Cleavage of the Sulphur–Sulphur Bond in Alkyl and Aryl Disulphides by Dicarbonylbis(η-cyclopentadienyl)titanium(II) and Bis(η-cyclopentadienyl)vanadium(II): Synthesis and Properties of Alkylthio- and Arylthio-derivatives of Titanium(IV), Titanium(III), Vanadium(IV), and Vanadium(III)

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A new synthesis of the complexes $[Ti(cp)_2(SR)_2]$, (II), *via* oxidative addition of alkyl and aryl disulphides to $[Ti(cp)_2(CO)_2]$, (I), is reported (cp = η-cyclopentadienyl). Reactions of (II) with (I) give binuclear titanium(III) complexes, $[(cp)_2Ti(\mu\text{-}SR)_2Ti(cp)_2]$, (III), and this type of reaction is proposed as a general synthetic route to such complexes. Complexes (III) show reduced paramagnetism, in agreement with titanium(III)–titanium(III) interaction, and unusual affinity for carbon monoxide. The oxidative addition of disulphides to $[V(cp)_2]$, (VI) affords, depending on the reactions conditions, $[V(cp)_2(SR)_2]$, (VIII), or $[V(cp)_2SR]$, (VII). The latter complexes can reversibly co-ordinate carbon monoxide.

THE sulphur–sulphur bond in organic disulphides may be cleaved by nucleophilic, electrophilic, and radical processes.[1] In addition, several transition-metal complexes, having a pattern of reactivity similar to organic intermediates,[2] have been shown to be effective reagents for cleavage of the sulphur–sulphur bond. The thiolate fragment produced as a result of sulphur–sulphur bond cleavage appears as a sulphur-containing ligand in the products of the reactions. The general interest in chemistry of transition-metal complexes containing sulphur-donor atoms,[3] and in homonuclear bond cleavage by metals, prompted us to try to insert a metal atom having 'carbene-like' behaviour into a sulphur–sulphur bond. For this purpose we choose two recent models, dicarbonylbis(η-cyclopentadienyl)titanium(II)[4] and bis(η-cyclopentadienyl)vanadium(II),[5] which are known to cleave a number of other homonuclear bonds *via* oxidative addition.[4,5]

RESULTS AND DISCUSSION

Bis(alkylthio)- and Bis(arylthio)-bis(η-cyclopentadienyl)-titanium(IV) *Complexes*.—Such complexes, $[Ti(cp)_2(SR)_2]$, were first obtained[6,7] by reaction of $[Ti(cp)_2Cl_2]$ with the corresponding RSH in the presence of an amine. This was the only useful synthesis, if we do not take into account the reaction between disulphides and so-called titanocene,[8] which is not a genuine source of 'carbene-like' $[Ti(cp)_2]$.[9] The reaction of $[Ti(cp)_2(CO)_2]$, (I), with dialkyl or diaryl disulphides, RSSR, represents an interesting and general synthesis to $[Ti(cp)_2(SR)_2]$ complexes, and shows a new aspect of reacting ability of this d^2 'nucleophile' with S–S bonds. On addition of alkyl or aryl disulphides as pure reagents or in hydrocarbon solutions to a heptane solution of $[Ti(cp)_2(CO)_2]$, CO was evolved and a deep violet solution was formed from which, on standing, good red-violet crystals of complexes (II) were obtained. Complexes (II) were fully characterised by elemental analysis (Table), and n.m.r. and i.r. spectra were fundamentally in agreement with those reported earlier.[7] The

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[1] J. L. Kice, 'Sulphur in Organic and Inorganic Chemistry,' ed. A. Senning, Marcel Dekker, New York, 1971, vol. 1, p. 153.

[2] J. Halpern, *Adv. Chem. Series*, 1968, **70**, 1.

[3] L. F. Lindoy, *Co-ordination Chem. Rev.*, 1969, **4**, 41.

[4] C. Floriani and G. Fachinetti, *J.C.S. Chem. Comm.*, 1972, 790.

[5] G. Fachinetti, G. Fochi, and C. Floriani, *J. Organometallic Chem.*, 1973, **57**, C51; G. Fachinetti and C. Floriani, unpublished work.

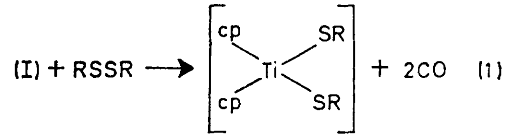
[6] S. A. Giddings, *Inorg. Chem.*, 1967, **6**, 849.

[7] H. Höpf and M. Schmidt, *Z. anorg. Chem.*, 1965, **340**, 139.

[8] H. Köpf and B. Block, *Z. Naturforsch.*, 1968, **B23**, 1536.

[9] H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1970, **92**, 6182.

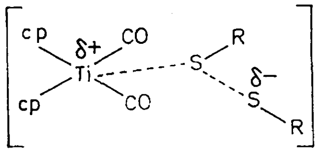
molecular-weight determinations in benzene (Table) confirmed the monomeric nature of the complexes,

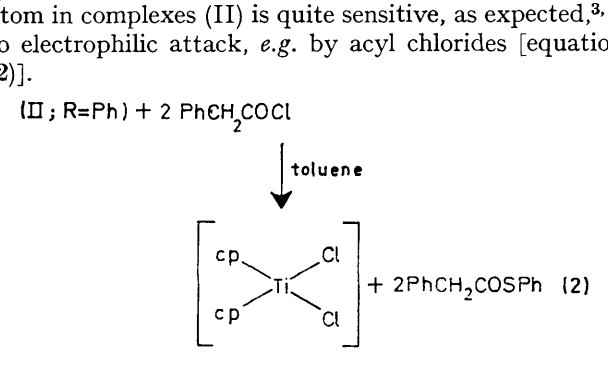


(II) R=Me,Ph,PhCH$_2$, or p-MeC$_6$H$_4$

except for (II; R = Me). Complexes (II) have high thermal and oxidative stabilities and are easily hydrolysed.

The initial step in reaction (1) may be regarded as nucleophilic attack by the titanium atom at one of the sulphur atoms of the disulphide. Since, at least from a qualitative point of view, the rate of reaction depends on the electron-attracting power of the substituent R (Ph $\simeq$ p-MeC$_6$H$_4$ $\simeq$ PhCH$_2$ $\gg$ Me > Pr^i), in the ground state the sulphur atoms would be expected to be slightly positive, and susceptible to nucleophilic attack. This assumption can be justified on the basis of the recent mechanism proposed in the reaction between Vaska's compound and an activated disulphide,[10] and from the well known basicity–nucleophilicity of [M(cp)$_2$X$_2$] systems having a d^2 metal atom.[11] The sulphur-donor atom in complexes (II) is quite sensitive, as expected,[3,12] to electrophilic attack, *e.g.* by acyl chlorides [equation (2)].



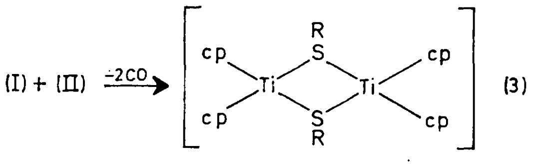


Analytical and magnetic results for the titanium and vanadium complexes

Complex	Analyses (%) [a] C	H	S	$\mu_{\text{eff.}}$[b]/B.M. (T/K)	M[a,c]
[Ti(cp)$_2$(SMe)$_2$] (II)	53·1 (52·9)	5·7 (5·9)	27·8 (27·2)		
[Ti(cp)$_2$(SPh)$_2$] (II)	66·4 (66·7)	5·1 (5·1)	16·6 (16·2)		341 (396)
[Ti(cp)$_2$(SCH$_2$Ph)$_2$] (II)	68·0 (67·9)	5·7 (5·7)	14·6 (15·1)		430 (424)
[Ti(cp)$_2$(SC$_6$H$_4$Me-p)$_2$] (II)	67·2 (67·9)	5·7 (5·7)	14·9 (15·1)		369 (424)
[(cp)$_2$Ti(μ-SPh)$_2$Ti(cp)$_2$] (III)	66·3 (66·9)	5·2 (5·2)	10·8 (11·1)	1·43 (291)	
[(cp)$_2$Ti(μ-SC$_6$H$_4$Me-p)$_2$Ti(cp)$_2$] (III)	67·3 (67·8)	5·8 (5·7)	10·3 (10·6)	1·43 (292)	
[(cp)$_2$Ti(μ-SEt)$_2$Ti(cp)$_2$] (III)	60·4 (60·3)	6·9 (6·3)	13·4 (13·4)	1·13 (295)	
[V(cp)$_2$SMe] (VII)	58·3 (57·9)	6·2 (5·7)	13·5 (14·0)	2·71 (292)	255 (228)
[V(cp)$_2$SEt] (VII)	59·5 (59·5)	6·5 (6·2)	12·6 (13·2)		
[V(cp)$_2$SPh] (VII)	65·7 (66·2)	5·5 (5·2)	11·2 (11·0)	2·75 (293)	290 (290)
[V(cp)$_2$SCH$_2$Ph] (VII)	67·0 (67·1)	5·5 (5·6)	10·4 (10·5)	2·76 (293)	318 (304)
[V(cp)$_2$(SPh)$_2$] (VIII)	66·6 (66·2)	4·6 (5·0)	16·5 (16·0)	1·84 (296)	

[a] Calculated values are given in parentheses. [b] Results expressed per metal atom; 1 B.M. = 0·927 × 10^{-23} A m^2. [c] By cryoscopy in benzene.

Di-μ-alkylthio- and Di-μ-arylthio-bis[bis(η-cyclopentadienyl)titanium(III)] *Complexes*.—These complexes, [(cp)$_2$Ti(μ-SR)$_2$Ti(cp)$_2$], were synthesised by reacting together (I) with the appropriate derivative (II) [equation (3)]. This reaction can be used as a general synthetic route to titanium(III) derivatives, [(cp)$_2$Ti(μ-X)$_2$Ti(cp)$_2$] (X = halogen,[13] O, or S). Complexes (III) were obtained by heating under reflux a toluene solution of (I) and (II; R = Ph and p-MeC$_6$H$_4$) for *ca.* 30 min. Rapid evolution of CO was observed during crystallisation of (III). The complexes were also obtained by reacting 0·5 mol of RSSR with 1 mol of (I) heating under reflux in toluene, as in the case of (III; R = Et or Ph). Complex (III; R = Ph) was also synthesised by displacement of chloride from [(cp)$_2$Ti(μ-Cl)$_2$Ti(cp)$_2$] using Na[SPh].



(III) R=Ph or p-MeC$_6$H$_4$

More than one synthesis was used for (III; R = Ph), because the same complex obtained from [(cp)$_2$Ti(μ-NMe$_2$)$_2$Ti(cp)$_2$] and PhSH [14] was reported, contrary to our results, to be diamagnetic and soluble in benzene. The three routes above yielded the same complex as confirmed by analyses, i.r. and mass spectra, and magnetic moment. Complexes (III) are generally insoluble in non-co-ordinating solvents; in co-ordinating solvents, dissolution seems to occur *via* bridge-splitting reactions [equation (4)],[13] although it was not always possible to isolate the monomeric species (IV). Evaporation of

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[10] C. T. Lam and C. V. Senoff, *Canad. J. Chem.*, 1973, **51**, 3790.

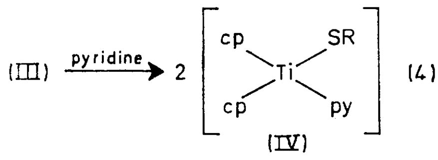
[11] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 4854.

[12] M. G. Harris, M. L. H. Green, and W. E. Lindsell, *J. Chem. Soc.* (*A*), 1969, 1453.

[13] C. Floriani and G. Fachinetti, *J.C.S. Dalton*, 1973, 1954 and refs. therein.

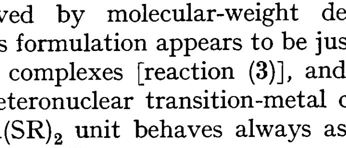
[14] M. F. Lappert and A. R. Sanger, *J. Chem. Soc.* (*A*), 1971, 1314.

the brown pyridine solution or addition of toluene or heptane always resulted in separation of (III).



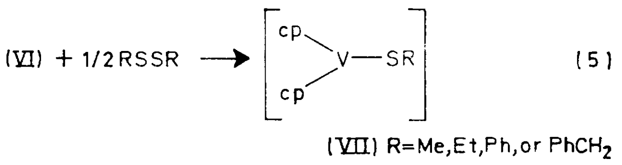
Due to their low solubility, formulation of complexes (III) as di-μ-alkylthio- or di-μ-arylthio-derivatives could not be proved by molecular-weight determination. However, this formulation appears to be justified by the origin of the complexes [reaction (3)], and by analogy with some heteronuclear transition-metal complexes in which the $Ti(SR)_2$ unit behaves always as a chelating disulphide ligand.[15] The mass spectra showed no molecular ion, but peaks were observed corresponding to the ions $[Ti(cp)_2(SR)_2]^+$, $[Ti(cp)_2]^+$, $[Ti(cp)_2SR]^+$, and $RSSR^+$. The absence of the parent peak is not surprising since, for example, complexes (III) readily undergo symmetric [reaction (4)] or asymmetric bridge-splitting reactions. All derivatives (III) were found to be paramagnetic (Table) with reduced magnetic moments. These values are the result either of the interaction of unpaired electrons *via* sulphur bridges or of triplet and singlet states in thermal equilibrium, as reported for $[(cp)_2Ti(\mu\text{-}X)_2Ti(cp)_2]$.[16]

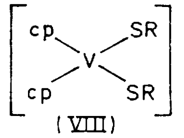
Synthetic route (3) deserves some comment. It can be interpreted as the result of interaction between acidic titanium(IV) and basic titanium(II) species. The acid–base intermediate, (V), not isolated, evolves as a consequence of reduced electron density at titanium(II),



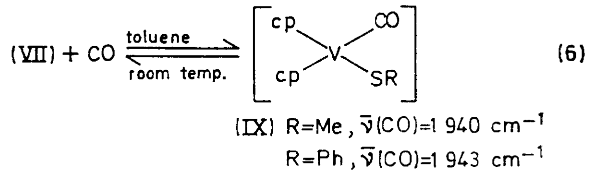
corresponding to decreased back bonding to CO. The reaction conditions (refluxing toluene) were chosen in order to reduce the partial pressure of carbon monoxide in the system. It was shown that complexes (III) absorb carbon monoxide at 1 atm and room temperature giving (I) and (II) quantitatively. This asymmetric splitting of the sulphur bridge and the mass-spectral results shows that the complexes behave as adducts of the units $[Ti(cp)_2]$ and $[Ti(cp)_2(SR)_2]$.

Alkylthio- and Arylthio-bis(η-cyclopentadienyl) Complexes of Vanadium(III) *and Vanadium*(IV).—Reaction of alkyl or aryl disulphides with bis(η-cyclopentadienyl)-vanadium(II), (VI), in toluene solution at room temperature gave, on addition of heptane and cooling, green crystals of $[V(cp)_2(SR)]$, (VII). Compounds (VII) were monomeric in benzene. Their i.r. spectra showed η-cyclopentadienyl groups, while magnetic moments suggested that we are dealing with derivatives of high-spin vanadium(III) (Table). Treatment of (VII; R = Ph) with dry hydrogen chloride under a dinitrogen atmosphere gave $[V(cp)_2Cl]$ and PhSH quantitatively. It seems impossible to say whether reaction (5) is a one-electron oxidative addition, or whether insertion of vanadium into the S–S bond to give (VIII) was followed by fast redox between vanadium(II) and vanadium(IV) with ligand transfer. Interaction between (VIII) and (VI) is reminiscent of reaction (3) and that between $[V(cp)_2Cl_2]$ and (VI).[17] Further support comes from the very rapid reaction between (VIII; R = Ph) and (VI) observed in toluene to give (VII; R = Ph).





One of the more interesting properties of complexes (VII; R = Me or Ph) is reversible addition of carbon monoxide in hydrocarbon solution [equation (6)]. A similar reaction was recently observed and quantitatively evaluated for bis(η-cyclopentadienyl)iodovanadium(III).[18] The CO stretching values can be compared with those of, for example, $[V(cp)_2(I)CO]$ (1 953) [18] and $[V(cp)_2(COR)CO]$ (*ca.* 1 905 cm^{-1}).[19]



We can exclude that the synthesis of complexes (VII) [equation (5)] is the result of instability of (VIII), as the non-existence of $[V(cp)_2R_2]$ alkyl [20] derivatives might have suggested. In fact, the synthesis of, for example, complex (VIII; R = Ph) can be quite easily realised. Either the displacement of chlorine in $[V(cp)_2Cl_2]$ by Na[SPh] or further reaction of PhSSPh with (VII; R = Ph) heated under reflux in toluene gives the

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[15] P. S. Braterman, V. A. Wilson, and K. K. Joshi, *J. Chem. Soc.* (*A*), 1971, 191; G. R. Davies and B. T. Kilbourn, *ibid.*, p. 87; P. S. Braterman and V. A. Wilson, *J. Organometallic Chem.*, 1971, **31**, 131.

[16] R. S. P. Coutts, R. L. Martin, and P. C. Wailes, *Austral. J. Chem.*, 1973, **26**, 2101.

[17] H. J. de Liefde Meijer, M. J. Jansson, and G. J. M. van der Kerk, *Rec. Trav. chim.*, 1961, **80**, 831.

[18] F. Calderazzo, G. Fachinetti, and C. Floriani, *J. Amer. Chem. Soc.*, 1974, **96**, 3695.

[19] G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1974, 516.

[20] F. W. Siegert and H. J. de Liefde Meijer, *Rec. Trav. chim.*, 1970, **89**, 764.

same product, (VIII; R = Ph) [equations (7) and (8)]. The vanadium(IV) complex was obtained as black-green

$$[V(cp)_2Cl_2] + 2Na[SPh] \longrightarrow (VIII;\ R = Ph) + 2NaCl \quad (7)$$

$$(VII;\ R = Ph) + 1/2PhSSPh \longrightarrow (VIII;\ R = Ph) \quad (8)$$

crystals, slightly soluble in aromatic hydrocarbons. The magnetic moment for (VIII; R = Ph) was in agreement with that of a vanadium(IV) complex (Table).

EXPERIMENTAL

Unless otherwise stated, all the reactions described here were carried out under an atmosphere of purified dinitrogen; solvents were purified by standard methods. Dicarbonylbis(η-cyclopentadienyl)titanium(II), (I),[21] bis(η-cyclopentadienyl)vanadium(II), (VI),[22] and di-μ-chloro-bis[bis(η-cyclopentadienyltitanium(III)] [12] were prepared as previously described. All the commercially available disulphides were purified by distillation or crystallisation before use.

I.r. spectra were measured with a Perkin-Elmer 337 spectrometer and n.m.r. spectra with a T-60 Varian spectrometer. Magnetic-susceptibility measurements were carried out with a Gouy balance.

Some of the typical reactions are described in detail, the preparations of the other complexes being carried out under similar conditions.

Preparations.— *Bis(η-cyclopentadienyl)bis(p-tolylthio)titanium*(IV), (II). To a heptane (25 cm^3) solution of complex (I) (0·52 g, 2·22 mmol), pure di(p-tolyl) disulphide (0·6 g, 2·44 mmol) was added. Fast evolution of CO was observed, and the colour of the solution changed from maroon to violet. After 1 h, red-violet crystals of (II) were collected and washed with heptane (*ca.* 62%). All complexes (II) are soluble in aromatic hydrocarbons, thermally stable, and sensitive to moisture.

Di-μ-phenylthio-bis[bis(η-cyclopentadienyl)titanium(III)], (III). *Method* (a). A toluene (50 cm^3) solution of complexes (I) (0·97 g, 4·15 mmol) and (II; R = Ph) (0·65 g, 4·15 mmol) was heated under reflux for *ca.* 30 min. Fast evolution of CO was observed, during precipitation of a black-violet crystalline solid. The collected solid was washed with toluene, dried, and analysed without further purification (*ca.* 67%).

Method (b). A toluene solution (100 cm^3) containing complex (I) (6·8 g, 29·0 mmol) and PhSSPh (3·0 g, 13·8 mmol) was heated under reflux for *ca.* 30 min. The solution became violet, and CO evolution was observed during precipitation of a black-violet crystalline solid. The solid was washed with toluene and analysed without further purification (*ca.* 90%).

Method (c). The complex $[(cp)_2Ti(\mu\text{-}Cl)_2Ti(cp)_2]$ (3·15 g, 7·4 mmol) suspended in toluene (200 cm^3) was treated with Na[SPh] (2·21 g, 16·7 mmol) and the suspension stirred for 2 days at room temperature. The solution became dark violet, but most of the solid remained insoluble. Extraction of the solid with hot toluene gave black-violet crystals of (III) (*ca.* 21·4%). The low yield results from the insolubility of the μ-thio-derivatives in hydrocarbons.

All complexes (III) are sensitive to dioxygen, especially in solution, and they are sparingly soluble in non-co-ordinating solvents. The more abundant ions in the mass spectra are m/e 300 and 239; 178 and 122 [for (III; R = Et)]; and 424, 301, and 246 [for (III; R = Ph)]. CO-Absorption measurements in toluene suspension gave the following results: (III; R = Et) (0·235 g, 0·98 mmol) absorbed, in 30 min at 19·1 °C, 0·95 mmol of CO (CO : Ti = 0·97 : 1); and (III; R = Ph) (0·195 g, 0·68 mmol) absorbed, in 2 h at 25·9 °C, 0·67 mmol of CO (CO : Ti = 0·99 : 1). The presence of complexes (I) and (II) in the resulting solutions was confirmed by n.m.r. (C_6D_6) and i.r. spectra (toluene).

Bis(η-cyclopentadienyl)phenylthiovanadium(III), (VII). A toluene (50 cm^3) solution of complex (VI) (0·83 g, 4·59 mmol) was treated with pure PhSSPh (1·1 g, 5·05 mmol) at room temperature. The reaction took place immediately, and in a short time a black-green solid crystallised. The solution was concentrated under reduced pressure and treated with heptane causing further product formation (*ca.* 75·1%).

Complex (VII) (0·386 g, 1·33 mmol) was dissolved in toluene (25 cm^3) and treated with dry HCl under N_2. The colour of the solution turned rapidly from green to deep violet. Addition of heptane gave $[V(cp)_2Cl]$ (0·2 g, 0·92 mmol) and PhSH determined by g.l.c. (0·137 g, 1·25 mmol).

Bis(η-cyclopentadienyl)bis(phenylthio)vanadium(IV), (VIII). *Method* (a). The addition of a tetrahydrofuran (thf) (50 cm^3) suspension of the complex $[V(cp)_2Cl_2]$ (1·4 g, 5·55 mmol) to Na[SPh] (1·6 g, 12·12 mmol) resulted in formation of a black-green solution. After evaporation of the solution to dryness under reduced pressure, the resulting green residue was extracted with toluene (100 cm^3) at 50 °C and the toluene solution was filtered then concentrated to 30 cm^3. On addition of heptane (100 cm^3) a black-green solid crystallised (*ca.* 67·7%).

Treatment of complex (VIII) (0·48 g, 1·20 mmol) in toluene (25 cm^3) with dry HCl gave $[V(cp)_2Cl_2]$ (0·256 g, 1·02 mmol), while the solution contained PhSH (0·250 g, 2·27 mmol) determined by g.l.c.

Method (b). To a toluene (20 cm^3) solution of complex (VII; R = Ph) (0·7 g, 2·41 mmol), PhSSPh was added (1·4 g, 6·42 mmol). The resulting solution was heated under reflux for *ca.* 15 min, then cooled, and the amount of black-green crystals then formed was increased by addition of heptane (*ca.* 83·2%).

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[21] J. G. Murray, *J. Amer. Chem. Soc.*, 1961, **83**, 1287.
[22] E. O. Fischer and S. Vigoureux, *Chem. Ber.*, 1958, **91**, 2205.