewis acids, *e.g.*, silver salts, to form compounds $LM(CO)_5$. It was proposed[2] that transient $M(CO)_5$ species are formed and immediately trapped by the ligand L. Accordingly, we allowed solutions of the 1,6,6aλ^4-trithiapentalenes (**1**)—(**3**) and tetraethylammonium pentacarbonyliodotungstate(0) $\{Et_4N^+[W(CO)_5I]^-\}$[3] in dichloromethane to react under argon with aqueous silver nitrate. Chromatography of the resulting blue solutions on silica (benzene) followed by recrystallisation from benzene–hexane at temperatures not exceeding 25 °C gave the complexes (**5**)—(**7**)† as deep blue–black crystals with a bronze reflex [(**5**) (84%), decomp. >120 °C, ν_{max}(CO) (cyclohexane) 2064(w), 1977(vw), 1940(s), and 1921(m) cm^{-1}; (**6**) (75%), decomp. >139 °C, ν_{max}(CO) (cyclohexane) 2056(w), 1973(vw), 1938(s), and 1916(m) cm^{-1}; (**7**) (82%), decomp. >126 °C, ν_{max}(CO) (cyclohexane) 2066(w), 1978(vw), 1938(s), and 1919(m) cm^{-1}].



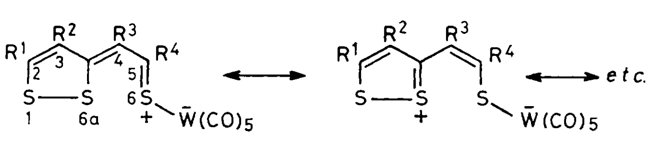
	R1	R2	R3	R4
(**1**)	H	[CH2]3		H
(**2**)	Me	H	H	Me
(**3**)	Bu^t	H	H	H



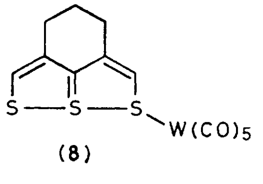
(**4a**)



(**4b**)



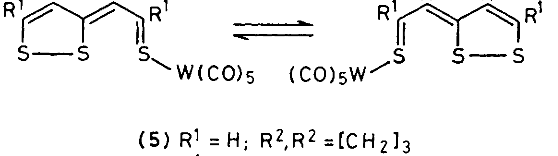
	R1	R2	R3	R4
(**5**)	H	[CH2]3		H
(**6**)	Me	H	H	Me
(**7**)	Bu^t	H	H	H



(**8**)

An *X*-ray single crystal structure determination[4] has established that the complex from the 1,6,6aλ^4-trithiapentalene (**1**) has the pentacarbonyl(thioaldehyde)tungsten(0) structure (**5**) rather than structure (**8**). Thus the S(1)–S(6a)‡ bond length (2.08 Å) falls in the range for two-electron covalent S–S bond lengths (*ca.* 2.00—2.10 Å), and the S(6a) · · · S(6) distance (2.75 Å) lies far outside the range (*ca.* 2.20—2.50 Å) for three-centre S–S bonds in 1,6,6aλ^4-trithiapentalenes.[5]

Compounds (**5**) and (**6**) display fluxional behaviour in solution. The ^{1}H n.m.r. spectrum ($CDCl_3$) of compound (**5**) shows at −10 °C two sharp singlets at δ 8.182(2-H) and 9.457(5-H) which broaden with increase of temperature and coalesce at 34 °C to a broad singlet at δ 8.79. Further heating to 60 °C causes this singlet to become progressively sharper. This behaviour is reversed by cooling the solution. The coalescence temperature (T_c) and line shape were independent of the concentration of the complex (**5**) over the range 0.075—0.4 M. From the spectral data [ν(5-H) − ν(2-H), 102 Hz], $\Delta G^{\ddagger}(T_c)$ is calculated to be 14.7 kcal mol^{-1} (1 kcal = 4.184 kJ). The ^{1}H n.m.r. spectrum ($CDCl_3$) of the complex (**6**) at −20 °C shows two sharp ring signals at δ 7.453(3-H) and 7.660(4-H) and two sharp methyl signals at δ 2.666(2-Me) and 2.733(5-Me). The ring signals coalesce at 1 °C, and at 33 °C appear as a sharp singlet at δ 7.517. The methyl signals coalesce at *ca.* 4 °C, and at 33 °C give rise to a sharp singlet at δ 2.669. In contrast, the ^{1}H n.m.r. spectrum ($CDCl_3$) of the complex (**7**) comprises one set of signals whose pattern is temperature-invariant. At 33 °C these signals appear at δ 1.507(Bu^t), 7.541(s, 3-H), 7.564(d, 4-H), and 9.645(d, 5-H) ($J_{4,5}$ 7.5 Hz). We conclude that the fluxional process is intramolecular (Scheme 1).



(**5**) R^1 = H; R^2,R^2 = [CH$_2$]$_3$
(**6**) R^1 = Me; R^2 = H

Scheme 1

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† Satisfactory analytical data were obtained for compounds (**5**)—(**7**).

‡ For clarity of discussion, the complexes (**5**)—(**7**) are here numbered in the same way as the corresponding 1,6,6aλ^4-trithiapentalenes.

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References

1 D. Leaver and D. M. McKinnon, *Chem. Ind.* (*London*), 1964, 461.

2 J. A. Connor, E. M. Jones, and G. K. McEwen, *J. Organomet. Chem.*, 1972, **43**, 357.

3 Prepared in 90% yield essentially by the method of E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 1963, 2068. Equimolar quantities of tetraethylammonium iodide and hexacarbonyltungsten(0) were heated in boiling n-butyl alcohol for 1.5 h.

4 Full details are being published elsewhere (C. Glidewell, D. C. Liles, and P. J. Pogorzelec, *Acta Crystallogr.*, *Sect. B*, in the press).

5 In compound (**1**), the S–S distances are 2.300 and 2.385, and 2.276 and 2.412 Å, respectively, for two crystallographically independent molecules (P. L. Johnson, E. C. Llaguno, and I. C. Paul, *J. Chem. Soc.*, *Perkin Trans.* 2, 1976, 234).