Notes

Formation of Carbonato and Hydroxo Complexes of Vanadium(IV) on Reaction of Carbonylbis(η-pentamethylcyclopentadienyl)vanadium(II) with Dinitrogen Oxide

Frank Bottomley* and James Darkwa
Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

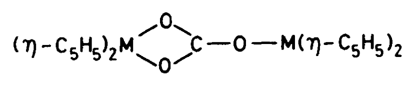
The reaction between $[V(\eta\text{-}C_5Me_5)_2(CO)]$ and N_2O in toluene at 20 °C gave a mixture of the vanadium(IV) carbonate $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$ and a polymer proposed to be $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$. The reaction is compared with analogous ones of $[V(\eta\text{-}C_5H_5)_2(CO)]$ and $[Ti(\eta\text{-}C_5R_5)_2(CO)_2]$ (R = H or Me).

The reactions between N_2O and $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$ or $[V(\eta\text{-}C_5H_5)_2(CO)]$ proceeded according to equations (1) and (2) respectively ($n = 1$ or 2).[1,2] The common feature of these

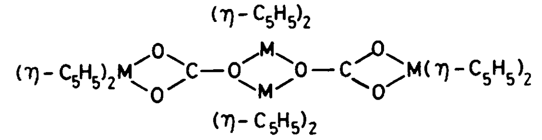
$$4[Ti(\eta\text{-}C_5H_5)_2(CO)_2] + 4N_2O \longrightarrow \tfrac{1}{n}[\{Ti(\eta\text{-}C_5H_5)_2\}_{2n}(CO_3)_n] + 4N_2 + 6CO \quad (1)$$

$$2[V(\eta\text{-}C_5H_5)_2(CO)] + 2N_2O \longrightarrow \tfrac{1}{2}[\{V(\eta\text{-}C_5H_5)_2\}_{2n}(CO_3)_n] + 2N_2 + CO \quad (2)$$

reactions was oxidation of the metal from the II to the III oxidation state with concomitant oxidation of CO to CO_3^{2-} The structures of the products were similar, (**I**) for $n = 1$ and



(**I**)



(**II**)

(**II**) for $n = 2$.[2,3] There was no reaction between $[Ti(\eta\text{-}C_5Me_5)_2(CO)_2]$, $[Zr(\eta\text{-}C_5Me_5)_2(CO)_2]$, or $[V(\eta\text{-}C_5H_5)_2(CO)_2]^+$ and N_2O; with $[Zr(\eta\text{-}C_5H_5)_2(CO)_2]$ only ZrO_2 was obtained.[2,4]

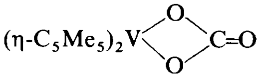
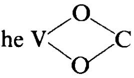
In order to extend these reactions and to find, if possible, a pattern which would allow a mechanism to be suggested for them, we investigated the reaction between $[V(\eta\text{-}C_5Me_5)_2(CO)]$ and N_2O. The results, which are reported here, were unexpected; the oxidation took a completely different course from that of reactions (1) and (2).

Results and Discussion

Two products containing vanadium were obtained from the reaction between $[V(\eta\text{-}C_5Me_5)_2(CO)]$ and N_2O, which was conducted in toluene at room temperature. The first product was green $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$, obtained in 70% yield based on N_2O. This complex was insoluble in toluene but soluble in tetrahydrofuran. The second product was purple $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$, obtained in 17% yield based on N_2O. This product was insoluble in all common solvents. The only gaseous product of the reaction was N_2, neither CO, H_2, nor CH_4 being observed. The reaction between $[V(\eta\text{-}C_5Me_5)_2(CO)]$ and O_2 also gave a mixture of $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$ and $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$.

Formation of $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$.—Since no CO was evolved, the reaction forming $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$ can be represented by equation (3). The magnetic, analytical, and

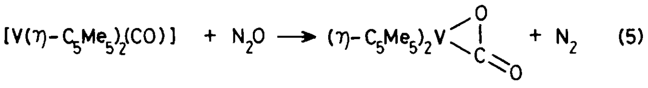
$$[V(\eta\text{-}C_5Me_5)_2(CO)] + 2N_2O \longrightarrow [V(\eta\text{-}C_5Me_5)_2(CO_3)] + 2N_2 \quad (3)$$

spectroscopic properties of the product of the reaction prove that it was the V^{IV}, d^1, carbonato complex, $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$, and not the expected V^{III}, d^2, complex $[\{V(\eta\text{-}C_5Me_5)_2\}_2(CO_3)]$ or one of its oligomers. The i.r. spectrum $[\nu_1(CO_3)^5$ at 1 660 cm^{-1}] and the e.s.r. spectrum (eight lines, $g = 1.995$, $A_{iso} = 32.05$ G) suggest that the CO_3^{2-} ligand is acting as a bidentate ligand and the complex has the structure . The low value of A_{iso} indicates delocalisation of the unpaired electron onto the CO_3^{2-} ligand (values of 60—75 G are found when the electron is localised on vanadium[6]). This could be accomplished by π overlap of the $1a_1$ orbital on the $V(\eta\text{-}C_5Me_5)_2$ unit[7] with filled sp^2 hybrid orbitals on the donor oxygen atoms, all these orbitals being in the plane of the  ring.

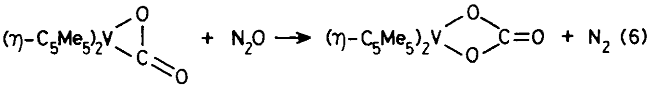
The yield of $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$ was much too high for it to have been formed by the simple oxidation of $[\{V(\eta\text{-}C_5Me_5)_2\}_2(CO_3)]$ by N_2O according to equation (4). Further

$$[\{V(\eta\text{-}C_5Me_5)_2\}_2(CO_3)] + N_2O \longrightarrow [V(\eta\text{-}C_5Me_5)_2(CO_3)] + \text{'}VO(\eta\text{-}C_5Me_5)_2\text{'} + N_2 \quad (4)$$

evidence on this possibility is provided by the properties of $[\{M(\eta\text{-}C_5H_5)_2\}_{2n}(CO_3)_n]$ (M = Ti or V; $n = 1$ or 2), which on oxidation by N_2O (excess) lost CO_2 giving intractable polymeric oxides. The V^{IV} carbonate must be formed directly from $[V(\eta\text{-}C_5Me_5)_2(CO)]$ by a different mechanism to that which formed $[\{V(\eta\text{-}C_5H_5)_2\}_2(CO_3)]$. We have suggested previously that the carbonate-bridged compounds $[\{M(\eta\text{-}C_5H_5)_2\}_2(CO_3)]$ were formed *via* oxo-bridged compounds such as $[\{Ti(\eta\text{-}C_5H_5)_2\}_2(\mu\text{-}O)]$.[1,8] In the case of $[V(\eta\text{-}C_5Me_5)_2(CO)]$, the steric bulk of the $\eta\text{-}C_5Me_5$ ligand would prevent such a dimer from being formed (the covalent radius of vanadium is 0.4 Å less than that of samarium for which $[\{Sm(\eta\text{-}C_5Me_5)_2\}_2(\mu\text{-}O)]$ is known[9]). The most reasonable route from $[V(\eta\text{-}C_5Me_5)_2(CO)]$ to $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$ is a direct double insertion of oxygen, equations (5) and (6). Initial co-ordination of N_2O to V is unlikely because of the lack of an available orbital on the 17-electron $[V(\eta\text{-}C_5Me_5)_2(CO)]$ complex.



(5)



(6)

Formation of $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$.—The second product of the reaction between $[V(\eta\text{-}C_5Me_5)_2(CO)]$ and N_2O was a purple compound which was insoluble in all common solvents. The most remarkable characteristic of this compound was an intense absorption band centred at 3 410 cm^{-1}, accompanied by bands of medium intensity centred at 1 565 and 918 cm^{-1} in the i.r. spectrum. The band at 3 410 cm^{-1} can only be assigned to ν(O–H). The possibility that the OH arose from extraneous water must be rejected. The reaction was repeatable, with low but constant yields of the purple product, and the same results were found when the most rigorous precautions were taken to exclude air or water. Microanalyses gave a C_5Me_5:V:O ratio of *ca.* 1:1:2, and the mass spectrum clearly indicated the presence of the tetrameric units $[V(\eta\text{-}C_5Me_5)O_2]_4$; a formulation which is in agreement with the results is the vanadium(IV) tetramer, $[\{V(\eta\text{-}C_5Me_5)(OH)(\mu\text{-}O)\}_4]$. This would be the hydroxo analogue of the planar cyclic tetramer $[\{V(\eta\text{-}C_5Me_5)Cl(\mu\text{-}O)\}_4]$,[8] and the related but non-planar $[\{Ti(\eta\text{-}C_5H_5)Cl(\mu\text{-}O)\}_4]$.[9,10] However such a tetramer would be expected to be soluble in toluene, whereas the purple compound was completely insoluble. We propose that the compound is a polymer formed by linking the tetramers together *via* oxo bridges; the limiting formula would then be $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$. The overall yield of the hydroxo complex is low, so that the CO which must be evolved from $[V(\eta\text{-}C_5Me_5)_2(CO)]$ during its formation would not be detected.

The formation of a hydroxo complex from $[V(\eta\text{-}C_5Me_5)_2(CO)]$ and N_2O is very surprising. It is believed that the proton derives from the $\eta\text{-}C_5Me_5$ ligand and the oxygen from N_2O. A precedent for the loss of a proton from a $\eta\text{-}C_5Me_5$ ligand is the formation of $[\{Ti(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}\sigma\text{:}\eta^5\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2]$ on reaction of $[Ti(\eta\text{-}C_5Me_5)_2]$ with N_2O.[11,12] We have also observed an hydroxo complex on reaction of $[Zr(\eta\text{-}C_5Me_5)_2(CO)_2]$ with NO.[13]

Experimental

All operations were conducted under rigorously air- and water-free conditions, under argon or in vacuum. The starting material $[V(\eta\text{-}C_5Me_5)_2(CO)]$ was prepared by the literature method.[14] Instruments used were a Perkin-Elmer 683 i.r. spectrometer (spectra being measured as Nujol or Fluorolube mulls between KBr plates) and a locally modified version of the Varian E-4 e.s.r. spectrometer. Microanalyses were by Beller Laboratorium, Göttingen, West Germany.

Reaction of $[V(\eta\text{-}C_5Me_5)_2(CO)]$ *with* N_2O*: Formation of* $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$ *and* $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$.—A solution of $[V(\eta\text{-}C_5Me_5)_2(CO)]$ (0.38 g, 1.09 mmol) in toluene (35 cm^3) was incubated with N_2O (1.05 mmol) for 72 h at room temperature. The green-brown solution gradually turned dark green and a very dark green solid was precipitated. The solid was collected by filtration and then extracted with tetrahydrofuran (30 cm^3). Dark purple $[\{[\{V(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_4(OH)_2](\mu\text{-}O)\}_n]$ was collected by filtration, washed with tetrahydrofuran, and dried under vacuum. Yield: 0.09 g, 17% (based on N_2O) (Found: C, 54.1; H, 7.3; V, 23.4. Calc. for $C_{40}H_{62}O_7V_4$: C, 55.9; H, 7.3; V, 23.7%). Infrared: 3 410s [ν(O–H)], 1 565m [ν(C=C)], and 918m cm^{-1} [δ(VOH) and/or ν(V–O)].

The volume of the filtrate was reduced to 15 cm^3 and diethyl ether (15 cm^3) added to precipitate light-green $[V(\eta\text{-}C_5Me_5)_2(CO_3)]$. This was collected by filtration and dried in vacuum. Yield: 0.14 g, 70% (based on N_2O) (Found: C, 66.2; H, 7.9. Calc. for $C_{21}H_{30}O_3V$: C, 66.1; H, 7.9%). Infrared: 1 660s, 1 640s, and 1 605s cm^{-1} [ν(C–O)]. Magnetic moment 1.67 B.M. (B.M. $\approx 9.274 \times 10^{-24}$ J T^{-1}) at 20 °C (by the Faraday method). E.s.r.: eight sharp lines centred at $g = 1.995$, $A_{iso} = 32.05$ G (G = 10^{-4} T). Molecular weight (osmometric in tetrahydrofuran): found 406; calc. 381.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

References

1 F. Bottomley, I. J. B. Lin, and M. Mukaida, *J. Am. Chem. Soc.*, 1980, **102**, 5238.
2 F. Bottomley and J. Darkwa, *J. Chem. Soc., Dalton Trans.*, 1983, 399.
3 G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 1767.
4 F. Bottomley, D. F. Drummond, G. O. Egharevba, and P. S. White, *Organometallics*, 1986, **5**, 1620.
5 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley-Interscience, Toronto, 1970, p. 171.
6 E. G. Müller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.*, 1976, **111**, 73; G. Doyle and R. S. Tobias, *Inorg. Chem.*, 1968, **7**, 2479.
7 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
8 F. Bottomley, J. Darkwa, L. Sutin, and P. S. White, *Organometallics*, 1986, **5**, 2165.
9 J. L. Petersen, *Inorg. Chem.*, 1980, **19**, 181.
10 A. C. Skapski and P. G. H. Troughton, *Acta Crystallogr., Sect. B*, 1970, **26**, 716.
11 F. Bottomley, I. J. B. Lin, and P. S. White, *J. Am. Chem. Soc.*, 1981, **103**, 703.
12 F. Bottomley, G. O. Egharevba, I. J. B. Lin, and P. S. White, *Organometallics*, 1985, **3**, 550.
13 F. Bottomley and G. O. Egharevba, unpublished work; G. O. Egharevba, Ph.D. Thesis, University of New Brunswick, 1986.
14 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1984, **23**, 1739.

Received 14*th August* 1987; *Paper* 7/1500