Molybdenum Complexes of Sterically Hindered Thiols. The Preparation and Structure of $[Mo(CO)_2(SC_6H_2Pr^i_3)_3]^-$

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The reaction of $[MoCl_4(thf)_2]$ (thf = tetrahydrofuran) with $NaSC_6H_2Pr^i_3$ in thf under CO gives $[Mo(CO)_2(SC_6H_2Pr^i_3)_3]^-$ (**1**); an *X*-ray crystal structure shows a trigonal bipyramidal structure with axial CO groups.

Despite intense recent interest in molybdenum sulphur complexes with their potential relevance to molybdoenzymes[1,2] there have been few examples of such complexes interacting with small molecules. The formation of sulphur bridged oligomers is one of the principal obstacles to the generation of small molecule binding sites in metal thiolate chemistry. We here report the synthesis of complexes of sterically hindered arenethiols where we hoped both bridge formation and sulphide formation *via* carbon–sulphur bond cleavage would be inhibited.

The molybdenum(IV) complex $[MoCl_4(thf)_2]$ (thf = tetrahydrofuran) reacts with the sodium salt of 2,4,6-tri-isopropylbenzenethiol, Na(tipt), in thf under CO to give the Mo^{II} complex $[Mo(CO)_2(tipt)_3]^-$ (**1**) which can be isolated from methanol as a pink-purple crystalline tetraphenylphosphonium salt. The same complex can also be prepared from the reaction of $[MoBr_2(CO)_4]$ with the thiol in methanol in the presence of triethylamine. Analogous complexes are formed with 2,6-di-isopropylbenzenethiol and also with $[WBr_2(CO)_4]$.

$$[Mo(CO)_2(SC_6H_2Pr^i_3)_3]^-$$

(**1**)

The complexes show a single strong band in their i.r. spectra in the solid state at about 1830 cm^{-1} assigned to ν(CO). The single C–O stretching frequency is consistent with a trigonal bipyramidal structure with axial CO ligands and equatorial thiols with overall local C_{3v} symmetry. Pink-purple crystals of (**1**) suitable for an *X*-ray determination were obtained from dichloromethane–methanol.

Crystal data: $[Mo(CO)_2(SC_6H_2Pr^i_3)_3][P(C_6H_5)_4]$, $C_{71}H_{89}MoO_2PS_3$, M = 1197.59, triclinic, space group $P\bar{1}$, a =

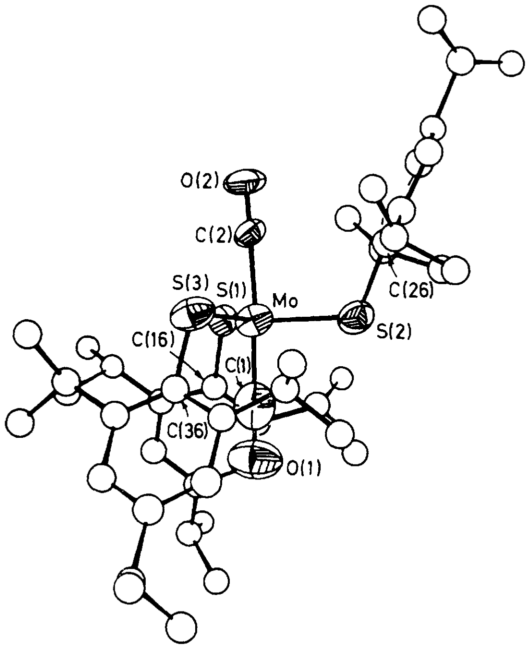

Figure 1. An ORTEP view of the $[Mo(CO)_2(SC_6H_2Pr^i_3)_3]^-$ anion showing for clarity a partial numbering scheme. Some distances in Å and bond angles in ° are: Mo–S(1), 2.332(4); Mo–S(2), 2.317(5); Mo–S(3), 2.342(5); Mo–C(1), 1.922(21); Mo–C(2), 1.987(16); C(1)–O(1), 1.203(24); C(2)–O(2), 1.164(19); and C(1)–Mo–C(2), 177.3(7); C(1)–Mo–S(1), 93.8(5); C(1)–Mo–S(2), 90.5(6); C(1)–Mo–S(3), 90.7(5); S(1)–Mo–S(2), 115.3(2); S(2)–Mo–S(3), 117.0(2); S(1)–Mo–S(3), 127.4(2); C(2)–Mo–S(1), 86.2(4); C(2)–Mo–S(2), 91.9(5); C(2)–Mo–S(3), 87.1(4).

13.451(2), b = 14.229(2), c = 19.862(3) Å, α = 96.11(1), β = 94.11(1), γ = 111.04(1)°; U = 3502.9(8) Å^3, D_c = 1.11 g cm^{-3}, Z = 2, F(000) = 1244.0. The structure analysis is based on 2939 reflections with $I_{obs} > 3.0\sigma(I_{obs})$, Mo-$K_\alpha$ radiation, μ = 3.26 cm^{-1}. R is currently 0.076.†

The stereochemistry of the $[Mo(CO)_2(SC_6H_2Pr^i_3)_3]^-$ anion is shown in Figure 1, and pertinent bond lengths and angles are summarised in the caption.

As implied by the i.r. data, the geometry about the Mo^{II} centre is essentially trigonal bipyramidal with axial CO and equatorial thiolato-ligands. The deviation of the S–Mo–S angles from the idealised value of 120° is a consequence of the relative orientations of the bulky aryl groups. Two of these adopt an *endo*-configuration relative to the C(1)–O(1) carbonyl with the two phenyl rings aligned parallel to leave a cleft for the carbonyl group. Steric interactions cause the S(1)–Mo–S(3) angle to expand to 127.4°. The third mercapto-ligand is disposed *exo* to the C(1)–O(1) group to reduce the steric congestion that would arise from all three mercapto-ligands adopting *endo*-configurations. This is in contrast with the situation in trigonal bipyramidal thiophenolate complexes such as $[WCl(SPh)_3(NO)]^-$,[3] and $[Re(SPh)_3(MeCN)(PPh_3)]$[4] where the three benzene rings adopt *endo*-configurations relative to the NO and MeCN ligands, respectively.

The bulky thiols affect a stabilisation of a co-ordinatively unsaturated carbonyl with formally 14 electrons in the valence shell. However, complex (**1**) reacts reversibly with CO to form $[Mo(CO)_3(tipt)_3]^-$ although the equilibrium markedly favours the five co-ordinate species. It is also very reactive towards acetylenes and isocyanides to give products which will be described elsewhere.

If the reaction of $[MoCl_4(thf)_2]$ with Na(tipt) is carried out under N_2, the purple crystalline complex Na[MoO(tipt)$_4$] can eventually be isolated from diethyl ether. The source of the oxo group may be adventitious dioxygen or the solvent. The e.s.r. spectrum of this complex is extremely similar to $[MoO(SPh)_4]^-$ and suggests that despite the bulky thiols the geometry is also essentially square pyramidal with an axial oxo-group.[5]

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