DI(η^5-CYCLOPENTADIENYL)PENTACARBONYLDIVANADIUM. A PROTOTYPAL EXAMPLE OF SEMIBRIDGING CARBONYL GROUPS *

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Summary

The crystal and molecular structures of the title compound have been determined; they provide an explanation of the unusual infrared spectrum, which is inconsistent with a symmetrical, singly-bridged structure. Instead it is found that there are three terminal CO groups of a completely conventional type and two which are intermediate between strictly terminal and strictly bridging. The (η^5-C$_5$H$_5$)V moieties are structurally normal. The V—V distance, 2.462(2) Å, is indicative of some multiple bond character. From the structure and infrared spectrum of the pentacarbonyl together with the infrared spectrum of the substitution product, (η^5-C$_5$H$_5$)$_2$V$_2$(CO)$_4$PPh$_3$, the position of the PPh$_3$ is predicted. The principal crystallographic data are: space group, $P2_1/n$; $a = 8.246(2)$, $b = 15.769(5)$, $c = 11.729(2)$ Å; $\beta = 91.66(2)°$; $Z = 4$. Using 1134 independent reflections with intensities greater than three times their esd's, the structure was refined to residuals of $R_1 = 0.044$ and $R_2 = 0.070$.

Introduction

The dark green compound, (η^5-C$_5$H$_5$)$_2$V$_2$(CO)$_5$, which is sensitive to oxygen, moisture, and temperature above about 45°C was first reported by E.O. Fischer and R.J.J. Schneider in 1967 [1] and described in more detail by them a few years later [2]. On the basis of physical and chemical data they suggested structures Ia or Ib and they also showed that a characteristic mode of reaction with donors such as phosphines and arsines, L, was to form monosubstituted products, (η^5-C$_5$H$_5$)$_2$V$_2$(CO)$_4$L.

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* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

(Ia)   (Ib)
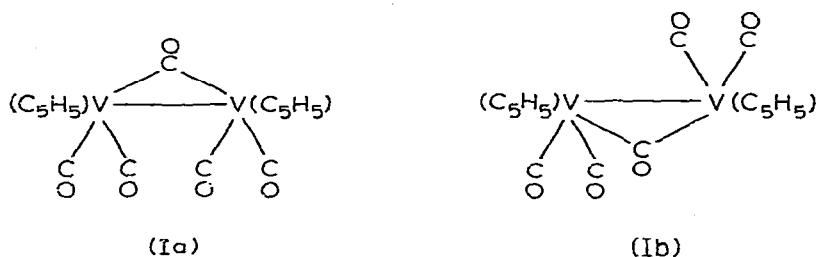
Our interest in studying this unusual compound began with a question about the possible intramolecular scrambling of terminal and bridging CO groups, but we immediately became dubious about whether the distribution of CO stretching frequencies in the infrared spectrum was satisfactorily explained by either of the suggested structures. It is, of course, true that these are very reasonable structures. Although they give only 16-electron configurations to the metal
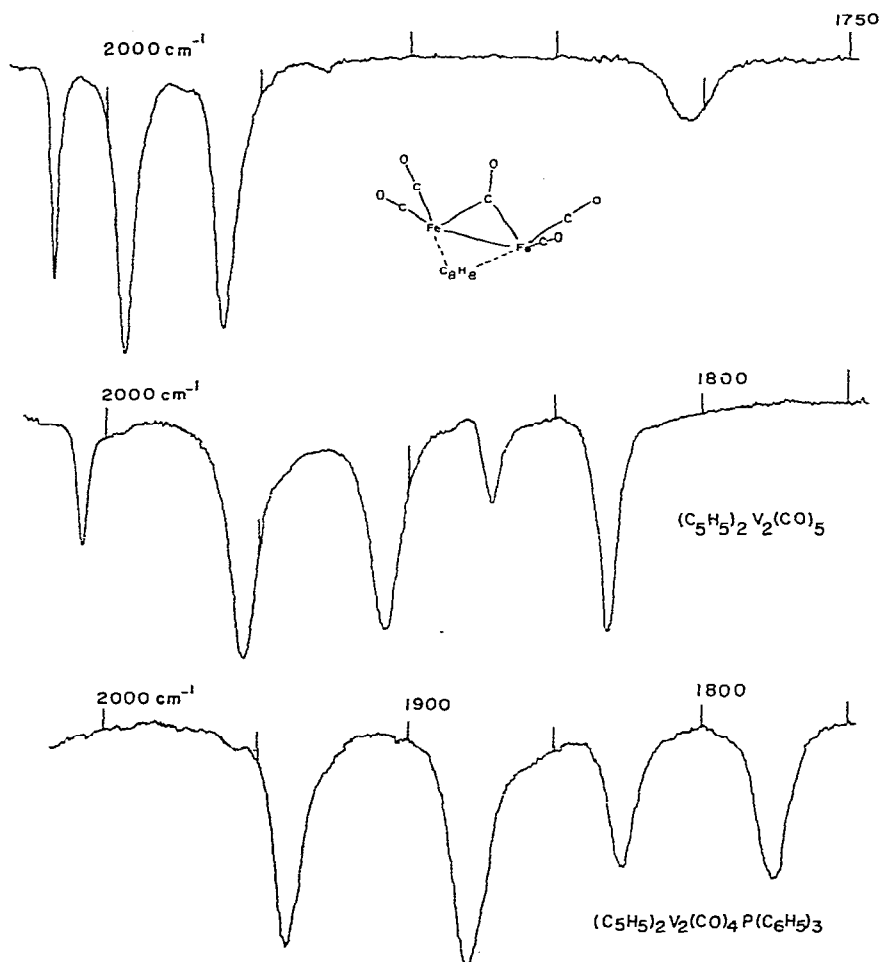

Fig. 1. Infrared spectra in the CO stretching region for $(C_8H_8)Fe_2(CO)_5$, $(C_5H_5)_2V_2(CO)_5$ and $(C_5H_5)_2V_2(CO)_4PPh_3$.

atoms this could be simply remedied, if necessary, by making the V—V bonds triple bonds. However, it seemed to us that they might have been expected to give rise to an IR spectrum with three or four bands well above 1900 cm^{-1} and one around 1800 cm^{-1} or below, as in the case of $C_8H_8Fe_2(CO)_5$ [4], Fig. 1. In fact, as shown also in Fig. 1, there are five rather evenly spaced bands from 2009 to 1832 cm^{-1}. An X-ray crystallographic investigation was considered to be the only certain way to resolve this seeming inconsistency.

Experimental

Both $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ and $(\eta^5\text{-}C_5H_5)_2V_2(CO)_4PPh_3$ were prepared by procedures essentially the same as those published by Fischer and Schneider [2]. During all preparative procedures and subsequent operations the compounds were kept in an atmosphere of nitrogen. Infrared spectra of mineral oil mulls were recorded on a Perkin—Elmer Model 451 infrared spectrometer. Crystals were grown from methylcyclohexane at —20°C.

Crystallographic procedures were those used routinely in this Laboratory and previously described in detail [4,5]. The compound crystallizes in the space group $P2_1/n$ with $a = 8.246(2)$, $b = 15.769(5)$, $c = 11.729(2)$ Å, $\beta = 91.66(2)°$ and $Z = 4$. The cell dimensions were determined by centering 15 intense reflections in the 2θ range 20—30°. No absorption correction was made since the crystal was nearly equidimensional. Data were collected with Mo-K_α radiation within a sphere in reciprocal space bounded by $2\theta = 43°$. Using 1134 reflections with intensities greater than 3σ the structure was solved using a conventional combination of Patterson functions, least squares refinements and electron density difference functions. Using a model in which hydrogen atoms were included but not refined and all others were refined anisotropically, refinement converged with residuals [5] of $R_1 = 0.044$ and $R_2 = 0.070$ *. The error in an observation of unit weight was 1.288 and the largest shift in any parameter in the last cycle of refinement was 0.46 times its esd.

Results and discussion

The atomic positional and thermal vibration parameters are listed in Table 1. The molecular structure is shown in Fig. 2, which also defines the atom numbering scheme used in all of the tables. The bond distances and bond angles are listed in Tables 2 and 3. The results reported here are essentially the same as those reported in our preliminary communication [6] but are more complete and more precise.

The positions of the cyclopentadienyl carbon atoms could not be accurately determined; nearly all of them have high thermal vibration amplitudes, and it is not impossible that there may be some partial disorder although we could

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* The table of structure factors has been deposited as NAPS Document No. 03297 (5 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a]

Atom	X	Y	Z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
V(1)	0.0285(2)	0.25713(10)	0.2149(1)	3.39(7)	3.83(7)	3.72(6)	-0.25(7)	0.31(6)	-0.23(6)
V(2)	-0.0859(2)	0.11291(9)	0.2143(1)	3.89(7)	3.45(6)	3.93(7)	0.06(7)	0.23(6)	-0.22(6)
O(1)	-0.0335(11)	0.3496(5)	0.4439(6)	10.3(5)	6.9(4)	5.5(3)	-1.5(4)	3.2(3)	-1.6(3)
O(2)	0.2395(10)	0.0489(4)	0.1260(7)	6.0(4)	6.1(4)	10.3(5)	1.2(3)	2.4(4)	-0.2(4)
O(3)	-0.1448(11)	0.1421(5)	-0.0419(6)	10.4(6)	7.8(4)	4.3(3)	-1.0(4)	-1.6(4)	-0.0(3)
O(4)	-0.3439(8)	0.2668(5)	0.2062(7)	3.5(3)	5.1(4)	13.3(6)	0.5(3)	0.2(4)	0.0(4)
O(5)	0.2005(11)	0.1455(5)	0.3978(6)	10.8(6)	8.1(4)	7.5(4)	0.2(5)	-4.6(4)	1.4(4)
C(1)	0.100(2)	0.3845(7)	0.1527(11)	14.6(7)	2.8(5)	17.7(8)	1.1(6)	13.1(5)	1.3(5)
C(2)	0.237(2)	0.3444(8)	0.1849(9)	10.2(6)	13.6(7)	4.6(5)	-9.7(5)	0.0(5)	0.4(5)
C(3)	0.252(1)	0.2797(8)	0.1189(11)	4.5(5)	8.5(7)	11.3(8)	2.0(6)	3.4(5)	3.0(6)
C(4)	0.138(2)	0.2777(8)	0.0467(8)	11.0(7)	11.0(7)	3.6(5)	-7.5(6)	1.5(5)	-2.1(5)
C(5)	0.034(1)	0.3401(10)	0.0640(11)	2.7(5)	20.6(9)	14.8(7)	-2.3(7)	-2.1(5)	14.0(6)
C(6)	-0.323(1)	0.0739(6)	0.2942(9)	5.5(6)	4.3(5)	8.4(6)	-0.5(5)	2.0(5)	0.0(5)
C(7)	-0.198(2)	0.0532(6)	0.3660(9)	7.8(7)	4.8(5)	5.3(5)	-0.1(5)	1.2(5)	0.7(4)
C(8)	-0.099(1)	-0.0072(7)	0.3178(10)	7.3(6)	4.7(5)	8.3(6)	1.4(6)	1.4(5)	3.1(4)
C(9)	-0.165(1)	-0.0240(6)	0.2078(9)	8.7(7)	4.3(4)	8.0(6)	-2.0(5)	3.6(5)	-0.7(5)
C(10)	-0.306(1)	0.0265(7)	0.1941(9)	5.7(6)	7.0(6)	6.7(6)	-2.9(5)	-0.5(1)	1.3(5)
C(11)	-0.013(1)	0.3153(6)	0.3595(8)	5.0(5)	4.7(5)	5.6(5)	-1.1(4)	1.4(4)	0.4(4)
C(12)	0.117(1)	0.0738(6)	0.1599(9)	5.2(5)	3.4(4)	6.7(5)	-0.2(4)	0.5(5)	0.5(4)
C(13)	-0.124(1)	0.1339(6)	0.0644(9)	5.9(6)	5.1(5)	5.5(5)	-0.1(5)	-0.9(5)	-0.1(4)
C(14)	-0.205(1)	0.2546(6)	0.2105(8)	5.3(4)	6.4(5)	-0.2(4)	0.2(5)	0.2(5)	-0.3(4)
C(15)	0.127(1)	0.1796(6)	0.3261(8)	6.1(6)	5.0(5)	5.0(5)	-0.2(6)	-1.1(5)	0.3(4)

[a] The form of the anisotropic thermal parameter is: $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE 2

TABLE OF BOND DISTANCES IN ÅNGSTROMS

V(1)—V(2)	2.462(2)	V(2)—C(8)	2.254(10)	O(5)—C(15)	1.155(11)
V(1)—C(1)	2.222(13)	V(2)—C(9)	2.255(10)	C(1)—C(2)	1.34(2)
V(1)—C(2)	2.238(12)	V(2)—C(10)	2.276(10)	C(1)—C(5)	1.35(3)
V(1)—C(3)	2.214(11)	V(2)—C(12)	1.911(12)	C(2)—C(3)	1.29(2)
V(1)—C(4)	2.218(11)	V(2)—C(13)	1.922(11)	C(3)—C(4)	1.24(2)
V(1)—C(5)	2.202(14)	V(2)—C(14)	2.440(10)	C(4)—C(5)	1.32(3)
V(1)—C(11)	1.967(11)	V(2)—C(15)	2.402(10)	C(6)—C(7)	1.352(15)
V(1)—C(14)	1.925(11)	O(1)—O(11)	1.144(10)	C(6)—C(10)	1.403(15)
V(1)—C(15)	1.947(11)	O(2)—C(12)	1.164(11)	C(7)—C(8)	1.382(15)
V(2)—C(6)	2.276(11)	O(3)—C(13)	1.144(10)	C(8)—C(9)	1.41(2)
V(2)—C(7)	2.235(10)	O(4)—O(14)	1.161(11)	C(9)—C(10)	1.416(15)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 3

TABLE OF BOND ANGLES IN DEGREES

V(2)—V(1)—C(1)	159.9(9)	C(11)—V(1)—C(15)	78.2(4)	C(9)—V(2)—O(13)	95.3(5)
V(2)—V(1)—C(2)	149.7(8)	C(14)—V(1)—C(15)	113.7(4)	C(9)—V(2)—C(14)	139.5(5)
V(2)—V(1)—C(3)	118.1(5)	V(1)—V(2)—C(6)	125.6(3)	C(9)—V(2)—C(15)	130.0(5)
V(2)—V(1)—C(4)	107.4(4)	V(1)—V(2)—C(7)	123.6(3)	C(10)—V(2)—C(12)	118.4(5)
V(2)—V(1)—C(5)	124.3(9)	V(1)—V(2)—C(8)	143.1(4)	C(10)—V(2)—C(13)	83.9(4)
V(2)—V(1)—C(11)	110.9(3)	V(1)—V(2)—C(9)	173.9(4)	C(10)—V(2)—C(14)	103.2(5)
V(2)—V(1)—C(14)	66.3(3)	V(1)—V(2)—C(10)	149.1(4)	C(10)—V(2)—C(15)	152.4(4)
V(2)—V(1)—C(15)	64.8(3)	V(1)—V(2)—C(12)	87.7(3)	C(12)—V(2)—C(13)	81.4(4)
C(1)—V(1)—C(2)	35.0(6)	V(1)—V(2)—C(13)	84.0(3)	C(12)—V(2)—C(14)	130.2(4)
C(1)—V(1)—C(3)	57.0(5)	V(1)—V(2)—C(14)	46.2(3)	C(12)—V(2)—C(15)	71.9(4)
C(1)—V(1)—C(4)	57.1(6)	V(1)—V(2)—C(15)	47.2(3)	C(13)—V(2)—C(14)	76.7(4)
C(1)—V(1)—C(5)	35.6(7)	C(6)—V(2)—C(7)	34.9(4)	C(13)—V(2)—C(15)	123.6(4)
C(1)—V(1)—C(11)	85.2(6)	C(6)—V(2)—C(8)	59.6(4)	C(14)—V(2)—C(15)	84.1(4)
C(1)—V(1)—C(14)	106.5(8)	C(6)—V(2)—C(9)	60.3(4)	V(1)—C(11)—O(1)	178.5(9)
C(1)—V(1)—C(15)	133.(1)	C(6)—V(2)—C(10)	35.9(4)	V(2)—C(12)—O(2)	178.9(9)
C(2)—V(1)—C(3)	33.6(5)	C(6)—V(2)—C(12)	145.2(4)	V(2)—C(13)—O(3)	176.4(9)
C(2)—V(1)—C(4)	55.6(4)	C(6)—V(2)—C(13)	109.3(5)	V(1)—C(14)—V(2)	67.5(3)
C(2)—V(1)—C(5)	58.3(5)	C(6)—V(2)—C(14)	84.6(4)	V(1)—C(14)—O(4)	169.2(9)
C(2)—V(1)—C(11)	90.1(6)	C(6)—V(2)—C(15)	121.1(5)	V(2)—C(14)—O(4)	123.2(8)
C(2)—V(1)—C(14)	141.4(8)	C(7)—V(2)—C(8)	35.8(4)	V(1)—C(15)—V(2)	68.0(3)
C(2)—V(1)—C(15)	100.6(6)	C(7)—V(2)—C(9)	59.9(4)	V(1)—C(15)—O(5)	168.4(9)
C(3)—V(1)—C(4)	32.6(5)	C(7)—V(2)—C(10)	59.0(4)	V(2)—C(15)—O(5)	123.7(8)
C(3)—V(1)—C(5)	57.2(5)	C(7)—V(2)—C(12)	121.0(5)	C(2)—C(1)—C(5)	107.(2)
C(3)—V(1)—C(11)	122.1(8)	C(7)—V(2)—C(13)	142.2(5)	C(1)—C(2)—C(3)	107.0(2)
C(3)—V(1)—C(14)	146.6(6)	C(7)—V(2)—C(14)	103.0(4)	C(2)—C(3)—C(4)	110.0(2)
C(3)—V(1)—C(15)	96.0(5)	C(7)—V(2)—C(15)	93.5(4)	C(3)—C(4)—C(5)	111.0(2)
C(4)—V(1)—C(5)	34.8(7)	C(8)—V(2)—C(9)	36.4(4)	C(1)—C(5)—C(4)	105.0(1)
C(4)—V(1)—C(11)	141.6(5)	C(8)—V(2)—C(10)	60.1(4)	C(7)—C(6)—C(10)	107.0(1)
C(4)—V(1)—C(14)	114.3(7)	C(8)—V(2)—C(12)	88.1(4)	C(6)—C(7)—C(8)	111.0(1)
C(4)—V(1)—C(15)	121.0(8)	C(8)—V(2)—C(13)	131.4(5)	C(7)—C(8)—C(9)	107.0(1)
C(5)—V(1)—C(11)	115.0(1)	C(8)—V(2)—C(14)	138.8(4)	C(8)—C(9)—C(10)	107.0(1)
C(5)—V(1)—C(14)	92.1(5)	C(8)—V(2)—C(15)	96.9(4)	C(6)—C(10)—C(9)	108.0(1)
C(5)—V(1)—C(15)	153.2(6)	C(9)—V(2)—C(10)	36.4(4)		
C(11)—V(1)—C(14)	80.5(4)	C(9)—V(2)—C(12)	86.2(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
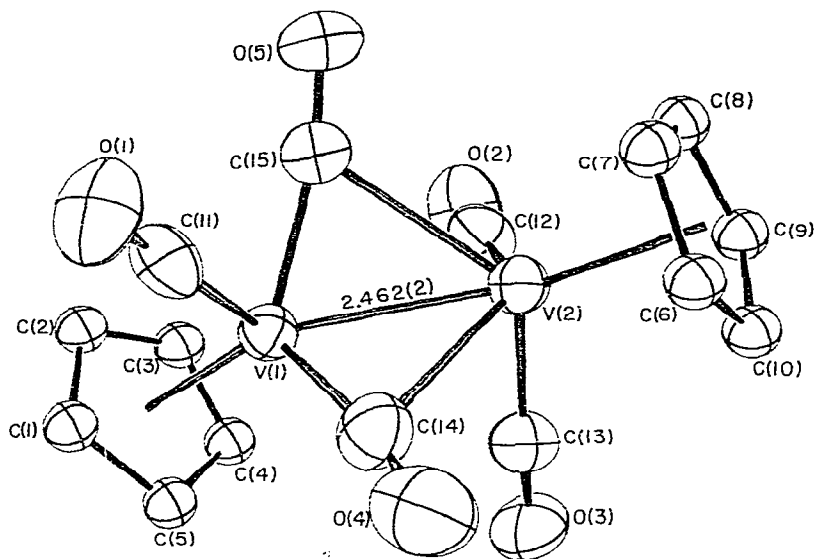
Fig. 2. A view of the $(C_5H_5)_2V_2(CO)_5$ molecule prepared with the program ORTEP. The atom numbering scheme is defined. The cyclopentadienyl carbon atoms are represented by arbitratily small spheres for the sake of clarity. The other atoms are represented by ellipsoids of thermal vibration scaled to enclose 50% of their electron density.

find no results to justify any attempt to refine such a disordered model. It may be recalled that for $(\eta^5\text{-}C_5H_5)V(CO)_4$ considerable disorder was found [7], and that this is not uncommon for $\eta^5\text{-}C_5H_5$ groups generally. Within the limited accuracy of this and other structures [7,8] containing $(\eta^5\text{-}C_5H_5)V$ units, the mean V—C distance here, 2.24(3) Å, is in good agreement with those found elsewhere, typically ~2.25 Å.

The V—V distance clearly implies the existence of a direct metal—metal bond, but there is no objective way to assign it a bond order. We suggest the following approach to explaining the molecular and electronic structure of this molecule. First let us think of it as a combination of a $(\eta^5\text{-}C_5H_5)V(CO)_3$ and a $(\eta^5\text{-}C_5H_5)V(CO)_2$ group. The former has a 16-electron configuration and the latter a 14-electron configuration. The former may use an electron pair to form a donor, V→V, bond, thus affording each V atom a 16-electron configuration. In the early transition groups 16-electron configurations are often entirely stable, as in $(C_5H_5)_2TiX_2$ and $(C_5H_5)_2VCl$, and this single bond may well constitute essentially all of the V—V bonding in this compound. It is also possible that some additional sharing of electrons may occur thus raising the bond order somewhat. A distance of 2.46 Å is not inconsistent with an essentially single bond but there is little data for direct comparison since the only other V—V bond characterized is the presumably triple one (2.200(2) Å) in $V_2(2,6\text{-dimethoxyphenyl})_4$ [5].

The curious posture of two of the CO groups, for which the designation *semi-bridging* has been proposed and widely used, C(14)—O(4) and C(15)—O(5), which have V—C—O angles of 169.2(9) and 168.4(9)° and C—V(2) distances of 2.44(1) Å and 2.40(1) Å, respectively, can now be explained. Assuming that the V—V bond is essentially single and very polar, it may be proposed that there

is donation of excess electron density on V(2) into the π^* orbitals, especially the carbon atom components thereof, on these two CO groups. This may be represented as follows:

$$(\eta^5\text{-}C_5H_5)(OC)V\underset{\underset{O}{C}}{\overset{\overset{O}{C}}{\rule{3cm}{0.4pt}}}V(CO)_2(\eta^5\text{-}C_5H_5)$$
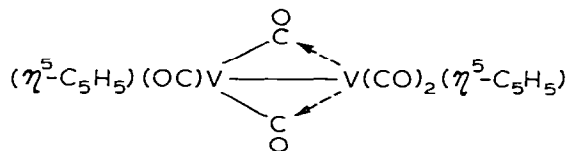
Semibridging CO groups, which may occur for electronic reasons, as in this case, or for purely steric ones [9], have been widely discussed [10] since our preliminary communication on this structure and further discussion is not needed here. It should be emphasized, however, that this compound played a pivotal role in establishing both the existence of, and one of the most common electronic explanations for, semibridging CO groups.

Infrared spectrum *. On the basis of the structure we have found for $(C_5H_5)_2V_2(CO)_5$ we can suggest an assignment of the infrared spectrum. Three of the CO groups (which can be conveniently identified by the numbers, n, of their oxygen atoms, the corresponding carbon atoms having numbers $n + 10$), namely 1, 2, and 3, are standard terminal CO groups. It is reasonable to expect that they will give rise to the three $\nu(CO)$ bands above 1900 cm^{-1}. In each of these the V—C—O angle is in the range 176—179° and the V—C distances are similar to those in $(\eta^5\text{-}C_5H_5)V(CO)_4$ [7]. Moreover, the C(12)—V(2)—C(13) angle of 81° is such that the symmetric and antisymmetrically coupled modes arising from this pair of *geminal* CO groups would be expected to have quite similar intensities, with the symmetric mode being a little more intense. Since coupling constants between CO groups attached to the same metal atom are always positive, the symmetric mode should have the higher frequency. Also, the magnitudes of such coupling constants for CO groups roughly at right angles to each other typically cause splittings of 30—60 cm^{-1}. All of these considerations lead straight-forwardly — and unequivocally — to the assignment of the symmetric and anti-symmetric modes in the CO groups 2 and 3 to the bands at 1955 and 1910 cm^{-1}, respectively. This leaves the band at 2009 cm^{-1} to be assigned to CO 1. Since the V(1)—C(11) distance is 0.05—0.06 Å longer than the V(2)—C(12) and V(2)—C(13) distances it is entirely reasonable that it have a weaker V—C bond, a stronger CO bond and hence a CO stretching frequency higher than the average of the other two.

The two remaining CO groups 4 and 5, must then be responsible for the bands at 1832 and 1871 cm^{-1}. The relative intensities of these two bands is consistent with the large (114°) angle they make at V(1) since this would require the antisymmetric (lower-frequency) mode to be considerably more intense than the symmetric (higher-frequency) mode, as observed.

This compound thus serves to establish the very important point that as terminal CO groups begin to serve the role of semibridging CO groups, in the structural and electronic manner discussed above, their CO stretching frequencies drop rapidly into the 1900—1800 cm^{-1} range. This correlation of infrared

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* All of the principles and rules upon which the following arguments are based are explained in ref. 11.

frequency with semibridging character has proved to be extremely useful. For example, it was on the basis of a low $\nu(CO)$ that the existence of semibridging CO groups in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC{\equiv}CR')$ molecules was first indicated, thus leading to crystallographic studies which confirmed their existence [9]. It also supplies an essential contribution to the explanation of the anomalous infrared spectrum of $Fe_3(CO)_{12}$ [10,12].

As we noted several years ago [6], it is possible to deduce from the $(C_5H_5)_2V_2\text{-}(CO)_5$ structure together with the infrared spectra of this and the $(C_5H_5)_2V_2\text{-}(CO)_4L$ derivatives that the latter have structures basically similar to the parent compound with the $C(11)\text{—}O(1)$ ligand replaced by L. The reasoning behind this deduction (which has since been shown correct [13]) was as follows. When the spectrum of $(C_5H_5)_2V_2(CO)_4PPh_3$, a typical derivative, is compared with that of $(C_5H_5)_2V_2(CO)_5$, as is done in Fig. 1, it seems clear that there is only one acceptable interpretation. The replacement of one CO group by PPh_3 should lead to a general lowering of the CO stretching frequencies of the remaining four CO groups because PPh_3 is a better σ-donor and poorer π-acid than CO. Moreover, the effect should be considerably larger for the CO groups on the metal atom where the replacement has occurred. Finally, the terminal CO group on V(1) has the longest V—C distance and is thus the most weakly bound one in the parent compound. Thermodynamically, this should be the CO most susceptible to replacement, although we emphasize that this statement is not intended to convey the slightest implication as to the mechanism by which the derivatives are formed. All of these considerations are neatly, and we think uniquely, accommodated by assuming that CO 1 is replaced by PPh_3, thus (1) abolishing the band at 2009 cm^{-1} in the parent compound, (2) causing the bands due to CO's 2 and 3 to shift down an average of 22 cm^{-1} and (3) causing the bands due to the semibridging CO's, 4 and 5, to shift down by a greater amount, namely by an average of 49 cm^{-1}. The changes in relative intensities appear to imply that the C—V—C angle for CO's 4 and 5 may have contracted to a value closer to 90°.

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