Decamethylvanadocene forming a Disulphur Complex from Elemental Sulphur and Desulphurization Reactions

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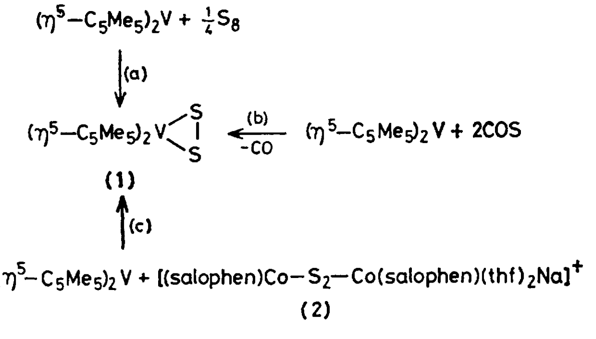
Bis(pentamethylcyclopentadienyl)vanadium(II) bonds to a disulphur ligand in reactions with elemental sulphur, COS, and [(salophen)Co–S_2–Co(salophen)(tetrahydrofuran)$_2$Na]$^+$ [salophen = *N,N'-o*-phenylenebis(salicylideneaminato)dianion] to form [(η^5-C_5Me_5)$_2$V(η^2-S_2)] which contains the persulphido-ligand [S–S, 2.028(4) Å].

Elemental sulphur reacting with transition metal complexes in a low oxidation state gives rise to a plethora of compounds that might be expected to form when a nucleophile or a free radical reacts with an S_8 molecule. This is a consequence of the co-ordinative unsaturation of the metal and of the versatile bonding behaviour of S_n species.[1] In a few cases, however, electronic or steric factors seem to control the selective formation of a single species from S_8; this may be seen, for example in d^8 complexes which bind an S_2 unit from elemental sulphur to form [M(dppe)$_2$(S_2)]Cl [M = Ir, Rh, dppe =



Scheme 1

bis(diphenylphosphino)ethane],[2] $[Ru(S_2)(CO)_2(PPh_3)_2]$,[3] and $[Os(S_2)(CO)_2(PPh_3)_3]$,[3] and in free radical-type d^7 cobalt(II) complexes which form $[CoS_2Co]$ units.[4] Cyclopentadienyl (cp) and substituted cyclopentadienyl complexes containing either the cpM[1,5] or the cp_2M[6] fragment are still receiving much attention owing to their ability to bind S_n units. The high number of co-ordination sites potentially available on a cpM unit leads to polynuclear complexes and to a variety of S_n ligands while the cp_2M moiety better controls both the molecular complexity of the final compound and the nature of the species formed either from the reaction with elemental sulphur or from the (more usual) reaction with polysulphides. Biscyclopentadienyl complexes have been found to form cp_2MS_5 (M = Ti, V),[6,7] cp_2MS_4 (M = Mo, W),[8] $(\eta^5\text{-}C_5Me_5)_2MS_3$ (M = Ti, Zr),[9] and $[cp_2Nb(S_2)X]$[10] (X = Cl, Br, I, SCN) complexes and the nature of the metal–sulphur ring seems to depend either on the presence of methyl substituents on the cp ligand or on the metal ion dimensions. The reaction with elemental sulphur has been reported only once.[7]

The present report concerns the reactivity of decamethylvanadocene[11] $(\eta^5\text{-}C_5Me_5)_2V$ which forms $[(\eta^5\text{-}C_5Me_5)_2V(\eta^2\text{-}S_2)]$ (Scheme 1) selectively from elemental sulphur, reaction (a), from the desulphurization of COS, reaction (b), or from the transfer of a disulphur ligand[4] from the cobalt complex (**2**) [salophen = *N,N′-o*-phenylenebis(salicylideneaminato) dianion, thf = tetrahydrofuran].

The reactions in Scheme 1 were performed using a thf [reactions (a) and (c)] or hexane [reaction (b)] solution of $(C_5Me_5)_2V$ and the reagent. Deep-yellow crystals of complex (**1**)† were recovered from all the reactions. The structure of (**1**) was elucidated by an *X*-ray analysis,‡ and an ORTEP view is shown in Figure 1 together with relevant bond distances and bond angles.

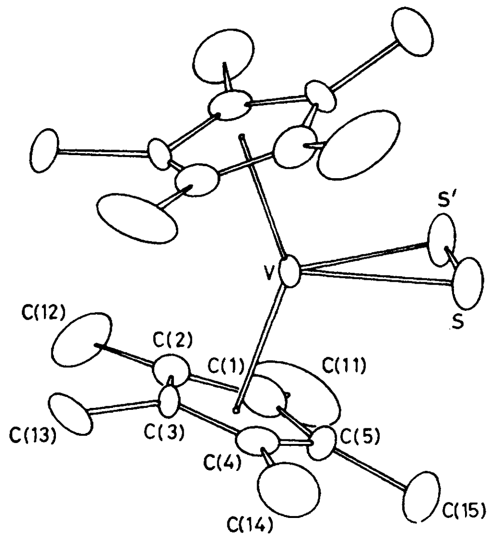


Figure 1. An ORTEP diagram of the complex $[(\eta^5\text{-}C_5Me_5)_2V(\eta^2\text{-}S_2)]$. Bond distances: V–S, 2.415(4), V–(C_5Me_5), 2.02(2), S–S′, 2.028(4) Å. Bond angles: (C_5Me_5)–V–$(C_5Me_5)'$, 141.7(4); S–V–(C_5Me_5), 108.8(3); S–V–$(C_5Me_5)'$, 105.9(3); S–V–S′, 49.7(1); V–S–S′, 65.2(2)°. Prime indicates a transformation of $(1.5 - x, 0.5 - y, z)$.

The two pentamethylcyclopentadienyl ligands are η^5-bonded to the metal in a bent arrangement to make a cavity in the equatorial plane for the disulphur ligand which is symmetrically and η^2-bonded to vanadium. The molecule has crystallographic C_2 symmetry with a two-fold axis through the S–S bond and the metal. The V–S bond distance [2.415(4) Å] is very close to those found in cp_2VS_5[7] and in other vanadocene derivatives containing V–S bonds.[12] The S–S bond distance [2.028(4) Å] falls within the range expected for the persulphido-dianion (*ca.* 2.03 Å).[2] Some characteristics of the structure of (**1**) are related to the presence of C_5Me_5 instead of cp ligands around vanadium. These include a significant lengthening of the (C_5Me_5)–V distance [2.02(2) Å] *vs.* the cp–V distance (1.92—1.96 Å),[12] and the value of the (C_5Me_5)–V–(C_5Me_5) angle [141.7(4)°] which is in the highest range found for vanadocene derivatives.[12] It is worth mentioning that the mutual repulsion of methyl groups on the rings is reduced by their significant deviation out of the plane of the ring [from 0.08(1) to 0.40(2) Å] which assumes a butterfly conformation. No intramolecular contact between the two rings at distances of less than 3.6 Å has been observed. The methyl substituents on the rings cause a significant change in the metal basicity and also give rise to steric control of the reactivity of the metal *via* the dimension of the cavity provided by the bent $(C_5Me_5)_2V$ unit.[11] This may be a larger influence than for other metals because of the relatively smaller ionic radius of the vanadium ion. The reactions in Scheme 1 suggest that $(C_5Me_5)_2V$ is a good model compound for binding the S_2 unit. Its formation from the desulphurization of COS, reaction (b) is rather surprising;[13] the transfer of the S_2 ligand from complex (**2**) occurs while the polynuclear structure remains intact and the cobalt(III) is reduced to cobalt(II).[14] The vanadocene moiety has been found to bind an S_5 unit (as titanocene does).[6,7] It has previously been observed that methyl substituents on the rings can affect the metal–sulphur ring size and so under the same conditions $(C_5Me_5)_2MS_3$ (M = Ti, Zr) may form.[9]

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† Satisfactory elemental analytical data were obtained.

‡ *Crystal data:* $C_{20}H_{30}S_2V$, orthorhombic, space group *Fdd*2, a = 17.664(9), b = 26.199(14), c = 8.664(3) Å, U = 4009(3) Å^3, $Z = 8$, D_c = 1.28 g cm^{-3}, $F(000)$ = 1640 e, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 6.8 cm^{-1}. The structure was solved by the heavy atom method, assuming the vanadium atom to lie on the two-fold axis according to the number of molecules in the unit cell. Refinement was by full-matrix least-squares. All calculations were carried out using the SHELX-76 program. For 996 unique observed structure amplitudes [$I > 3\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range $5 < 2\theta < 53°$ the current R is 0.060.

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.

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