sufficiently great to affect the d^{10} electrons in the metal atoms.

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Structure of Dicyclopentadienylpentacarbonyldivanadium. A New Example of Grossly Unsymmetrical Carbonyl Bridging

Sir:

The molecule $(C_5H_5)_2V_2(CO)_5$[1] initially attracted our interest in connection with our studies of intramolecular carbonyl scrambling in metal carbonyls.[2-4] However, assigning a satisfactory molecular structure constituted a problem in itself. Structures had been suggested[1] but we were not satisfied that they were consistent with the reported ir spectrum (five CO stretching bands). Moreover, structures with four terminal CO groups and one bridging CO group appeared likely to incorporate also some unusual features such as 16-electron configurations for the V atoms or a triple bond between the V atoms. X-Ray study of this molecule thus promised to be of more than routine interest. The results fulfill that promise but in a remarkable and unanticipated way.

Crystals grown from methylcyclohexane at −20° belong to space group $P2_1/n$ with a = 8.246 (2) Å, b = 15.769 (5) Å, c = 11.729 (2) Å, β = 91.66 (2)°, and Z = 4. A conventional procedure employing Patterson and electron density functions and least-squares refinement, using 1149 reflections with intensities exceeding 3σ, in the range $0 < 2\theta \leqslant 43°$ (Mo Kα) led to the present agreement indices of R_1 = 0.044 and R_2 = 0.050. Hydrogen atoms were included but not refined; all other atoms were refined anisotropically.

The structure is shown in Figure 1. Other dimensions are 1.40 Å for the average ring C–C bond; 2.22 (1) and 2.26 (1) Å for the mean distances of V(1) and V(2) to ring carbon atoms and 1.93 (1) Å for the V(2)–C(12) distance. Each vanadium atom is bonded to one h^5-C_5H_5 ring and to one or two ordinary terminal CO groups.[5]

The remaining two CO groups have an anomalous relationship to the two vanadium atoms. The V(1)–C(14)–O(4) and V(1)–C(15)–O(5) chains are nearly, but not exactly linear (angles of 169°), the V(1)–C(14) and V(1)–C(15) bonds are somewhat shorter than the other V–CO bonds, and the C(14)–V(2) and C(15)–V(2) distances, 2.40 and 2.44 Å, respectively, are too short to be regarded as mere nonbonded contacts.

There does not appear to be any straightforward way to specify the electronic structure of this molecule. For V(1), the V atom itself, the h^5-C_5H_5 group, and the three CO groups contribute a total of 16 electrons to the valence shell orbitals of the metal atom. For V(2), the V atom itself, the h^5-C_5H_5 group, and the two CO groups contribute a total of 14 electrons. It is clear that there are three important interactions between these two [$C_5H_5V(1)(CO)_3$ and $C_5H_5V(2)(CO)_2$] parts of the molecule. There is obviously a metal–metal bond; however, the order of this bond is uncertain. It seems to us that the V(1)–V(2) distance is shorter than would be expected for a simple single bond but also too long to be a full triple bond. It exceeds the recently reported length (2.22 Å) of an Fe–Fe double bond,[6a] as well as that (2.28 Å) of a Cr–Cr triple bond,[6b] but this may be due mainly to the greater intrinsic size of the vanadium atoms. The second and third interactions are between V(2) and the carbonyl groups C(14)–O(4) and C(15)–O(5): these are doubtless weak, but the C–V distances involved leave no doubt that they are real, bonding interactions. In short, C(14)–O(4) and C(15)–O(5) are not simply terminal CO groups, but are grossly unsymmetrical bridging carbonyl groups.

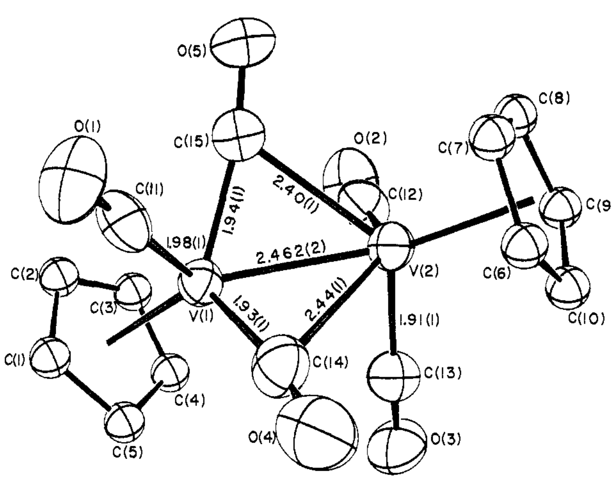

Figure 1. A view of the $(C_5H_5)_2V_2(CO)_5$ molecule, showing some important bond lengths and bond angles. Thermal parameters for the cyclopentadienyl carbon atoms have been arbitrarily reduced for clarity. See text for other important distances.

Grossly unsymmetrical carbonyl bridges are relatively rare but have been observed in at least ten compounds[7] before, the first such observation having been in the $Fe_4(CO)_{13}^{2-}$ ion[8] and the most recent in $H_2Ru_4(CO)_{13}$.[9] The exact nature and function of such bridges are not clear. The present compound displays them under relatively uncomplicated circumstances, and may thus help to increase our understanding of these points. Detailed discussion must be reserved for a later paper, however.

Only slightly unsymmetrical CO bridges have been observed in other molecules, *e.g.*, in both $Fe_3(CO)_{11}PPh_3$ isomers.[10] Markedly unsymmetrical NO bridges have also been observed in $(h^5$-$C_5H_5)_2Mn_2(NO)_3NO_2$.[11]

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(4) R. D. Adams and F. A. Cotton, *ibid.*, **94**, 619 (1972).

(5) The $(C_5H_5)V$ and VCO dimensions are quite comparable to those in $(h^5$-$C_5H_5)V(CO)_4$, as reported by J. B. Wilford, A. Whitla, and H. M. Powell, *J. Organometal. Chem.*, **8**, 495 (1967).

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(7) We are grateful to R. J. Doedens for a bibliography.

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Only one accurate study of bridging isocyanide groups has been reported, *i.e.*, for $[(h^5\text{-}C_5H_5)Ni(CNCH_3)]_2$, and only a very slight asymmetry was observed.[12]

The structure affords a good basis for understanding the complex reactivity patterns[1] of the compound with phosphines and other donors. It also can account for the infrared spectrum of $(C_5H_5)_2V_2(CO)_5$ and *mutatis mutandis* of the $(C_5H_5)_2V_2(CO)_4L$ derivatives if C(11)-O(1) is assumed to be replaced by L.

Finally, this structure is significant with respect to carbonyl scrambling processes since these presumably occur and account for the appearance of only one cyclopentadienyl proton resonance at 25°. Of particular interest is the likelihood that the orientation and bonding of each of the grossly unsymmetrical CO bridges resembles the transition configuration for a CO group as it passes back and forth from bridge to terminal positions in molecules such as $(C_5H_5)_2Fe_2(CO)_4$.[13]

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Reaction between Azide and Nitronium Ions. Formation and Decomposition of Nitryl Azide

Sir:

Although a significant effort has been associated with studies of the preparation and decomposition of nitrosyl azide (N_4O),[1] there has been no report of any attempt to prepare or examine the decomposition of the analogous nitryl azide (N_4O_2). By analogy to nitrosyl azide, which decomposes at temperatures as low as −50° to nitrogen and nitrous oxide,[1h] nitryl azide might also be expected to be unstable and exhibit the loss of nitrogen. We wish to report that nitryl azide can be directly prepared from nitronium and azide salts in organic solvents, is significantly more stable than nitrosyl azide, and decomposes solely to nitrous oxide.

When an equimolar amount (2.2 mmol) of nitronium tetrafluoroborate[2] in anhydrous acetonitrile (10 ml) is added to a stirred solution of lithium azide in the same solvent (160 ml) at temperatures below −10°, no apparent change is observed. When the solution is warmed above 0°, however, 4.4 mmol (2.0 equiv based on the amount of $NO_2^+BF_4^-$ used) of a colorless gas is rapidly evolved. Similar results are observed with sodium and potassium azides[3] and when carbon tetrachloride or chloroform is used as the solvent.[4] Spectrometric analyses of the acetonitrile and carbon tetrachloride solutions immediately after the nitronium and azide salts are added and mixed gives good evidence for the existence of nitryl azide.

The ir spectra of solutions obtained from the reaction between $NO_2^+BF_4^-$ and LiN_3 in both carbon tetrachloride and acetonitrile exhibit absorptions, given in Table I, that are consistent with the nitryl azide formulation. The band at 1609 (1602) cm^{-1} is consistent with the asymmetric stretching vibration of the nitro group.[5] The asymmetric stretching vibration of the azido group is commonly found between 2080 and 2200 cm^{-1};[6] however, the multiplicity of bands observed in this region does not permit this assignment to any single absorption given in Table I. Ir samples were filtered solutions obtained after mixing LiN_3 and $NO_2^+BF_4^-$ in the appropriate solvent. No attempt was made to examine the spectra at frequencies less than 1400 cm^{-1}. Each absorption assigned to nitryl azide was observed to decrease in intensity with time as the solution was warmed. Other absorptions, also observed, were assignable to dinitrogen tetroxide,[7] dinitrogen pentoxide,[7] or nitrous oxide based on the spectra of authentic samples (Table I); with the exception of those due to N_2O, these absorptions did not change in intensity with time as the solution was warmed. No absorption assignable to hydrazoic acid or nitric acid was observed.

Table I. Ir Absorption Frequencies of the Nitronium–Azide Reaction Product and of Related Compounds[a]

Bands assigned to N_4O_2,[b] cm^{-1} in CCl_4	in CH_3CN	Related compounds, cm^{-1}
2330 (m)	*c*	$NO_2^+BF_4^-$; 2360 (Nujol)[d]
2185 (s)	2190 (s, b)	LiN_3; 2100 (KBr)
2165 (s)		HN_3; 2140 (CCl_4)
2070 (m)	2090 (m)	N_2O_5; 1680 (CCl_4), 1660 (CH_3CN)
1609 (s)	1602 (s)	N_2O_4; 1810 (CCl_4), 1850 (CH_3CN)

[a] Spectra were taken on a Perkin-Elmer Model 621 recording spectrophotometer using, except when noted otherwise, NaCl salt plates. Frequencies from 4000 to 1400 cm^{-1} were recorded. Nitryl chloride was not observed in any spectrum. [b] Bands exhibiting greater than 20% transmission are reported; s = strong, m = medium, b = broad. [c] Band obscured by solvent absorption. [d] AgCl plates were used; spectrum was identical with that previously obtained: D. Cook, S. J. Kuhn, and G. A. Olah, *J. Chem. Phys.*, **33**, 1669 (1960).

The ir spectra obtained exhibit absorptions at 2330 and 2070 (2090) cm^{-1} which are approximately those frequencies that would be expected for NO_2^+ and N_3^-, respectively. For spectra in acetonitrile the assignment of these bands to solvated nitronium and azide ions must be considered, since both $NO_2^+BF_4^-$ and LiN_3 are soluble in this solvent. However, similar spectra are observed in carbon tetrachloride in which neither $NO_2^+BF_4^-$ nor LiN_3 is soluble to any extent.[8] We must reasonably conclude that the absorptions given in Table I are due to covalently bound nitryl azide, and that this

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(1) (a) H. Thiele, *Ber.*, **41**, 2681 (1908); (b) F. Sommer, *ibid.*, **48**, 1884 (1915); (c) T. Werner, *Proc. Roy. Soc., London*, **28**, 257 (1911); (d) E. Oliveri-Mandala, *Gazz. Chim. Ital.*, **51**, 101 (1922); (e) F. Seel, R. Wölfe, and G. Zwarg, *Z. Naturforsch. B*, **13**, 136 (1958), and preceding papers; (f) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers; (g) K. Clusius and H. Knopf, *Chem. Ber.*, **89**, 681 (1956); (h) H. W. Lucien, *J. Amer. Chem. Soc.*, **80**, 4458 (1958).

(2) Obtained from Ozark-Mahoning Co. and purified prior to use.

(3) These salts are much less soluble in acetonitrile; although the same number of equivalents of gas is produced, gas evolution is slower than with lithium azide under similar conditions.

(4) The nitronium and azide salts are insoluble in these solvents. However, nitryl azide is readily detectable in the filtered solutions.

(5) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); B. G. Gowenlock and W. Lüttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1958).

(6) E. Lieber, C. N. R. Rao, A. E. Thomas, E. Oftedahl, R. Minnis, and C. V. N. Nambury, *Spectrochim. Acta*, **19**, 1135 (1963); D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1258 (1955).

(7) The amounts of these compounds were variable in different solutions and, when present, were due to the reaction of $NO_2^+BF_4^-$ with traces of water.

(8) Evaporation of carbon tetrachloride solutions that were used to obtain the ir spectra summarized in Table I left no residue.