Reactions of Bis(η-cyclopentadienyl)vanadium Derivatives with Dinitrogen Oxide (Nitrous Oxide) †

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The reaction between $[V(cp)_2(CO)]$ and N_2O quantitatively gave $[\{V(cp)_2\}_{2n}(CO_3)_n]$ where $n = 1$ or 2. This is analogous to the reaction of $[Ti(cp)_2(CO)_2]$ with N_2O which gave $[\{Ti(cp)_2\}_4(CO_3)_2]$. Derivatives of V^{III} such as $[V(cp)_2X]$ (X = Cl or I) or $[V(cp)_2(CO)_2]^+$ did not react with N_2O, although $[V(cp)_2X]$ did react with O_2. The oxidising properties of N_2O are discussed, as are the properties of $[\{V(cp)_2\}_{2n}(CO_3)_n]$.

We have previously studied the reactions between dinitrogen oxide (nitrous oxide, N_2O) and bis(η-cyclopentadienyl)titanium derivatives.[1-3] Depending on the conditions the reaction of N_2O with '$Ti(cp)_2$' (cp = η-C_5H_5) gave $[\{Ti(cp)_2\}_2O]$,[2] $[\{Ti(cp)_2O\}_n]$[2] or '$Ti_2(cp)_3O_2$' which is presumed to have a bridged structure analogous to $[\{Ti(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}O)_2(\mu\text{-}\sigma{:}\eta^5\text{-}CH_2C_5Me_4)]$ obtained from '$Ti(\eta\text{-}C_5Me_5)_2$' and N_2O.[3] The reaction between $[Ti(cp)_2(CO)_2]$ and N_2O quantitatively gave $[\{Ti(cp)_2\}_4(CO_3)_2]$ which was shown to exist as $[\{Ti(cp)_2\}_4(CO_3)_2]$ in the solid state, but as $[\{Ti(cp)_2\}_2(CO_3)]$ in solution.[2] It was found that N_2O oxidised a variety of $Ti^{III}(cp)_2$ complexes to $Ti^{IV}(cp)_2$, an example being $[\{Ti(cp)_2Cl\}_2]$ which gave $[\{Ti(cp)_2Cl\}_2O]$.[2] We have now extended these reactions to bis(η-cyclopentadienyl)vanadium derivatives and report the similarities and differences here. The reaction between bis(η-cyclopentadienyl)vanadium and N_2O which gave the cluster $[V_5(cp)_5O_6]$ has been discussed elsewhere.[4,5]

Results and Discussion

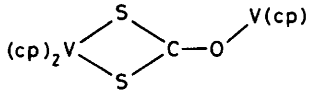
There was a slow but quantitative reaction between excess $[V(cp)_2(CO)]$ and N_2O in toluene at 25 °C [equation (1)],

$$2\,[V(cp)_2(CO)] + 2\,N_2O \longrightarrow \frac{1}{n}\,[\{V(cp)_2\}_{2n}(CO_3)_n] + 2\,N_2 + CO \quad (1)$$

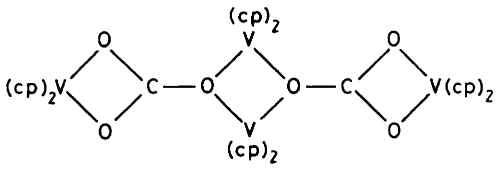
where $n = 1$ or 2. This may be compared to the analogous reaction of the carbonyl $[Ti^{II}(cp)_2(CO)_2]$ [equation (2)].[2]

$$4\,[Ti(cp)_2(CO)_2] + 4\,N_2O \longrightarrow [\{Ti(cp)_2\}_4(CO_3)_2] + 4\,N_2 + 6\,CO \quad (2)$$

The steel-blue extremely air-sensitive $[\{V(cp)_2\}_{2n}(CO_3)_n]$ complex is formulated mainly as a monomer in contrast to the dimeric $[\{Ti(cp)_2\}_4(CO_3)_2]$. The related complex $[\{V(cp)_2\}_2\{C(O)S_2\}]$ has the structure (I),[6] and a magnetic moment of 2.72 B.M.; $[\{V(cp)_2\}_2(CO_3)]$ with a magnetic moment of 2.62 B.M. is assumed to have a similar structure. The vanadium co-ordinated by either two oxygen or sulphur donors will have one pair of *d* electrons and be diamagnetic, since only three orbitals are available to hold the two donor pairs and two *d* electrons.[7,8] The vanadium atom co-ordinated by one oxygen will have two unpaired electrons. In contrast the dimer analogous to $[\{Ti(cp)_2\}_4(CO_3)_2]$ would have structure (II)[2,9] and would be diamagnetic. However, the i.r. spectrum of $[\{V(cp)_2\}_{2n}(CO_3)_n]$ showed four absorption bands at 1 532, 1 500, 1 415, and 1 360 cm⁻¹. Dimeric $[\{Ti(cp)_2\}_4(CO_3)_2]$ showed two absorptions at 1 475 and 1 425 cm⁻¹ whereas monomeric $[\{Ti(cp)_2\}_2(CO_3)]$, which was present in tetrahydrofuran solution, showed bands at 1 580 and 1 355 cm⁻¹.[2] Therefore the i.r. spectrum indicates that some dimeric $[\{V(cp)_2\}_4(CO_3)_2]$ was present in the solid product of reaction (1). This would account for the slightly low magnetic moment.



(I)



(II)

Oxidation of $[V(cp)_2(CO)]$ by O_2 also occurred, see equation (3), although the reaction was only stoicheiometric if a very large excess of $[V(cp)_2(CO)]$ was used to prevent further oxidation of $[\{V(cp)_2\}_{2n}(CO_3)_n]$ by O_2. Even then small quantities of a brown insoluble material were obtained as a by-product.

$$2\,[V(cp)_2(CO)] + O_2 \longrightarrow \frac{1}{n}\,[\{V(cp)_2\}_{2n}(CO_3)_n] + CO \quad (3)$$

Attempts to follow the course of reaction (1) using i.r. or e.s.r. spectroscopies failed because of the insolubility of $[\{V(cp)_2\}_{2n}(CO_3)_n]$ as compared to $[V(cp)_2(CO)]$; only the spectra of the latter were observed.

There was no reaction between the V^{III} complexes $[V(cp)_2(CO)_2]^+$, $[V(cp)_2X]$ (X = Cl or I), or $[\{V(cp)_2\}_{2n}(CO_3)_n]$ and N_2O; $[V(cp)_2(CO)_2]^+$ was even stable with respect to oxidation by O_2. On the other hand the complexes $[V(cp)_2X]$ were oxidised by O_2. With $[V(cp)_2I]$ the oxidation gave an intractable polymer but with $[V(cp)_2Cl]$ a dark green solid was obtained which by microanalysis, mass spectral fragmentation pattern, and magnetic moment (1.45 B.M., uncorrected for

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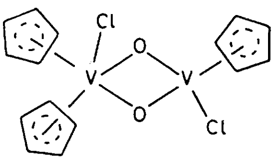
† *Non-S.I. unit employed:* 1 B.M. = 0.927 × 10⁻²³ A m².



(III)

diamagnetism) is formulated as $V_2(cp)_3O_2Cl_2$. The same material could also be prepared by oxidising $[V(cp)_2Cl]$ with NO. The suggested structure is (III).

Since V–O bonds are known to be strong (at least 325 kJ mol^{-1})[10] and the N–O bond in N_2O has a bond energy of only 166 kJ mol^{-1},[11] the lack of reactivity of $V^{III}(cp)_2$ complexes towards N_2O cannot be thermodynamic in origin. The three frontier orbitals of $[V(cp)_2X]$ complexes are occupied by one donor pair and two unpaired electrons. Hence a mechanistic barrier similar to that proposed[8,12] for the inability of the d^2 complex $[Mo(cp)_2(H)(olefin)]^+$ to form an alkyl (R), $[Mo(cp)_2R]^+$, may be preventing reaction with N_2O. However, $[V(cp)_2(CO)_2]^+$ is isoelectronic and essentially isostructural to $[Ti(cp)_2(CO)_2]$[13] and we cannot see a reason why insertion of an oxygen atom in the V–CO bond does not occur as happens with Ti–CO.

Experimental

The starting materials $[V(cp)_2(CO)]$,[14] $[V(cp)_2Cl]$,[15] $[V(cp)_2I]$,[16] and $[V(cp)_2(CO)_2]I$[14] were prepared by the literature methods. Instruments used were a Perkin-Elmer 683 i.r. spectrophotometer (spectra being measured as Nujol or Fluorolube mulls between KBr plates), a locally modified version of the Varian E-4 e.s.r. spectrometer, and an Alpha Scientific magnet/Cahn electrobalance system to measure magnetic moments at room temperature.

Reaction of $[V(cp)_2(CO)]$ *with Dinitrogen Oxide; Formation of* $[\{V(cp)_2\}_{2n}(CO_3)_n]$.—In a typical experiment a solution of $[V(cp)_2(CO)]$ (0.54 g, 2.58 mmol) in toluene (30 cm^3) was incubated with N_2O (2.49 mmol) at 25 °C for 4 d. The solution turned from dark green to blue-black and precipitated a steel-blue solid. The gaseous products were CO (1.25 mmol) and N_2 (2.50 mmol), determined by exhaustively pumping (Toepler) first through liquid nitrogen traps then over Cu-CuO heated to 300 °C. The extremely air-sensitive solid was removed by filtration and washed several times with toluene (yield 0.37 g, 70% based on N_2O used) [Found: C, 59.5; H, 4.6; V (as V_2O_5) 24.7. Calc. for $C_{21}H_{20}O_3V_2$: C, 59.7; H, 4.8; V, 24.1%]. Magnetic moment = 2.62 B.M.; i.r. spectrum, $\nu(CO_3)$ bands at 1 532vs, 1 500vs, 1 415vs, and 1 360m cm^{-1}. An average of five experiments of this type established the stoicheiometry shown in equation (4).

$$2\ [V(cp)_2(CO)] + 2\ N_2O \longrightarrow [\{V(cp)_2\}_2(CO_3)] + (2.44 \pm 0.28)\ N_2 + (1.14 \pm 0.32)\ CO \quad (4)$$

Reaction of $[V(cp)_2(CO)]$ *with Dioxygen; Formation of* $[\{V(cp)_2\}_{2n}(CO_3)_n]$.—To a solution of $[V(cp)_2(CO)]$ (0.66 g, 3.15 mmol) in toluene (40 cm^3) was added O_2 (1.49 mmol), and the solution stirred at room temperature for 18 h. At the end of this period a grey-black solid had precipitated. The residual gases were collected and analysed by Toepler techniques, an average of four experiments establishing the stoicheiometry as reaction (3) above. The reaction mixture was filtered and the dark grey precipitate of $[\{V(cp)_2\}_{2n}(CO_3)_n]$ washed well with tetrahydrofuran (thf). The spectroscopic, magnetic, and chemical properties of the product were identical to those of $[\{V(cp)_2\}_{2n}(CO_3)_n]$ obtained from the reaction between $[V(cp)_2(CO)]$ and N_2O.

Reaction of $[V(cp)_2Cl]$ *with Dioxygen.*—A solution of $[V(cp)_2Cl]$ (0.49 g, 2.26 mmol) in thf (30 cm^3) was incubated with O_2 (0.57 mmol) for 1 h at 25 °C. The green solid which precipitated was collected by filtration, washed with thf and hexane, and dried in vacuum. Yield 0.2 g (Found: C, 44.9; H, 3.9. Calc. for $C_{15}H_{15}Cl_2O_2V_2$: C, 45.0; H, 3.8%). Magnetic moment = 1.45 B.M. There were no absorption bands in the i.r. spectra except those assignable to cp.

Acknowledgements

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