Reactions of Bis(cyclopentadienyl)vanadium Derivatives with Nitrogen Mono-oxide and the Crystal Structure of an Oxo-bridged Nitrosyl Complex of Vanadium†

Frank Bottomley,* James Darkwa, and Peter S. White
Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

The reaction between $[V(\eta\text{-}C_5H_5)_2]$ and NO has been shown to have a 1:1 stoicheiometry but the initial product, presumed to be $[V(\eta\text{-}C_5H_5)_2(NO)]$, undergoes disproportionation to give a mixture of final products. The reaction between $[V(\eta\text{-}C_5H_5)_2(CO)]$ and NO occurred with a 2:1 stoicheiometry and gave a complex containing NCO which could not be separated from a polymeric oxide. The complex $[V(\eta\text{-}C_5H_5)_2(NCO)]$ was obtained independently from $[VCl(\eta\text{-}C_5H_5)_2]$ and NCO^- in aqueous solution. The reaction between $[V(\eta\text{-}C_5H_5)_2(CO)]$ and NOCl gave a mixture of products including one or more containing NCO^-, and there was no reaction between NO and $[V(\eta\text{-}C_5H_5)_2(CO)_2]^+$. The reaction between $[VI(\eta\text{-}C_5H_5)_2]$ and NO gave two products, both analysing as $VI(C_5H_5)_2NO$. One was a brown insoluble polymer with ionic iodide which is believed to have bridging $N_2O_2^{2-}$ ligands. The second product was green, monomeric $[VI(C_5H_5)_2(NO)]$. This is a fluxional molecule as shown by e.s.r. and i.r. spectroscopy in tetrahydrofuran (thf) solution. The two forms of the molecule have different ν(NO) frequencies (1 670 and 1 590 cm^{-1}). The form with the lower frequency [which is presumed to be $VI(C_5H_5)_2(NO)$ with either a bent {VNO} group or a linear {VNO} group but a long N–O bond] predominates at low temperature. The form with the higher ν(NO) frequency has a linear {VNO} group with a short N–O distance and is presumed to have at least one C_5H_5 ring with less than pentahapticity. When a solution of $[VI(C_5H_5)_2(NO)]$ in thf was set aside at room temperature, diamagnetic $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ was formed. The structure of this complex, determined by *X*-ray diffraction, showed that it has an eight-membered ring of alternating V and O atoms with a two-fold axis in the centre of the ring. The V atoms alternately carry I or NO ligands, which are arranged in *trans* fashion to one another. The O–V–O angles are all similar, averaging 104.7(3)°, but the V–O–V angles are in two sets, two of 179.3(3) and two of 148.1(3)°. The four oxygen atoms lie in a plane with the V atoms carrying the iodo-ligand displaced 0.261 Å out of the plane towards the iodo-ligand and the V atoms carrying the NO ligand displaced 0.157 Å in the opposite direction. The reaction between $[VBr(\eta\text{-}C_5H_5)_2]$ and NO gave a complicated mixture of insoluble nitrosyl products and a soluble green monomer, $[VBr(C_5H_5)_2(NO)]$ which was analogous to $[VI(C_5H_5)_2(NO)]$ but lost NO far more readily. With $[VCl(\eta\text{-}C_5H_5)_2]$ and NO insoluble nitrosyls were again produced, as well as N_2O and $[V_2O_2Cl_2(\eta\text{-}C_5H_5)_3]$ which could also be obtained from $[VCl(\eta\text{-}C_5H_5)_2]$ and O_2. There was no reaction between $[VCl_2(\eta\text{-}C_5H_5)_2]$ and NO, but on addition of BF_3 reduction of $[VCl_2(\eta\text{-}C_5H_5)_2]$ to $[VCl(\eta\text{-}C_5H_5)_2]$ occurred.

Whereas reactions of nitrogen mono-oxide (nitric oxide, NO) with the later transition metals are well established and the reaction products well characterised, the same is not true of the early transition metals. We have embarked on a systematic investigation of the reactions between NO and organometallic complexes of Groups 4A and 5A. In previous papers we reported on the reactions of bis(cyclopentadienyl)titanium derivatives with NO: $[Ti(\eta\text{-}C_5H_5)_2]$ formed a polymer containing $N_2O_2^{2-}$; $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$ gave $[Ti(\eta\text{-}C_5H_5)_2(NCO)]$; and $[TiX(\eta\text{-}C_5H_5)_2]$ (X = Cl or NCO) were oxidised to $[\{TiX(C_5H_5)_2\}_2(\mu\text{-}O)]$ with concomitant production of N_2O.[1,2] In order to extend this chemistry we have investigated the reactions of derivatives of $[V(C_5H_5)_2]$ with NO, and report the results here. Previous work on vanadium nitrosyls is scattered. $[V(C_5H_5)(NO)_2(CO)]$ has been prepared by a variety of methods,[3–6] and its spectroscopic properties investigated.[7,8] Reaction of this complex with NO^+ gave[6] the rare trinitrosyl $[V(C_5H_5)(NO)_3]^+$ (another unstable trinitrosyl, $[\{VCl_2(NO)_3\}_n]$, is known[9]); the cyano-nitrosyls $[V(CN)_5(NO)]^{3-}$ (ref. 10) and $[V(CN)_6(NO)]^{4-}$ (refs. 11—13) and derivatives of them[9,14,15] have been known for some time. The thermally unstable and reactive $[V(CO)_5(NO)]$ has been prepared,[16] and a series of more stable $[V(CO)_{5-n}L_n(NO)]$ complexes can be readily obtained by nitrosyl transfer.[17] Recently a remarkable series of vanadium nitrosyls which also contain the η^2-NH_2O ligand has been obtained from reactions of hydroxylamine with vanadium(V) complexes.[15,18–20] The d^1 alkyl $[V(CH_2SiMe_3)_4]$ was oxidised to $[VO(CH_2SiMe_3)_3]$ by NO.[21] A report on the reactions of $[V(\eta\text{-}C_5H_5)_2]$ with NO and NOX (X = Cl or Br)[22] is discussed below later in relation to the results presented here.

A brief report on part of this work has been given.[23] A second report on the reactions of derivatives of $[V(\eta\text{-}C_5Me_5)_2]$ with NO, which are markedly different from those of $[V(\eta\text{-}C_5H_5)_2]$ will be given separately.[24]

Results and Discussion

The Reaction between $[V(\eta\text{-}C_5H_5)_2]$ *and* NO.—At any temperature between −70 and 20 °C $[V(\eta\text{-}C_5H_5)_2]$ and NO

---

† *Supplementary data available* (No. SUP 56221, 5 pp.): H-atom co-ordinates, thermal parameters, plane data and distances and angles involving the C_5H_5 rings, full numbering scheme. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

reacted rapidly in a 1:1 mol ratio. There were no gaseous products. The air-sensitive black solid which precipitated could be recrystallised from diethyl ether–tetrahydrofuran (thf) and was diamagnetic. It showed very strong absorption bands at 1 650 and 1 550 cm^{-1} in the i.r. spectrum in addition to bands assignable to η-C_5H_5. Microanalyses showed that the V:N and C:H ratios were always 1:1 but the V:C and V:O ratios varied from experiment to experiment, and the V:O ratio was always $>1:1$. Since the initial reaction always showed a 1:1 stoicheiometry we conclude that the '[$V(\eta$-$C_5H_5)_2(NO)$]' initially formed undergoes some form of disproportionation in solution.

Moran and Gayoso[22] apparently obtained the air-stable complex [$\{V(\eta$-$C_5H_5)(NO)_2\}_2$] by passing NO gas through an ethereal solution of [$V(\eta$-$C_5H_5)_2$]. We have found that large excesses of NO invariably oxidise low-valent bis(cyclopentadienyl)metal complexes of the early transition elements. In the case of [$V(\eta$-$C_5H_5)_2$] we obtained an insoluble air-stable brown material of empirical formula $V_3(C_5H_5)_3NO_7$.

The Reaction between [$V(\eta$-$C_5H_5)_2(CO)$] *and* NO.—At room temperature in toluene the reaction between [$V(\eta$-$C_5H_5)_2(CO)$] and NO proceeded relatively slowly. The ratio of [$V(\eta$-$C_5H_5)_2(CO)$] consumed to NO consumed was 2:1 and the ratio of NO consumed to CO produced was 1:1. Addition of hexane to the resultant toluene solution gave a black paramagnetic solid with a strong absorption at 2 209 cm^{-1} in the i.r. spectrum. The analogous reaction between [$Ti(\eta$-$C_5H_5)_2(CO)_2$] and NO has the stoicheiometry in equation (1)

$$[Ti(\eta\text{-}C_5H_5)_2(CO)_2] + NO \longrightarrow [Ti(\eta\text{-}C_5H_5)_2(NCO)] + \tfrac{1}{n}[\{TiO(\eta\text{-}C_5H_5)_2\}_n] + 3CO \quad (1)$$

and [$Ti(\eta$-$C_5H_5)_2(NCO)$] [$\nu_1(NCO) = 2\,202$ cm^{-1}] could be isolated from the reaction as a pure crystalline material.[2] In the reaction of [$V(\eta$-$C_5H_5)_2(CO)$] with NO, neither repeated recrystallisation of the black solid from ether–thf nor chromatography succeeded in producing pure [$V(\eta$-$C_5H_5)_2(NCO)$]. The black solid always showed a broad absorption at 920 cm^{-1} in the i.r. spectrum in addition to bands attributable to NCO and η-C_5H_5; this band is probably due to a V–O vibration. It is clear that [$V(\eta$-$C_5H_5)_2(CO)$] and NO produce NCO, but the exact nature of the complex remains uncertain.

In order to establish that [$V(\eta$-$C_5H_5)_2(NCO)$] exists, this complex was prepared by addition of excess NCO^- to [$VCl(\eta$-$C_5H_5)_2$] dissolved in water. The product analysed reproducibly as [$V(\eta$-$C_5H_5)_2(NCO)$], was dark violet in colour, showed a strong absorption at 2 209 cm^{-1} in the i.r. spectrum [$\nu_1(NCO)^{25}$] and had a magnetic moment of 2.38×10^{-23} A m^2 which is slightly lower than usually obtained for a spin-free d^2 complex.[26]

We were surprised to find that there was no reaction whatever between [$V(\eta$-$C_5H_5)_2(CO)_2$]$^+$ and NO in thf or water as solvent at temperatures up to 50 °C. There are no structural differences which are chemically significant between [$V(\eta$-$C_5H_5)_2(CO)_2$]$^+$ and the isoelectronic [$Ti(\eta$-$C_5H_5)_2(CO)_2$][27,28] which reacts according to equation (1). The first step in reaction (1) is believed to be replacement of a CO in the co-ordinatively saturated [$Ti(\eta$-$C_5H_5)_2(CO)_2$] by NO.[2] If loss of CO occurred in [$V(\eta$-$C_5H_5)_2(CO)_2$]$^+$, we would have observed at least a substitution product under the forcing conditions used. We conclude therefore that substitution of CO does not occur. The analogous [$Nb(\eta$-$C_5H_5)_2(CO)_2$]$^+$ is also inert towards NO and unlike [$V(\eta$-$C_5H_5)_2(CO)_2$]$^+$ which slowly oxidises, [$Nb(\eta$-$C_5H_5)_2(CO)_2$]$^+$ is even stable towards air.[29,30]

The reaction between [$V(\eta$-$C_5H_5)_2(CO)$] and NOCl is discussed below.

The Reactions between [$VX(\eta$-$C_5H_5)_2$] (X = Cl, Br, *or* I) *and* NO.—The reaction between a toluene solution of [$VI(\eta$-$C_5H_5)_2$] and NO occurred rapidly in a 1:1 mol ratio giving a dark brown precipitate and no gaseous products. Extraction of the precipitate with thf gave a light brown residue and a green solution from which a green solid was obtained by concentrating the solution and adding hexane. Both the light brown and green products analysed reproducibly as $VI(C_5H_5)_2NO$.

The light brown $VI(C_5H_5)_2NO$ was insoluble in all common solvents, had a magnetic moment of 6.02×10^{-24} A m^2 [calculated for the formula $VI(C_5H_5)_2NO$ and uncorrected for ligand diamagnetism] and showed no absorptions in the i.r. spectrum which could be assigned to co-ordinated NO. On washing with water the washings showed a strongly positive test for ionic iodide, the brown solid remaining undissolved. We conclude that the light brown form of $VI(C_5H_5)_2NO$ is polymeric: $\{[V(C_5H_5)_2NO]^+\}_n[I^-]_n$. Since $\{[V(C_5H_5)_2NO]^+\}_n$ is isoelectronic with $[Ti(C_5H_5)_2NO]_n$, which is believed to contain bridging N_2O_2 units,[2] a similar structure is likely for $\{[V(C_5H_5)_2NO]^+\}_n$. The weak paramagnetism may be due either to coupling between the electrons of the formally V^{IV} (d^1) atoms or a different geometry and oxidation state of the individual V atoms in the polymer.

The other product, air-sensitive green [$VI(C_5H_5)_2(NO)$], was very soluble in thf, in which solvent it was monomeric. The i.r. spectrum (Nujol mull) of the complex after precipitation at room temperature showed two strong rather broad absorption bands at 1 670 and 1 590 cm^{-1} whose intensities were in the approximate ratio of 1:3. In thf solution the absorption bands (1 688 and 1 588 cm^{-1}) were strong and sharp with an intensity ratio of 1:2. When the [$VI(C_5H_5)_2(NO)$] was precipitated from thf at −70 °C the i.r. spectrum (Nujol mull, measured at room temperature) showed that the absorption bands at 1 670 and 1 590 cm^{-1} now had an intensity ratio of 1:6.4. Dissolution of the material precipitated at low temperature in thf and reprecipitation at room temperature returned the intensity ratio of the absorption bands to their former value.

The e.s.r. spectrum of [$VI(C_5H_5)_2(NO)$] is shown in Figure 1. This spectrum is very similar to that of [$V(\eta$-$C_5H_5)_2\{C_2(CO_2CH_3)_2\}$].[31] On warming, the spectrum collapsed until at +60 °C an approximately isotropic spectrum was obtained (Figure 1). The changes in the spectrum between −100 and 0 °C were completely reversible. However, above 20 °C irreversible changes slowly occurred, due to the decomposition of [$VI(C_5H_5)_2(NO)$] which is discussed below. There were no observable signals due to the C_5H_5 rings of [$VI(C_5H_5)_2(NO)$] in either the ^{13}C or ^1H n.m.r. spectra (thf solution, 220 MHz, −70 °C).

That the changes with temperature observed in the e.s.r. spectrum are due to a molecular rearrangement is clearly shown by the spectrum of [$VI(\eta$-$C_5Me_5)_2(NO)$].[24] This complex shows only one ν(NO) absorption in the i.r. spectrum at 1 710 cm^{-1} and the e.s.r. spectrum is independent of temperature except for changes in linewidth. There is no fluxionality in [$VI(\eta$-$C_5Me_5)_2(NO)$].

The i.r. and e.s.r. evidence indicates that monomeric [$VI(C_5H_5)_2(NO)$] is a fluxional molecule. By the criteria of Haymore and Ibers,[32] the two forms of the molecule would be one with a linear $\{VNO\}^3$ group [$\nu(NO) = 1\,670$ cm^{-1}] and one with a bent $\{VNO\}^3$ group [$\nu(NO) = 1\,590$ cm^{-1}].† An interconversion between forms of the molecule with linear and bent $\{VNO\}^3$ groups would be in accord with the proposals of Enemark and Feltham[33] on the stereochemical control of valence in metal nitrosyls, and such fluxional interconvensions have been observed previously.[34,35] However, the criteria of

---

† The notation $\{\ \}^n$ is explained at length in ref. 33.

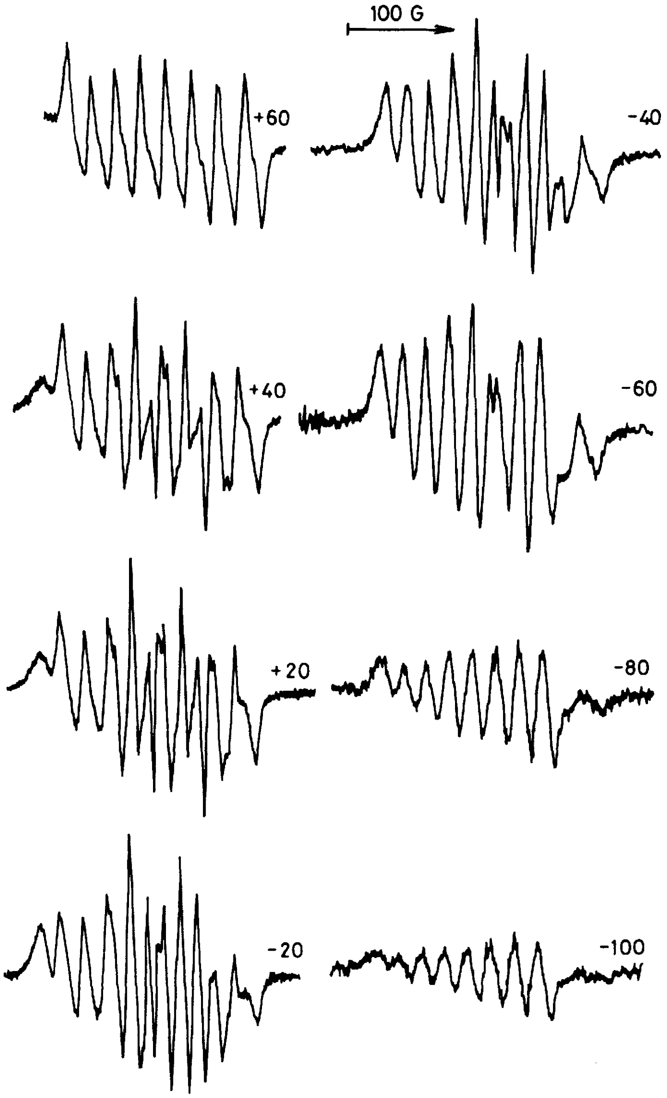

Figure 1. The e.s.r. spectrum of $[VI(C_5H_5)_2(NO)]$ in thf as a function of temperature (°C)

Haymore and Ibers[32] were developed for nitrosyls of the Group 8A metals and it is by no means certain that they can be applied to nitrosyls of the early transition metals. Indeed at least one vanadium nitrosyl, $[V(dipic)(H_2O)(NH_2O)(NO)]^-$ (dipic = pyridine-2,6-dicarboxylate), has ν(NO) at 1 530 cm^{-1} but the $\{VNO\}^4$ group is linear (175.7°).[18] It has also been pointed out that nitrosyls *formally* having an NO^- ligand can have a linear $\{MNO\}^n$ group,[36–39] and in the 19-electron complex $[W(\eta\text{-}C_5H_5)\{P(OPh)_3\}(NO)_2]$ the WNO angles are 165.7(1.3) and 174.9(1.2)°. The W–N distances [1.80(1) and 1.78(1) Å] are much shorter than in the analogous 18-electron complex $[WCl(\eta\text{-}C_5H_5)(NO)_2]$ [WNO 168.4(8) and 169.0(1.0)°; W–N 1.832(9) and 1.819(8) Å]. On the other hand, the N–O distances in $[W(\eta\text{-}C_5H_5)\{P(OPh)_3\}(NO)_2]$ [1.20(2) and 1.22(2) Å] are longer than in $[WCl(\eta\text{-}C_5H_5)(NO)_2]$ [1.15(1) and 1.17(1) Å]. The ν(NO) frequencies in $[W(\eta\text{-}C_5H_5)\{P(OPh)_3\}(NO)_2]$ are 1 613 and 1 553 cm^{-1}.[36] Hence the two forms of $VI(C_5H_5)_2(NO)$ could both have essentially linear VNO groups but in one [that with ν(NO) = 1 590 cm^{-1}] the V–N distance would be shorter and the N–O distance longer than in the other.

The form of $VI(C_5H_5)_2(NO)$ with ν(NO) at 1 670 cm^{-1} will have a linear $\{VNO\}^3$ group in any case, and therefore will be *formally* a 19-electron molecule, with one electron in an antibonding orbital involving the $\eta\text{-}C_5H_5$ and NO ligands.[37,39] Two 20-electron complexes are known, $[MoX(C_5H_5)_2(NO)]$ (X = I,[40] $\eta^1\text{-}C_5H_5$,[41] or CH_3[42]) and $[W(C_5H_5)_2(CO)_2]$.[43–45] In $[Mo(CH_3)(C_5H_5)_2(NO)]$ and $[Mo(\eta^1\text{-}C_5H_5)(C_5H_5)_2(NO)]$, two C_5H_5 rings in each are planar but the Mo–C distances are markedly unequal: two are 2.34, one is 2.44, and two are 2.61 Å (averages). The rings are not η^5 but what their hapticity actually is, is not clear.[41] In $[W(C_5H_5)_2(CO)_2]$ there is one $\eta^5\text{-}C_5H_5$ and one $\eta^3\text{-}C_5H_5$ ring, the latter being not planar but bent along its 1,3 axis by 20°.[43] No 19-electron $[MX_2(C_5H_5)_2]$ complex is known but extrapolating from $[MoX(C_5H_5)_2(NO)]$ and $[W(C_5H_5)_2(CO)_2]$ we would expect $[VI(C_5H_5)_2(NO)]$ to have either two planar C_5H_5 rings, both having unequal V–C distances or one planar η^5 ring and one bent of η^3 or η^4 hapticity. We have not been able to crystallise either form of $[VI(C_5H_5)_2(NO)]$; because of the decomposition discussed below only recrystallisation below −30 °C is possible and this gives microcrystals.

Although the fluxional behaviour is the most reasonable explanation for the physical properties of $[VI(C_5H_5)_2(NO)]$, there is the possibility that the equilibrium (2) takes place;

$$[VI(\eta\text{-}C_5H_5)_2(NO)] \rightleftharpoons [V(\eta\text{-}C_5H_5)_2(NO)]^+ + I^- \quad (2)$$

$[VI(\eta\text{-}C_5H_5)_2(NO)]$ would have ν(NO) at 1 590 and $[V(\eta\text{-}C_5H_5)_2(NO)]^+$, at 1 670 cm^{-1}. There was no evidence of ionic iodide in thf solutions of $[VI(C_5H_5)_2(NO)]$ but in order to test further this possibility attempts were made to prepare $[V(\eta\text{-}C_5H_5)_2(NO)]^+$ by reaction of $[V(\eta\text{-}C_5H_5)_2(CO)]$ with NOCl. The reaction (in toluene) was extremely complicated. There was i.r. evidence for NCO, presumably produced by dissociation of NOCl and subsequent attack of NO on $[V(\eta\text{-}C_5H_5)_2(CO)]$ (see above). There were also a wealth of i.r. absorption bands attributable to carbonyl and nitrosyl species which are presumed to arise *via* disproportionation of complexes containing NO, Cl, and CO ligands. Using $NOBF_4$ in place of NOCl gave a material having a single strong ν(NO) absorption band at 1 555 cm^{-1}, but the presumed $[V(\eta\text{-}C_5H_5)_2(NO)]BF_4$ was insoluble in all common solvents and could not be purified. A final attempt to obtain $[V(\eta\text{-}C_5H_5)_2(NO)]^+$ used the reaction between $[VI(\eta\text{-}C_5H_5)_2]$ and NO in water. This gave a brown-green product with ν(NO) at 1 521 cm^{-1}. The complex could not be dehydrated and was insoluble in thf, and we cannot be certain whether it is to be formulated as $[V(\eta\text{-}C_5H_5)_2(NO)]I{\cdot}H_2O$ or as $[V(\eta\text{-}C_5H_5)_2(H_2O)(NO)]I$. It was in any event not a fluxional molecule and had neither the solubility nor i.r. spectral properties of $[VI(C_5H_5)_2(NO)]$.

On setting a green thf solution of $[VI(C_5H_5)_2(NO)]$ aside under vacuum at room temperature, it slowly turned brown and over a period of several days golden-brown crystals were deposited. These were shown by *X*-ray diffraction to be the remarkable oxo-bridged nitrosyl $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ [ν(NO) = 1 780 cm^{-1}]. Microanalysis of the bulk material obtained when $[VI(C_5H_5)_2(NO)]$ decomposed revealed that it was homogeneous and therefore $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ was the only insoluble product of the decomposition. Formation of this complex must be accompanied by other products, but we have been unable to detect any of the obvious possibilities (N_2O, I_2, pyridine, or cyclopentadienylvanadium derivatives) and have no idea how this most improbable transformation takes place. We do note that the transformation was readily reproducible and $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ could be obtained in relatively large quantities.

The reaction between $[VBr(\eta\text{-}C_5H_5)_2]$ and NO gave a brown product showing three absorption bands in the ν(NO) region of the i.r. spectrum (1 660, 1 582, and 1 560 cm^{-1}).

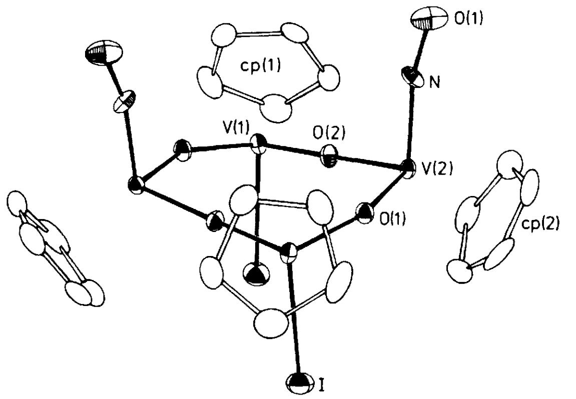

Figure 2. The molecular structure of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$

Extraction with thf gave a green solution and a light brown solid which still showed the three i.r. bands but analysed as $VBr(C_5H_5)_2NO$. From the solution, a green solid could be crystallised. Room-temperature crystallisation gave a complex having two ν(NO) bands at 1 660 and 1 560 cm^{-1}, a molecular weight of 290 [calc. for $VBr(C_5H_5)_2(NO)$: 291.1] and which transformed in solution into brown $[\{VBr(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ [ν(NO) = 1 775 cm^{-1}]. However microanalysis of the presumed $[VBr(C_5H_5)_2(NO)]$ always gave a very low nitrogen content. Crystallisation of the green complex at −30 °C gave only the form having ν(NO) at 1 560 cm^{-1}. We believe that the green material is $[VBr(C_5H_5)_2(NO)]$ which is fluxional like $[VI(C_5H_5)_2(NO)]$ but which also loses NO rather readily. The brown $VBr(C_5H_5)_2NO$ is obviously more complicated than the analogous $VI(C_5H_5)_2NO$ polymer.

Reaction of $[VCl(\eta\text{-}C_5H_5)_2]$ with NO in thf gave once again a brown solid showing three absorption bands (1 655, 1 581, and 1 538 cm^{-1}) in the ν(NO) region of the i.r. spectrum. However, unlike the reactions of $[VI(\eta\text{-}C_5H_5)_2]$ or $[VBr(\eta\text{-}C_5H_5)_2]$, N_2O was also produced in the reaction. Removal of the brown solid by filtration gave a green solution which precipitated a green solid on addition of hexane. Chemical and physical analysis showed the product to be the same $[V_2O_2Cl_2(\eta\text{-}C_5H_5)_3]$ dimer which we have described previously as the product of the reaction between $[VCl(\eta\text{-}C_5H_5)_2]$ and O_2.[46]

The Reaction between $[VCl_2(\eta\text{-}C_5H_5)_2]$ *and* NO.—There was no reaction between $[VCl_2(\eta\text{-}C_5H_5)_2]$ and NO. In order to provide a free co-ordination site, BF_3 was added to toluene solutions of $[VCl_2(\eta\text{-}C_5H_5)_2]$ resulting in a colour change from the light green of $[VCl_2(\eta\text{-}C_5H_5)_2]$ to black and precipitation of a dark olive-green solid whose i.r. spectrum showed bands ascribable to BF_4^- and BCl_4.[25] It is known that mixed $BCl_nF_{4-n}^-$ anions rapidly redistribute to give the parent anions.[47] Addition of NO to the dark mixture (after removal of BF_3) gave an immediate colour change to light blue-green. The solid which was formed showed several absorption bands in the region 1 800—1 950 cm^{-1} in the i.r. spectrum, but these all disappeared on attempted recrystallisation or washing, leaving blue $[VCl(\eta\text{-}C_5H_5)_2]$ as the only product. We conclude that NO reduced $[VCl_2(\eta\text{-}C_5H_5)_2]$ to $[VCl(\eta\text{-}C_5H_5)_2]$, itself giving various NO^+ salts ($NOBF_4$, NOCl, $NOBCl_4$) which adsorbed on the $[VCl(\eta\text{-}C_5H_5)_2]$. As discussed above, $[VCl(\eta\text{-}C_5H_5)_2]$ is at least partially oxidised by NO, and the unusual situation in which reactions (3) and (4) can occur together probably contributes to the complicated chemistry observed in the reactions between $[VCl(\eta\text{-}C_5H_5)_2]$ and NO.

Table 1. Important distances (Å) in $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$

V(1)–I	2.653(2)	V(2)–N	1.760(7)
V(1)–O(1)	1.698(5)	V(2)–O(1)	1.885(5)
V(1)–O(2)	1.694(5)	V(2)–O(2)	1.874(5)
V(1)–cp(1)*	1.978	V(2)–cp(2)*	1.964
		N–O(3)	1.128(10)

* Distances to the centroids of the $\eta^5\text{-}C_5H_5$ rings (cp).

Table 2. Important angles (°) in $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$

I–V(1)–cp(1)	114.50(6)	N–V(2)–cp(2)	121.4(3)
		O(1)–V(2)–cp(2)	116.4(2)
O(1)–V(1)–cp(1)	119.7(2)	O(2)–V(2)–cp(2)	115.6(2)
O(2)–V(1)–cp(1)	117.0(2)	O(1)–V(2)–O(2)	103.4(2)
O(1)–V(1)–O(2)	106.1(3)	N–V(2)–O(2)	96.5(3)
I–V(1)–O(2)	97.8(2)	N–V(2)–O(1)	100.2(3)
I–V(1)–O(1)	98.0(2)	V(1)–O(2)–V(2)	179.3(3)
V(1)–O(1)–V(2)	148.1(3)	V(2)–N–O(3)	166.9(8)

$$[VCl(\eta\text{-}C_5H_5)_2]^+ + NO \longrightarrow [VCl(\eta\text{-}C_5H_5)_2] + NO^+ \quad (3)$$

$$2[VCl(\eta\text{-}C_5H_5)_2] + 2NO \longrightarrow N_2O + 2[VCl(\eta\text{-}C_5H_5)_2] + O^{2-} \quad (4)$$

Structure of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$.—The crystals are made up of layers of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ rings (Figure 2), the layers being perpendicular to the *b* axis. Each ring is packed directly over one in the next layer, the V–I vectors running in one direction approximately parallel to *b*, the V–NO vectors in the opposite direction. The shortest intermolecular contact is 2.44 Å between hydrogen atoms of $\eta\text{-}C_5H_5$ rings on adjacent molecules within one layer. The important bond distances and angles are listed in Tables 1 and 2. The basic geometry of the molecule is an eight-membered ring of alternating V and O atoms which is approximately planar (see Figure 2 and Table 3). The I and NO ligands are attached alternately to the V atoms around the ring. The nitrosyls are *cis* to each other, as are the iodides but the nitrosyls are *trans* to the iodide ligands. There is a crystallographic two-fold axis in the centre of the ring perpendicular to its approximate plane.

The $(V\text{-}O)_4$ ring may be described in two ways, each of which illustrates a different facet of the structure. Firstly the four oxygen atoms form a parallelogram whose opposite sides measure 2.950 and 2.711 Å and whose alternating internal angles are 105.0 and 74.7°. The V atoms are alternately above and below the plane of this parallelogram, those carrying the I ligands being 0.261 Å above (*i.e.* towards the I ligand), those carrying NO 0.157 Å below (*i.e.* towards the NO) (see Table 3). Thus described, the structure is a flattened version of that observed in the $[(VO_2)_4(\mu\text{-}O)_4]^{4-}$ ring in $[NBu_4][HV_4O_{12}]$,[48] which is in turn related to tetrametaphosphate and cyclotetrasilicate.[49] However, in addition to the flattening there are significant differences from these structures. Although the O–V–O angles are very similar to one another [103.4(2)° at V(2), carrying the NO, and 106.1(3)° at V(1), carrying I], the V–O–V angles are very different, 148.1(3) and 179.3(3)°. The V–O distances are also markedly unequal, those involving V(1) being 1.694(5) and 1.698(5) Å and those involving V(2) being 1.874(5) and 1.885(5) Å. With the O–V–O angles and V(1)–O or V(2)–O distances averaged, the second description of the ring is illustrated in Figure 3(*a*). It consists of two irregularly shaped

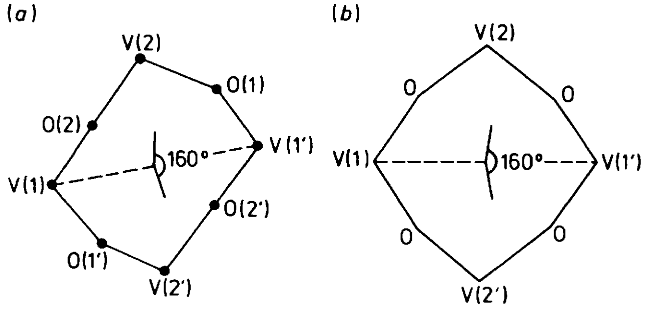

Figure 3. The $(V–O)_4$ ring of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$: (*a*) observed; (*b*) calculated, with all V–O–V angles of 162°

Table 3. Equations of planes and distances (Å) of atoms from the planes for $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$

Plane 1: O(1), O(2), O(1'), O(2')

$$0.0X + 1.0Y + 0.0Z = -2.5311$$

O(1)	−0.067	V(1)	+0.259
O(2)	+0.067	V(2)	−0.158
O(1')	−0.067	I	+2.909
O(2')	+0.067	N	−1.903

Plane 2: V(1), O(1), V(2), O(2'), V(1')

$$-0.1431X + 0.9851Y + 0.0955Z = -1.8247$$

V(1)	+0.025	O(2')	+0.011
O(1)	−0.047	V(1')	−0.012
V(2)	+0.023		

Plane 3: V(1), O(2), V(2'), O(1'), V(1')

$$+0.1431X + 0.9851Y - 0.0955Z = -2.6642$$

Angle between Plane 2 and Plane 3: 160.2°

planes fused at an angle of 160.2° on the V(1) ··· V(1') axis (Table 3). In Figure 3(*b*) the ring is shown as it would be if all four V–O–V angles were equal.

The large (0.184 Å) difference in the V–O distances is independent of the angle at the oxygen atom but dependent on the ligand attached to the vanadium atom, V(1)–O being the shorter distance. Considerable variation in V–O distances at the *same* V atom are often observed,[48] and are attributable to different V–O bond orders. In the present case the V–O distances are equal at the same V atom, but different between V(1) and V(2). The difference must be due to the different formal oxidation states of the vanadium atoms produced by the different ligands, I at V(1) or NO at V(2). However, assigning actual oxidation states to the V atoms is not easy. If the VNO angle of 166.9(8)° is considered as indicating that the nitrosyl ligand is formally NO^+ [ν(NO) is 1 780 cm^{-1}] and the C_5H_5, O, and I ligands are considered as being in their normal $\eta\text{-}C_5H_5^-$, O^{2-}, and I^- oxidation states, then we are dealing with V_4^{12+}. The assignment of each vanadium as V^{III} does not explain the different V–O distances. Because of the requirements of the NO^+ ligand for π back-bonding the only acceptable alternatives are V^{IV} (d^1) for V(1), with V^{II} (d^3) for V(2), or V^V (d^0) for V(1) with V^I (d^4) for V(2). The complex is diamagnetic at room temperature which is expected for the V^V/V^I formulation, but would only be compatible with the V^{IV}/V^{II} formulation if coupling of the unpaired electrons *via* the bridging oxygen occurred. With the exception of $[VI(C_5H_5)_2(NO)]$ (see above) all known vanadium nitrosyls have the $\{VNO\}^4$ configuration. We therefore favour the V^V (d^0) for V(1) with V^I (d^4) for V(2) formulation. It is then expected that the V^V–O distances would be shorter than V^I–O. However, it should be noted that unequal Ti–O distances were observed in the $(TiO)_4$ unit of $Cs_4[TiO(nta)]_4$ (nta = nitrilotriacetate; Ti–O 1.90 and 1.755 Å) though the Ti atoms are unequivocally all Ti^{IV}.[50] Also the V–I distance of 2.653(2) Å in $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ is longer than that in $[\{VI_2(\eta\text{-}C_5Me_5)\}_2O]$ (2.616 Å).[51] The latter unequivocally contains V^{IV}, and a V^{IV}–I distance would be expected to be longer than V^V–I. These two facts are in accord with a V^{III}/V^{III} formulation.

The average V(1)–O distance, 1.696(5) Å is extremely short even for a V^V–O bridging distance. In the $[(VO_2)_4(\mu\text{-}O)_4]^{4-}$ ring the bridging V–O distances average 1.80 Å and the terminal distances 1.62 Å.[48] The latter distance is close to that generally observed for the V–O double bond.[49,52] The overall average of the V–O bond distances in $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ is 1.788(5) Å, close to that in $[(VO_2)_4(\mu\text{-}O)_4]^{4-}$ and related vanadates.[48,49] It appears that the unequal vanadium oxidation states in $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ partitions the V–O distances into two sets, 1.879(5) Å at V(2) (V^I) and 1.696(5) Å at V(1) (V^V).

The structure of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$ is remarkable for the two very different V–O–V angles, 148.1(3) and 179.3(3)°. There is no chemical difference in the environments of the oxygen atoms which would account for the difference in the angles. Oxo-bridges between metal atoms with angles between 106 and 180° are known, and there is no obvious preference for particular angles in any particular case.[53] With the planar geometry of the two halves of the ring and the observed bond lengths and bond angles at the V atoms, it can be calculated that four equal V–O–V angles of 162° can easily be accommodated [see Figure 3(*b*)]. There are no steric constraints on either the observed or calculated geometries. Although V–O π-bonding will be affected by the V–O–V angles, we do not see any overall advantage in having such widely different angles.

Vanadium nitrosyls which have been structurally characterised previously have the $\{VNO\}^4$ configuration, VNO angles of 164—176°, and V–N distances of 1.66—1.81 Å.[10,12,18] The V–N distance observed here, 1.760(7) Å, is at the longer end of the range of these distances. The V(1)–cp(1) distance (the perpendicular distance from the centroid of the $\eta^5\text{-}C_5H_5$ ring to the vanadium) of 1.978 Å is longer than V(2)–cp(2) (1.964 Å), again suggesting that V(1) has a higher formal oxidation state than V(2). However, the V(1)–cp(1) distance is shorter than might have been expected for V^V, and the V(2)–cp(2) distance is longer than expected for V^I.[54] This reflects the π-electron withdrawing ability of the NO^+ ligand, and the π-electron donating capability of I^-.

Experimental

All experiments were carried out under argon or vacuum using standard vacuum-line techniques. Solvents were predried, stored over methyl-lithium, and distilled under vacuum. The complexes $[VCl(\eta\text{-}C_5H_5)_2]$,[55] $[VBr(\eta\text{-}C_5H_5)_2]$,[56] and $[VI(\eta\text{-}C_5H_5)_2]$[56] were prepared by literature methods; $[VCl_2(\eta\text{-}C_5H_5)_2]$ was purchased from Strem Chemicals. Nitric oxide (99%) was purified by passage through silica gel at −78 °C. All other chemicals were reagent grade. Volumes of gaseous reactants and products were measured using calibrated bulbs and gaseous products were separated by a Toepler pump using traps at different temperatures and a Cu–CuO bed at 300 °C. Instruments used were a Perkin-Elmer 683 i.r. spectrophotometer (spectra measured as Nujol or Fluorolube mulls or in solution between KBr plates), an Alpha Scientific electromagnet with a Cahn electrobalance to measure magnetic moments by the Faraday method, a locally modified version of the Varian E-4 e.s.r. spectrometer, and a Hitachi–Perkin-Elmer

Table 4. Positional parameters for the non-hydrogen atoms of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I	0.061 29(4)	0.046 32(9)	0.371 65(4)	C(13)	0.099 7(6)	−0.325 4(18)	0.496 1(5)
V(1)	0.068 81(7)	−0.278 70(20)	0.370 27(7)	C(14)	0.159 1(6)	−0.242 6(15)	0.465 2(6)
V(2)	−0.113 24(7)	−0.329 86(17)	0.324 75(7)	C(15)	0.187 9(5)	−0.342 1(15)	0.408 9(6)
O(1)	−0.021 7(3)	−0.318 7(7)	0.375 2(3)	C(21)	−0.154 1(6)	−0.068 0(13)	0.352 1(9)
O(2)	0.090 4(3)	−0.302 3(7)	0.277 8(3)	C(22)	−0.154 5(6)	−0.160 6(17)	0.417 7(6)
O(3)	−0.146 3(5)	−0.673 9(10)	0.322 6(4)	C(23)	−0.202 9(7)	−0.283 2(17)	0.406 5(7)
N	−0.125 4(4)	−0.543 9(9)	0.321 0(4)	C(24)	−0.232 7(5)	−0.269 1(16)	0.335 9(7)
C(11)	0.144 6(6)	−0.484 0(13)	0.406 0(6)	C(25)	−0.203 3(6)	−0.140 0(15)	0.302 3(6)
C(12)	0.093 6(6)	−0.472 1(15)	0.460 1(6)				

RMU-6D mass spectrometer. Microanalyses and molecular weight determinations (by osmometry) were by the Analytische Laboratorien, Engelskirchen, West Germany.

Bis(η-cyclopentadienyl)(isocyanato)vanadium(III), $[V(\eta\text{-}C_5H_5)_2(NCO)]$.—To a solution of $[VCl(\eta\text{-}C_5H_5)_2]$ (0.42 g, 1.94 mmol) in water (25 cm^3) was added KNCO (0.16 g, 1.97 mmol) also dissolved in water (25 cm^3). There was immediate precipitation of an extremely air-sensitive violet solid which was removed by filtration, washed twice with water (10 cm^3), and dried *in vacuo*. Recrystallisation from thf gave 0.26 g (60%) of $[V(\eta\text{-}C_5H_5)_2(NCO)]$ [Found: C, 59.0; H, 4.5; N, 6.4; V (as V_2O_5), 22.0. Calc. for $C_{11}H_{10}NOV$: C, 59.2; H, 4.5; N, 6.3; V, 22.8%]. Molecular weight (found by osmometry), 228; calc. for $[V(\eta\text{-}C_5H_5)_2(NCO)]$, 213. The magnetic moment (uncorrected for ligand diamagnetism) was 2.38×10^{-23} A m^2. The complex showed a strong sharp absorption at 2 209 cm^{-1} [ν_1(NCO)] in the i.r. spectrum.

Reaction of $[VI(\eta\text{-}C_5H_5)_2]$ *with* NO: *Bis(η-cyclopentadienyl)iodo(nitrosyl)vanadium*, $[VI(\eta\text{-}C_5H_5)_2(NO)]$.—To a solution of $[VI(\eta\text{-}C_5H_5)_2]$ (1.77 g, 5.75 mmol) in toluene (50 cm^3) was added NO (5.67 mmol). There was an immediate colour change from bright green to dark green-brown. The mixture was stirred for 24 h, after which time all the NO had been taken up. The mixture was filtered giving a dark brown solid which was dried and extracted with thf (50 cm^3) to produce a light brown solid (1.03 g) and a dark green filtrate.

The solid, which was insoluble in all common solvents, had a magnetic moment of 6.02×10^{-24} A m^2, showed no absorption bands in the region of the i.r. spectrum where ν(NO) vibrations are expected, and analysed as $[\{VI(C_5H_5)_2(NO)\}_n]$ (Found: C, 35.6; H, 3.0; N, 3.1. Calc. for $C_{10}H_{10}INOV$: C, 35.5; H, 3.0; N, 3.3%).

The volume of the green filtrate was reduced to approximately 25 cm^3 and then hexane (25 cm^3) was added to precipitate the product, $[VI(C_5H_5)_2(NO)]$, which was removed by filtration. The above operations were conducted as rapidly as possible to avoid the decomposition described below. Yield 0.35 g (18%) (Found: C, 35.3; H, 3.1; I, 37.8; N, 3.9. Calc. for $C_{10}H_{10}INOV$: C, 35.5; H, 3.0; I, 37.5; N, 3.3%). Molecular weight (by osmometry in thf), 354; calc., 338. I.r. spectrum: ν(NO) at 1 670, 1 590 cm^{-1} (Nujol); 1 688, 1 588 cm^{-1} (thf solution). $\mu_{eff.} = 6.30 \times 10^{-24}$ A m^2 at 20 °C. Mass spectrum: M/e = 308 $[VI(C_5H_5)_2]$.

Rearrangement of $[VI(C_5H_5)_2(NO)]$ *to Tetra-μ-oxo-bis[(η-cyclopentadienyl)iodovanadium]bis[(η-cyclopentadienyl)nitrosylvanadium]*, $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$.—A solution of $[VI(C_5H_5)_2(NO)]$ (0.29 g) in thf (30 cm^3) was set aside under vacuum at room temperature for 4 weeks. During this time the green solution turned brown and deposited golden brown crystals of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$·thf. These were removed by filtration, yield 0.13 g (Found: C, 31.5; H, 3.8; I, 27.8; N, 3.0. Calc. for $C_{24}H_{28}I_2N_2O_7V_4$: C, 31.5; H, 3.1; I, 27.8; N, 3.1%). I.r.: ν(NO) at 1 780 cm^{-1}.

Reaction of $[VBr(\eta\text{-}C_5H_5)_2]$ *with* NO.—To a solution of $[VBr(\eta\text{-}C_5H_5)_2]$ (0.67 g, 2.57 mmol) in toluene (30 cm^3) was added NO (2.45 mmol). The solution was stirred at room temperature for 72 h and filtered giving a green-brown solid. Extraction of the solid with thf (50 cm^3) gave a green solution and left a brown residue of $[VBr(C_5H_5)_2(NO)]_n$ (0.4 g) (Found: C, 41.1; H, 3.6; N, 4.6. Calc. for $C_{10}H_{10}BrNOV$: C, 41.0; H, 3.5; N, 4.8%). I.r.: ν(NO) at 1 660, 1 582, and 1 560 cm^{-1}.

The green solution was reduced to a volume of 25 cm^3 and then hexane (25 cm^3) was added. This procedure was conducted as rapidly as possible to avoid decomposition (see below). The green solid which precipitated was removed by filtration, yield 0.18 g, 24% assuming the product was pure $[VBr(C_5H_5)_2(NO)]$ [Found (two samples from different experiments): C, 38.2, 39.0; H, 3.3, 3.5; Br, 34.3, 32.8; N, 1.4, 1.8. $C_{10}H_{10}BrNOV$ requires C, 41.0; H, 3.5; Br, 27.3; N, 4.8%]. Molecular weight (osmometrically in thf), 290; $[VBr(C_5H_5)_2(NO)]$ has M = 291.1. $\mu_{eff.} = 4.63 \times 10^{-24}$ A m^2. I.r.: ν(NO) at 1 660 and 1 560 cm^{-1}.

Rearrangement of $[VBr(C_5H_5)_2(NO)]$ *to Tetra-μ-oxo-bis[bromo(η-cyclopentadienyl)vanadium]bis[(η-cyclopentadienyl)nitrosylvanadium]*, $[\{VBr(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$.—A solution of $[VBr(C_5H_5)_2(NO)]$ (0.28 g) in thf (30 cm^3) was set aside at room temperature for 4 weeks. The green solution became brown and a brown solid precipitated. This was removed by filtration, washed well with thf and dried *in vacuo*. Yield of the thf solvate 0.11 g (Found: C, 37.4; H, 3.5; N, 3.3. $C_{28}H_{36}Br_2N_2O_8V_4$ requires C, 37.6; H, 4.0; N, 3.1%); ν(NO) at 1 775 cm^{-1}.

Reaction of $[VCl(\eta\text{-}C_5H_5)_2]$ *with* NO.—A solution of $[VCl(\eta\text{-}C_5H_5)_2]$ (0.94 g, 4.34 mmol) in thf (30 cm^3) was incubated with NO (4.02 mmol) for 18 h. The colour of the solution changed rapidly from blue to brown and a brown solid was slowly precipitated. Analysis of the gases remaining after the reaction showed only N_2O (the exact amount could not be determined because of the vapour pressure of thf). The mixture was filtered giving the brown solid (yield 0.40 g) and a green filtrate. Hexane (10 cm^3) was added to the filtrate, precipitating green $[V_2O_2Cl_2(\eta\text{-}C_5H_5)_3]$. This was recrystallised from thf–hexane in 54% yield (0.34 g) (Found: C, 44.9; H, 3.9. Calc. for $C_{15}H_{15}Cl_2O_2V_2$: C, 45.0; H, 3.8%). $\mu_{eff.} = 1.33 \times 10^{-23}$ A m^2 (uncorrected for ligand diamagnetism). The material had the same chemical and physical properties as a sample obtained from the oxidation of $[VCl(\eta\text{-}C_5H_5)_2]$ by O_2.[46]

Reaction of $[VCl_2(\eta\text{-}C_5H_5)_2]$ *with* BF_3 *and* NO: *Formation of Chlorobis(η-cyclopentadienyl)vanadium*(III), $[VCl(\eta\text{-}C_5H_5)_2]$.—A solution of $[VCl_2(\eta\text{-}C_5H_5)_2]$ (7.7 g, 0.031 mol) in toluene (120 cm^3) was incubated with a large excess of BF_3 for 48 h with constant stirring. The solution absorbed BF_3 (which was recharged at intervals), changing colour from green to black in the process. A black precipitate formed during this period. After 48 h the BF_3 was pumped off and NO was added. The mixture was stirred for 24 h, the NO being occasionally replenished as it was absorbed. The mixture turned various shades of brown and finally became blue-green. Removal of *ca.* one-half of the toluene and filtration gave a blue solid which was recrystallised from toluene–hexane. Yield 5.5 g, 84% of $[VCl(\eta\text{-}C_5H_5)_2]$. The product was identified as $[VCl(\eta\text{-}C_5H_5)_2]$ by comparison of its physical and chemical properties with those of an authentic sample.[55]

Determination of the Crystal Structure of $[\{VI(\eta\text{-}C_5H_5)\}_2\{V(\eta\text{-}C_5H_5)(NO)\}_2(\mu\text{-}O)_4]$.—A brown crystal of dimensions 0.25 × 0.25 × 0.18 mm was coated with 'Apiezon' grease and mounted in a thin-walled capillary under argon. Weissenberg and precession photographs showed the monoclinic class and the systematic absences $h + k = 2n$ for $h\,k\,l$, $k = 2n$, $l = 2n$ for $h0l$ and $k = 2n$ for $0k0$, thus establishing the space groups as either *Cc* (no. 9) or *C*2/*c* (no. 15). The crystal was transferred to a Picker FACS 1 diffractometer and accurate determination of the settings of 12 Friedel pairs of reflections gave the cell dimensions $a = 18.358(3)$, $b = 8.152(1)$, $c = 17.590(2)$ Å, $\beta = 91.27(2)°$ (Mo-K_α radiation, 0.710 69 Å). With $Z = 4$ and $M = 842$, the calculated density was 2.12 Mg m^{-3} and $F(000) = 1600$. Data were collected by the ω–2θ scan technique to $2\theta_{max.} = 45°$, 1 304 reflections being observed $[I > 2\sigma(I)]$ out of a total of 1 720 unique reflections. The data were corrected for the usual effects as well as for absorption ($\mu = 3.69$ mm^{-1}) and extinction.

An initial structure solution was found using the MULTAN package.[57] This solution was in *Cc*, no solution being found in *C*2/*c*. Refinement by Fourier, difference Fourier, and least-squares techniques $\{$minimising $\Sigma w(\Delta F)^2$ with $w = 1/[\sigma(F)^2 + k(F)^2]$ with σ based on counting statistics$\}$ proceeded smoothly to $R = 0.032$.* However, inspection of the resulting structure revealed considerable distortion in the η-C_5H_5 rings and wide variations in apparently equivalent bond distances and angles. Hence the structure was re-refined in *C*2/*c*, which not only gave very good agreement between equivalent bond distances and angles but also produced a lower *R* value (0.030). Final refinement with all atoms except H having anisotropic thermal parameters gave $R\ [=(\Sigma\Delta|F|/\Sigma|F|] = 0.030$ and $R'\ \{=[\Sigma w(\Delta F)^2/\Sigma wF^2]^{\frac{1}{2}}\} = 0.052$ for 195 variables. The maximum residual intensity was 0.67 e Å^{-3}, approximately halfway along the V–I vector, the minimum -0.32 e Å^{-3}. Scattering factors were taken from ref. 58 and were corrected for both the real and the imaginary parts of the anomalous dispersion. The positional parameters of the non-hydrogen atoms are given in Table 4, the important derived bond distances and angles in Tables 1 and 2.

Acknowledgements

The exploratory experiments for this work were carried out by F. B. during the tenure of an Alexander von Humboldt Fellowship with Professor H. H. Brintzinger at the Universität Konstanz, Federal Republic of Germany. We thank the Natural Sciences and Engineering Research Council of Canada and the University of New Brunswick Research Fund for financial support, Tracy V. Bell, David I. McGee, Carolyn J. Jones, and Germaine C. Pataki for the preparation of starting materials, Rod McGregor and Professor Colin Mailer for assistance with the e.s.r. spectra, and Walter Brereton for technical assistance with the vacuum lines.

References

1 F. Bottomley and H. H. Brintzinger, *J. Chem. Soc., Chem. Commun.*, 1978, 234.
2 F. Bottomley and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 1981, 271.
3 E. O. Fischer, R. J. J. Schneider, and J. Müller, *J. Organomet. Chem.*, 1968, **14**, P4.
4 E. O. Fischer and R. J. J. Schneider, *Chem. Ber.*, 1970, **103**, 3684.
5 F. Näumann and D. Rehder, *J. Organomet. Chem.*, 1981, **204**, 411.
6 M. Herberhold, R. Klein, and P. D. Smith, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 220.
7 M. Herberhold, W. Kremnitz, H. Trampisch, R. B. Hitam, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 1261.
8 M. Herberhold and H. Trampisch, *Z. Naturforsch., Teil B*, 1982, **37**, 614.
9 W. Beck, H. G. Fick, K. Lottes, and K. H. Schmidtner, *Z. Anorg. Allg. Chem.*, 1975, **415**, 97; M. Herberhold and H. Trampisch, *Inorg. Chim. Acta*, 1983, **70**, 143.
10 S. Jagner and N-G. Vannerberg, *Acta Chem. Scand.*, 1970, **24**, 1988; *Chem. Scr.*, 1974, **6**, 19.
11 A. Müller, P. Werle, E. Diemann, and P. J. Aymonino, *Chem. Ber.*, 1972, **105**, 2419.
12 M. G. B. Drew and C. F. Pygall, *Acta Crystallogr., Sect. B*, 1977, **33**, 2838.
13 S. Jagner and E. Ljungström, *Acta Crystallogr., Sect. B*, 1978, **34**, 653.
14 R. Srivastava and S. Sarkar, *Transition Met. Chem.*, 1980, **5**, 122.
15 U. Quilitzsch and K. Wieghardt, *Z. Naturforsch., Teil B*, 1979, **34**, 640.
16 K. L. Fjare and J. E. Ellis, *J. Am. Chem. Soc.*, 1983, **105**, 2303.
17 F. Näumann and D. Rehder, *J. Organomet. Chem.*, 1982, **232**, 219.
18 K. Wieghardt, U. Quilitzsch, B. Nuber, and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 351.
19 K. Wieghardt and U. Quilitzsch, *Z. Anorg. Allg. Chem.*, 1979, **457**, 75.
20 K. Wieghardt and U. Quilitzsch, *Z Naturforsch., Teil B*, 1981, **36**, 683.
21 A. R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 1888.
22 M. Moran and M. Gayoso, *Z. Naturforsch., Teil B*, 1981, **36**, 434.
23 F. Bottomley, J. Darkwa, and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1039.
24 F. Bottomley, J. Darkwa, and P. S. White, *Organometallics*, in the press.
25 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley-Interscience, Toronto, 1970.
26 B. N. Figgis and J. Lewis, in 'Modern Coordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience Inc., New York, 1960.
27 J. L. Atwood, K. E. Stone, H. G. Alt, D. C. Hrncir, and M. D. Rausch, *J. Organomet. Chem.*, 1977, **132**, 367.
28 J. L. Atwood, R. D. Rogers, W. E. Hunter, C. Floriani, G. Fachinetti, and A. Chiesi-Villa, *Inorg. Chem.*, 1980, **19**, 3812.
29 E. E. H. Otto and H. H. Brintzinger, *J. Organomet. Chem.*, 1978, **148**, 29.
30 E. E. H. Otto and H. H. Brintzinger, personal communication.
31 J. L. Petersen and L. Griffith, *Inorg. Chem.*, 1980, **19**, 1852.
32 B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 2610.
33 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.
34 C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.
35 M. W. Schoonover, E. C. Baker, and R. Eisenberg, *J. Am. Chem. Soc.*, 1979, **101**, 1880.
36 Y. S. Yu, R. A. Jacobson, and R. J. Angelici, *Inorg. Chem.*, 1982, **21**, 3106.
37 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
38 B. J. Morris-Sherwood, B. W. S. Kolthammer, and M. B. Hall, *Inorg. Chem.*, 1981, **20**, 2771.
39 R. Hoffmann, M. M-L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, 1974, **13**, 2666.
40 R. B. King, *Inorg. Chem.*, 1968, **7**, 90.
41 J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, 1969, **91**, 2528.

---

* The programs used were those of A. C. Larson and E. J. Gabe described in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Haze-Kamp, H. van Korningsfeld, and G. C. Bassi, Delft University Press, Delft, The Netherlands, 1978, p. 81. Also used was 'ORTEP-II, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations,' C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., 1976.

42 F. A. Cotton and G. A. Rusholme, *J. Am. Chem. Soc.*, 1972, **94**, 402.
43 G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer, *J. Organomet. Chem.*, 1978, **145**, 529.
44 L. G. Bell and H. H. Brintzinger, *J. Organomet. Chem.*, 1977, **135**, 173.
45 K. L. T. Wong and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1975, **97**, 5143.
46 F. Bottomley and J. Darkwa, *J. Chem. Soc., Dalton Trans.*, 1983, 399.
47 J. C. Lockhart, *Chem. Rev.*, 1965, **65**, 131.
48 J. Fuchs, S. Mahjour, and J. Pickardt, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 374.
49 H. T. Evans, *Perspect. Struct. Chem.*, 1971, **4**, 1.
50 K. Wieghardt, U. Quilitzsch, J. Weiss, and B. Nuber, *Inorg. Chem.*, 1980, **19**, 2514.
51 F. Bottomley, J. Darkwa, and P. S. White, unpublished work.
52 F. Pintchovski, S. Soled, and A. Wold, *Inorg. Chem.*, 1976, **15**, 330.
53 W. P. Griffith, *Coord. Chem. Rev.*, 1970, **5**, 459.
54 F. Bottomley, D. E. Paez, and P. S. White, *J. Am. Chem. Soc.*, 1982, **104**, 5651.
55 L. E. Manzer, *J. Organomet. Chem.*, 1976, **110**, 291.
56 H. J. de Liefde Meijer, M. J. Janssen, and J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 1961, **80**, 831.
57 P. Main, M. M. Woolfson, and G. Germain, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
58 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, England, 1974, vol. 4.

Received 5*th September* 1984; *Paper* 4/1535