Synthesis of Different Thione Complexes from Pentacarbonyl-α-ethoxybenzylidenetungsten and Lithium Phenylethynethiolate

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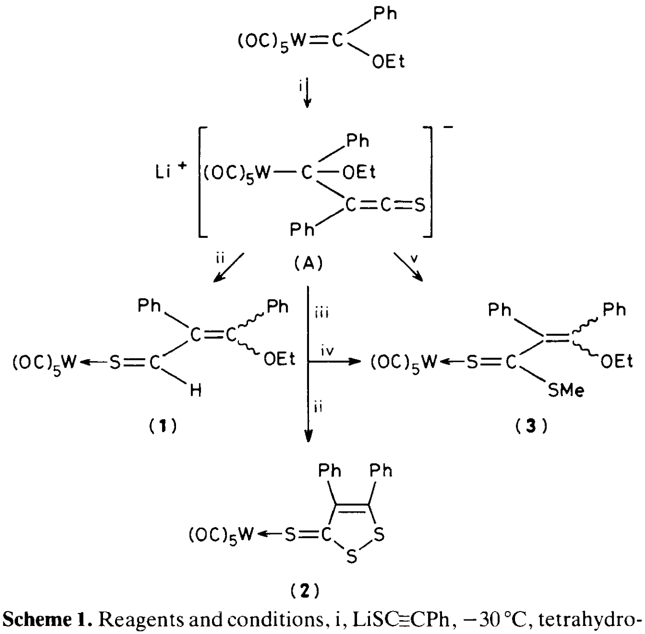
The adduct between pentacarbonyl-α-ethoxybenzylidenetungsten and lithium phenylethynethiolate is a promising nucleophilic reagent for the preparation of a variety of compounds such as tungsten co-ordinated 2,3-diphenyl-3-ethoxypropenethial (**1**), 4,5-diphenyl-1,2-dithiole-3-thione (**2**), and methyl 2,3-diphenyl-3-ethoxydithiopropenoate (**3**); the formation of the adduct has been confirmed by a crystal structure determination on (**2**).

Addition of lithium compounds to co-ordinated alkoxycarbene groups leads to important carbon–carbon and carbon–heteroatom bond formation.[1] Usually the alkoxy group is subsequently removed by acidification,[2] but the adduct has also been converted into compounds which still contain the alkoxy group.[3] We report here the formation of an unusual adduct during the title reaction from which pentacarbonyltungsten complexes of an α,β-unsaturated thioaldehyde,[4] a pseudo-aromatic 1,2-dithiole-3-thione,[5] and a dithioester[6] were synthesized.

Formation of the new complexes, purple (**1**) (20%),† purple (**2**) (87%), and brown (**3**) (21%), from the red adduct (A) upon treatment with respectively, HCl in Et_2O; S_8 and then HCl in Et_2O; and S_8 and MeI or only MeSSMe (33%), are explained in terms of Scheme 1. The thione complexes (**1**)—(**3**) were separated from other lower yield products by column chromatography and crystallized from ether–hexane [m.p.s respectively, 88, 91, and 182 (decomp.) °C]. Their structures are fully supported by n.m.r.‡, i.r.,[7] and mass spectral data, and elemental analysis.



Scheme 1. Reagents and conditions, i, LiSC≡CPh, −30 °C, tetrahydrofuran; ii, HCl–Et_2O, −30 °C; iii, S_8; iv, MeI, 25 °C; v, MeSSMe, 55 °C.

The crystal structure of compound (**2**) was determined by *X*-ray diffraction. The crystals are dark, reddish-brown, opaque, and block shaped, and a small (0.06 × 0.05 × 0.13 mm) crystal was used to minimise absorption effects.

Crystal data for (**2**): $C_{20}H_{10}O_5S_3W$, $M = 610.3$, monoclinic, space group $P2_1/n$, $a = 17.495(9)$, $b = 19.792(9)$, $c = 6.001(3)$ Å, $\beta = 95.9(1)°$, $U = 2067$ Å^3, $Z = 4$, $D_c = 1.96$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.7107$ Å), μ(Mo-K_α) = 57 cm^{-1}, 2331 (783 unobserved) reflections with $3° < \theta < 23°$. The structure was refined by full-matrix least-squares (SHELX 76) with anisotropic thermal parameters for the tungsten only and hydrogens in calculated positions. Final $R = 0.068$ and $R_w = 0.051$ (weights = $1/\sigma_F^2$).§

The molecular structure is shown in Figure 1. The 1,2-dithiole-3-thione part of the molecule is essentially flat and all its structural parameters are very similar to those of 4-methyl-1,2-dithiole-3-thione.[8] The carbonyl group *trans* to the sulphur shows little influence from the latter, with a W–C bond length similar to the others. The co-ordination around

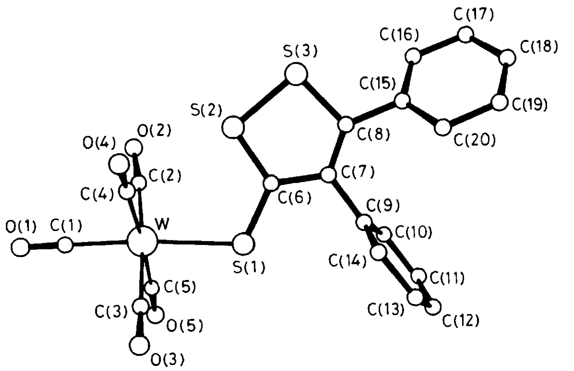
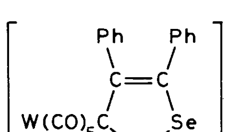


Figure 1. The *X*-ray crystal structure of (**2**). Some important distances (Å): W–S(1), 2.528(6); average W–C, 1.99(4); S(1)–C(6), 1.68(2); S(2)–S(3), 2.056(8); S(2)–C(6), 1.70(2); S(3)–C(8), 1.76(2); C(6)–C(7), 1.45(2); C(7)–C(8), 1.32(2).



(**4**)

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† Yields refer to analytically pure products and were not optimised.

‡ Selected n.m.r. spectroscopic data measured in $CDCl_3$ at room temperature. Compound (**1**): ^1H, δ 10.31 (s, 1H, S=CH), 7.65—6.90 (m, 10H, Ph), 3.90 (q, 2H, OCH_2), and 1.16 (t, 3H, OCH_2CH_3); ^{13}C-{^1H}, δ 217.1 (C-1), 174.4 (C-3), 137.4 (C-2), and 133.4—128.0 p.p.m. (Ph). (**2**): ^{13}C-{^1H}, δ 213.5 (C-3), 172.7 (C-5), 145.5 (C-4), and 134.0—129.4 p.p.m. (Ph). (**3**): ^1H, δ 7.49—6.95 (m, 10H, Ph), 3.67 (q, 2H, OCH_2), 2.50 (s, 3H, SMe), and 1.23 (t, 3H, OCH_2CH_3).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

the tungsten is in agreement with the previously determined structure of $[W(CO)_5\{S{=}\overline{CNH(CH_2)_2S}\}]$.[9]

These results are significant in several respects. First, the formation of the adduct (A) is in accord with the presence of an unproved equilibrium between thioacetylene and thioketene anions.[10] Secondly, the adduct (A) is a versatile nucleophilic reagent with a nucleophilic centre located β to a carbene carbon and α to a sulphur atom. Thirdly, the reactions with the adduct represent novel transformations under mild reaction conditions which extend the synthetic utility of carbene complexes as well as sulphur-containing organic compounds.[11]

$LiSeC{\equiv}CPh$ and the carbene complex similarly form an adduct, the unusual chemistry of which will be discussed in detail elsewhere. Preliminary results show that treatment of the adduct with Se_8 and HCl affords, after chromatography and crystallization, analytically pure crystals of the selenium analogue of (**2**) (20%) and, in addition, the 1,2-diselenole carbene complex (**4**) in 10% yield.

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