Inorg. Chem. **1981**, *20*, 1173-1178

NVE, which has been observed for the transitions *to* the 6e level: these transitions have indeed been considered to produce the bands lying below ca. 10 000, 11 000, and 15 000 cm^{-1} in the spectra of the complexes with 33, 32, and 31 valence electrons (there are no bands of this type for the 34-electron compounds).[2] This trend in the frequency values is obviously related to that one of decreasing bond distances and increasing overall strength of the interactions within the coordination sphere, which has been discussed above.

Acknowledgment. Thanks are expressed to Mr. F. Cecconi and Mr. D. Masi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. **1**, 66745-30-0; **2**, 76421-14-2; **3**, 76429-47-5; **4**, 76421-15-3; $[Fe(H_2O)_6](BF_4)_2$, 15279-59-1; $[Co(H_2O)_6](BF_4)_2$, 37041-75-1; $[Ni(H_2O)_6](BF_4)_2$, 14322-78-2.

Supplementary Material Available: Listings of structure factor amplitudes (18 pages). Ordering information is given on any masthead page.

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Activation of CO_2-like Molecules: η^1-O and η^2-C,O Carbonylic Functional Groups Metal Anchored to the Bis(cyclopentadienyl)vanadium Unit

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and CARLO GUASTINI

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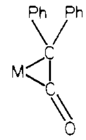
Vanadocene, Cp_2V ($Cp = \eta^5$-C_5H_5), reacts with diphenylketene, DPK, giving a monomeric complex $[Cp_2V(DPK)]$ ($\mu_{eff} = 1.77\ \mu_B$ at 293 K), suitable for studying the metal-controlled reactivity of a η^2-C,O bonded DPK. Vanadium is η^5 bonded to two Cp rings, which are in a bent arrangement (Cp–V–Cp = 139.4 (3)°), making a cavity in the equatorial plane for η^2-C,O bonded DPK. Metal-promoted C–O and long-range C–C bond lengthenings are observed (C–O = 1.290 (6), C–C = 1.340 (7) Å). $[Cp_2V(DPK)]$ reacts with I_2, giving DPK and the so far unreported Cp_2VI_2. The coordinated DPK is decomposed by organic acids to $(Ph_2CH)_2$ and CO. As $[Cp_2V(DPK)]$ represents a structural model for CO_2 η^2-C,O bonded, $[Cp_2V(acetone)](BPh_4)$ would be a model for η^1-O bonded CO_2. The C=O bond distance in acetone (C–O = 1.223 (5) Å) is only slightly affected upon coordination. This is the first structurally determined complex in the class of d^2 paramagnetic compounds $[Cp_2V–X]^+$. Crystallographic details for $[Cp_2V(DPK)]$: space group $P2_12_12_1$ (orthorhombic); $a = 18.510$ (2), b 9.712 (1), $c = 10.021$ (1) Å; $Z = 4$; $D_{calcd} = 1.383$ g cm^{-3}. The final R factor was 0.038 for 1632 observed reflections. Crystallographic details for $[Cp_2V(acetone)](BPh_4)$: space group $Pnam$ (orthorhombic); $a = 24.014$ (3), $b = 9.280$ (1), $c = 13.692$ (2) Å; $Z = 4$; $D_{calcd} = 1.216$ g cm^{-3}. The final R factor was 0.052 for 1809 observed reflections.

Introduction

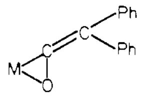
Metal-promoted transformations on some cumulenes, like X=C=Y, can simulate the metal-induced transformations on carbon dioxide,[1] whose activation is a problem of great interest.[2] Moreover, it is very well-known that CO_2-like cumulenes are highly versatile reagents in organic synthesis,[3] so their coordination to metal centers would have the following effects: (i) a drastic change on the reactivity depending on the functional group interacting with the metal; (ii) the control of some reactions (i.e., cycloadditions) occurring on free cumulenes.

For a metal-bonded organic molecule to be suitable for reactivity studies, two requirements must be fulfilled: (i) the examined molecule must form a stable 1:1 adduct with the metal; (ii) the functional group anchored to the metal must be easily released in its original form.

The interest in the metal–diphenylketene chemistry is centered on the characteristics of $Ph_2C=C=O$, DPK, as a CO_2-like molecule and on its metal-promoted reactivity. The coordination of DPK occurs through either the C=C bond in $[Pt(PPh_3)_2(DPK)]$[4] and $[MnCp(CO)_2(DPK)]$[5] or the C=O in $[Cp_2Ti(DPK)]_2$.[6]



M = Pt, Mn



M = Ti

While the first complexes are suitable models for studying the C=O reactivity, the titanium compound may permit the exploration of the reactivity of the C=C bond not engaged in bonding the metal. The titanium complex, however, is a dimer, where the DPK molecule is somewhat protected toward reagents, so that its utilization as a metal–diphenylketene model compound is not largely profitable. Moreover, the reaction of $[Cp_2Ti(DPK)]_2$ with DPK shows that the C—O unit bonded to the metal is a reactive site of the coordinated molecule.[6]

We report here a monomeric complex, $[Cp_2V(DPK)]$,[7] suitable for studying the metal-controlled reactivity of the C=C bond of a η^2-C,O metal-bonded DPK. Its reactivity toward organic acids and oxidizing agents is described. The reported structure of $[Cp_2VOC(CH_3)_2](BPh_4)$[8] represents a

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structural model for η^1-O metal-bonded carbonylic groups, including CO_2.

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Bis(η-cyclopentadienyl)vanadium(II)[9] and diphenylketene[10] were prepared as in the literature. IR spectra were measured with a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibility measurements were made with a Faraday balance. The synthesis of $[Cp_2V(\text{acetone})](BPh_4)$ was carried out as previously reported.[8] The solid recrystallized two times from acetone gave suitable crystals for an X-ray analysis.

Synthesis of $[Cp_2V(DPK)]$. A toluene solution (50 mL) of vanadocene (1.75 g, 9.67 mmol) was reacted at room temperature with neat diphenylketene (1.84 g, 9.48 mmol). The color of the solution changed rapidly from deep violet to green, and after 15 min deep green crystals of $[Cp_2V(DPK)]$ separated (64%). Anal. Calcd for $[Cp_2V(DPK)]$, $C_{24}H_{20}OV$: C, 76.80; H, 5.33. Found: C, 76.14; H, 5.40. The complex was recrystallized from hot toluene. ν_{CO}(Nujol) = 1620 cm^{-1}. $\mu_{eff} = 1.77$ μ_B at 293 K.

Reaction of $[Cp_2V(DPK)]$ with Iodine. The diphenylketene complex $[Cp_2V(DPK)]$ (1.12 g, 2.98 mmol) was suspended in THF (30 mL). The addition of iodine (1.14 g, 4.49 mmol) gave in a few mintues brown crystals of Cp_2VI_2 (ca. 63%), while the IR spectrum of the solution displayed a strong band at 2090 cm^{-1} (DPK). Anal. Calcd for Cp_2VI_2, $C_{10}H_{10}I_2V$: C, 27.60; H, 2.30; I, 58.37. Found: C, 27.78; H, 2.29; I, 57.47. $\mu_{eff} = 1.81$ μ_B at 293 K. The same reaction can be carried out in toluene or acetone. The final iodide derivative might contain variable amounts of solvent. In every case, the reaction with I_2 made free diphenylketene in a quantitative amount.

Reaction of $[Cp_2V(DPK)]$ with CH_3COOH. A THF (20 mL) suspension of $[CP_2V(DPK)]$ (0.98 g, 2.61 mmol) was reacted with acetic acid (6 mL). A fast reaction took place, evolving carbon monoxide and producing a deep blue solution from which $[CpV(CH_3COO)_2]_2$ crystallized (ca. 60%). The IR spectrum (Nujol) showed a strong, broad carbonylic band centered at 1630 cm^{-1}. Anal. Calcd for $[CpV(CH_3COO)_2]_2$, $C_{18}H_{22}O_8V_2$: C, 46.15; H, 4.70. Found: C, 46.53; H, 4.71. The solution evaporated to dryness gave a residue which, after the exposure to the air, was collected with hot hexane. The hexane solution gave, on cooling, $(Ph_2CH)_2$ (ca. 50%; mp 218 °C). When the reaction was carried out in a gas-volumetric apparatus, 0.9 mol of CO/g-atom of vanadium were measured.

Reaction of $[Cp_2V(DPK)]$ with HCOOH. THF (20 mL) containing $[Cp_2V(DPK)]$ (1.47 g, 3.92 mmol) was reacted with HCOOH (97%, 6 mL). The suspension reacted very fast, losing carbon monoxide and transforming into a blue solution. After the solution was allowed to stand overnight, a violet crystalline solid was obtained (45%). Anal. Calcd for $[CpV(HCOO)_2]_2$, $C_{14}H_{14}O_8V_2$: C, 40.77; H, 3.40. Found: C, 40.53; H, 3.66. The IR spectrum showed a strong, broad band centered at 1645 cm^{-1}. By addition of water the blue solution separated $(Ph_2CH)_2$ (70%).

When the reaction with HCOOH (excess) was carried out in toluene in a carbon monoxide atmosphere, a negligible evolution of CO was followed by an absorption of 0.95 mol of CO/g-atom of vanadium. The orange formic acid layer treated with an aqueous solution of $NaBPh_4$ gave $[Cp_2V(CO)_2](BPh_4)$[8] in an almost quantitative yield.

X-ray Data Collection and Structure Refinement for $[Cp_2V(DPK)]$. A summary of crystal data and intensity data collection is given in Table I. Cell dimensions were determined from rotation and Weissenberg photographs; the values quoted were obtained by a least-squares refinement of the 2θ values of 24 reflections ($2\theta > 33°$). The crystal examined was wedged into a thin-walled glass capillary and sealed under nitrogen. Data were collected at room temperature with a single-crystal Siemens AED automated diffractometer. The pulse height discriminator was set to accept 90% of the Mo $K\bar{\alpha}$ peak. One reflection was remeasured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. For intensity and background the "five point technique"[11] was used.

Table I. Summary of Crystal Data and Intensity Collection

	$[Cp_2V(Ph_2C_2O)]$	$[Cp_2V(Me_2CO)]BPh_4$
a, Å	18.510 (2)	24.014 (3)
b, Å	9.712 (1)	9.280 (1)
c, Å	10.021 (1)	13.692 (2)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
Z	4	4
M_r	375.4	558.4
calcd density, g/cm^3	1.383	1.216
space group	$P2_12_12_1$	*Pnam*
radiation	Nb-filtered Mo Kα radiation (λ 0.7107 Å)	Ni-filtered Cu Kα radiation (λ 1.541 Å)
μ, mm^{-1}	0.54	2.92
scan type	θ–2θ	θ–2θ
scan range	±5° from peak center	±5° from peak center
scan speeds	2.5–10° θ/min	2.5–10° θ/min
backgrounds	stationary crystal at ±0.5°	stationary crystal at ±0.5°
2θ limits, deg	5–58	6–120
criterion for observn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	1632	1809
unique total data	2707	2372
crystal dimensions, mm	0.11 × 0.47 × 0.48	0.18 × 0.26 × 0.39

The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by the Wilson's method.[12] No correction for absorption was applied ($\mu\bar{r} = 0.08$).

The analytical scattering factors for neutral atoms (ref 14a for V, ref 15 for O and C, ref 16 for H) were corrected for both the real and the imaginary components of anomalous dispersion.[14b] The function minimized during least-squares refinement was $\sum w|\Delta F|^2$, with unit weights.

Initial coordinates for the one independent vanadium atom were obtained from a vector analysis of a three-dimensional Patterson function.[13] Two successive Fourier syntheses yielded the positions of all other nonhydrogen atoms. Refinement was by full-matrix least squares, isotropically down to $R = 0.080$ and anisotropically down to $R = 0.063$. A subsequent difference Fourier map revealed all hydrogen atoms which were subjected to isotropic refinement. Convergence was reached with $R = 0.042$. Since the space group is *polar*, we tested the chirality of the crystal by inverting all the coordinates through 0, 0, 0 (i.e, $x, y, z \rightarrow \bar{x}, \bar{y}, \bar{z}$). Refinement to convergence led to the decreased residual $R = 0.038$ for the 1632 observed data. Clearly, the inverted coordinates define the correct crystal chirality. The largest peak on a difference Fourier synthesis was of height 0.29 e Å^{-3}. In the last stage of the refinement no parameter shifted by more than 0.3 times its standard deviation. No evidence for secondary extinction was found. The final atomic coordinates are listed in Table II.

X-ray Data Collection and Structure Refinement for $[Cp_2V(\text{acetone})]BPh_4$. A summary of crystal data and intensity data collection is given in Table I. Cell dimensions were determined from rotation and Weissenberg photographs; the values quoted were obtained by a least-squares refinement of the 2θ values ($2\theta > 60°$) of 31 reflections.

Data collection and data reduction techniques have been described above.[13] No correction for absorption was applied ($\mu\bar{r} = 0.3$).

The structure was solved by the heavy-atom technique, the vanadium atom being assumed to lie on a mirror plane of the centrosymmetric space group *Pnam*,[17] as indicated by the number of molecules in the unit cell ($Z = 4$). The Fourier map confirmed this

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(17) The transformation matrix from the *Pnam* space group to the standard *Pnma* (No. 62) space group is ($\bar{1}$00/001/010).

Table II. Atomic Coordinates ($\times 10^4$ for Nonhydrogen and $\times 10^3$ for Hydrogen Atoms), with Estimated Standard Deviations in Parentheses, for $[V(C_5H_5)_2(Ph_2C_2O)]$

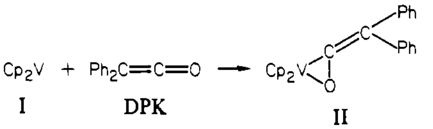
	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
V	−1442 (1)	−660 (1)	−1531 (1)	H(1)	−180 (3)	18 (7)	−422 (6)
O	−2532 (2)	−575 (4)	−1594 (4)	H(2)	−194 (3)	202 (6)	−249 (6)
C(11)	−2311 (3)	−1499 (5)	−2424 (5)	H(3)	−87 (3)	206 (6)	−109 (6)
C(12)	−2623 (2)	−2440 (5)	−3214 (5)	H(4)	−5 (3)	40 (7)	−206 (6)
C(1)	−1435 (4)	420 (7)	−3527 (7)	H(5)	−47 (3)	−66 (7)	−381 (6)
C(2)	−1542 (5)	1384 (7)	−2583 (9)	H(6)	−12 (3)	−218 (6)	−109 (6)
C(3)	−943 (5)	1450 (8)	−1804 (7)	H(7)	−55 (3)	−37 (7)	76 (6)
C(4)	−462 (3)	487 (10)	−2273 (9)	H(8)	−174 (3)	−68 (7)	141 (6)
C(5)	−785 (4)	−145 (7)	−3365 (8)	H(9)	−217 (3)	−264 (7)	−4 (6)
C(6)	−580 (3)	−1999 (7)	−602 (7)	H(10)	−115 (3)	−356 (6)	−126 (6)
C(7)	−769 (3)	−989 (6)	325 (6)	H(22)	−206 (3)	−497 (6)	−280 (6)
C(8)	−1481 (4)	−1190 (6)	693 (5)	H(23)	−134 (3)	−615 (6)	−406 (6)
C(9)	−1720 (3)	−2323 (8)	−7 (7)	H(24)	−97 (3)	−548 (7)	−622 (6)
C(10)	−1172 (4)	−2819 (6)	−803 (6)	H(25)	−139 (3)	−333 (6)	−701 (6)
C(21)	−2147 (3)	−3304 (5)	−4065 (5)	H(26)	−213 (3)	−204 (6)	−568 (6)
C(22)	−1915 (3)	−4610 (5)	−3659 (5)	H(32)	−375 (3)	−110 (6)	−207 (6)
C(23)	−1477 (3)	−5388 (5)	−4467 (6)	H(33)	−493 (3)	−169 (6)	−216 (6)
C(24)	−1279 (3)	−4912 (6)	−5703 (6)	H(34)	−541 (3)	−346 (6)	−346 (7)
C(25)	−1512 (3)	−3662 (6)	−6130 (5)	H(35)	−458 (3)	−485 (6)	−470 (6)
C(26)	−1936 (3)	−2857 (5)	−5314 (5)	H(36)	−336 (3)	−427 (7)	−461 (6)
C(31)	−3408 (2)	−2701 (5)	−3272 (5)				
C(32)	−3911 (3)	−1913 (5)	−2563 (6)				
C(33)	−4633 (3)	−2213 (6)	−2634 (6)				
C(34)	−4892 (3)	−3290 (6)	−3397 (7)				
C(35)	−4411 (3)	−4065 (5)	−4087 (5)				
C(36)	−3683 (3)	−3774 (5)	−4042 (5)				

assumption and revealed the atoms of acetone lying on the mirror plane and those of the BPh_4 anion showing a C_m symmetry. The carbon atoms of the one independent cyclopentadienyl ring were found in a successive difference map. Refinement was by full-matrix least squares in the *Pnam* space group, first isotropically down to $R = 0.126$ and then anisotropically down to $R = 0.083$. All the hydrogen atoms were located in a difference map and isotropically refined in the next to last cycle. The final R value was 0.052 for the 1809 observed data. In the last stage of refinement no parameter shifted by more than 0.4 times its standard deviation.

A final difference map showed no peaks with electron density greater than 0.2 e Å^{-3}. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$ and the reflections were weighted according to the scheme $w = 1.2917/(\sigma^2|F| + 0.003F^2)$ based on counting statistics. The atomic scattering factors were those indicated above and those from ref 15 for B. The final atomic coordinates are listed in Table III.

Results and Discussion

When a toluene solution of vanadocene is allowed to react with neat diphenylketene, DPK, a deep green solid is obtained (see eq 1), which can be recrystallized from hot toluene. The drastic lowering of the C═O stretching vibration to 1620 cm^{-1} (Nujol) shows that DPK bonds the metal through the C═O unit as in the corresponding titanium analogue. The monomeric nature of II was established by an X-ray analysis. The magnetic moment 1.77 μ_B at 293 K indicates one unpaired electron *per* vanadium atom. The sketch of the structure of II is drawn on the basis of the X-ray structure determination, which is reported below.



(1)

Description of the Structure of $Cp_2V(DPK)$ (II). The structure of complex II consists of monomeric units, shown in Figure 1. The two Cp rings, which are η^5 bonded to vanadium, make a cavity in the equatorial plane (not crystallographic) for the η^2-C,O bonded diphenylketene. The orientation of the Cp rings is staggered. V–C(Cp) and V–Cp(centroid) distances (Table IV) fall in the usual range,[18,19] as well as do the C–C bond distances within the Cp rings, which are planar. The structural characteristics of the unit reported in Figure 2 deserve the major attention. The more significant structural parameters associated with DPK coordinated to vanadium are given together with the parameters identifying the same ligand η^2-C,O bonded in $[(Cp_2Ti)_2(Ph_2C_2O)]_2$[6] (only the monomeric unit is shown for clarity) and η^2-C,C bonded in $[CpMn(CO)_2(Ph_2C_2O)]$.[5] The vanadium unit shown in Figure 2 is not planar, since C(12) is significantly outside (0.091 Å) the plane defined by V, O, and C(11) (Figure 1).

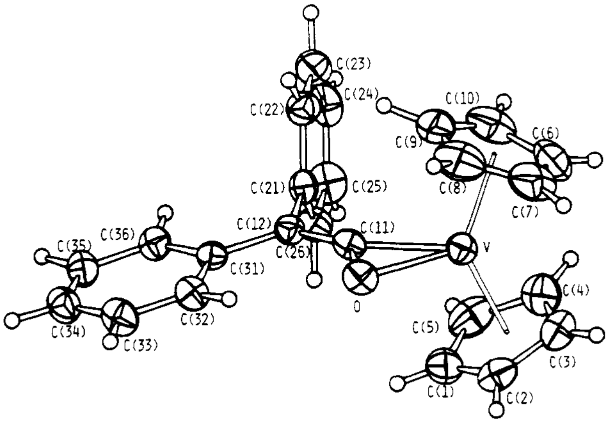


Figure 1. An ORTEP drawing of the complex $[Cp_2V(DPK)]$ displaying the thermal ellipsoids at 50% probability and showing the numbering scheme.

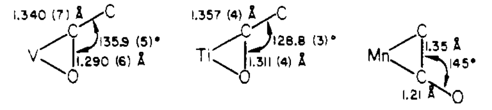


Figure 2.

It is interesting to note that Ph_2C_2O repeats the attachment mode of CO_2 in $[Ni(PCy_3)_2CO_2]$.[20] A significant shortening

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Table III. Atomic Coordinates ($\times 10^4$ for Nonhydrogen and $\times 10^3$ for Hydrogen Atoms), with Estimated Standard Deviations in Parentheses, for $[V(C_5H_5)_2(Me_2CO)]BPh_4$

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
V	1056 (1)	1355 (1)	2500 (–)	H(1)	113 (2)	314 (5)	84 (3)
O(1)	1702 (1)	2850 (4)	2500 (–)	H(2)	176 (2)	82 (5)	70 (3)
C(1)	1004 (2)	2123 (6)	928 (3)	H(3)	118 (2)	–125 (5)	145 (3)
C(2)	1336 (2)	908 (6)	953 (3)	H(4)	14 (2)	– 34 (5)	164 (3)
C(3)	1012 (3)	–246 (6)	1254 (4)	H(5)	11 (2)	262 (5)	145 (3)
C(4)	483 (3)	280 (7)	1422 (4)	H(71)	230 (3)	58 (8)	250 (–)
C(5)	474 (3)	1757 (8)	1216 (4)	H(72)	281 (2)	141 (5)	198 (4)
C(6)	2211 (2)	2819 (6)	2500 (–)	H(81)	227 (3)	506 (7)	250 (–)
C(7)	2531 (3)	1476 (10)	2500 (–)	H(82)	273 (2)	423 (5)	200 (3)
C(8)	2519 (3)	4215 (9)	2500 (–)	H(12)	108 (2)	102 (5)	594 (4)
B	1109 (2)	3141 (6)	7500 (–)	H(13)	100 (2)	–131 (5)	596 (4)
C(11)	1098 (2)	1368 (5)	7500 (–)	H(14)	94 (3)	–268 (8)	750 (–)
C(12)	1069 (2)	584 (4)	6639 (3)	H(22)	95 (2)	564 (5)	631 (3)
C(13)	1014 (2)	–920 (4)	6633 (3)	H(23)	148 (2)	638 (5)	499 (3)
C(14)	993 (3)	–1659 (6)	7500 (–)	H(24)	234 (2)	543 (5)	441 (4)
C(21)	1446 (2)	3787 (3)	6551 (2)	H(25)	261 (2)	320 (5)	524 (4)
C(22)	1297 (2)	5065 (4)	6064 (3)	H(26)	207 (2)	227 (5)	665 (3)
C(23)	1618 (2)	5645 (5)	5323 (3)	H(32)	35 (2)	357 (4)	906 (4)
C(24)	2098 (2)	4988 (5)	5028 (3)	H(33)	–60 (2)	414 (5)	899 (4)
C(25)	2261 (2)	3733 (5)	5485 (4)	H(34)	–116 (3)	450 (7)	750 (–)
C(26)	1939 (2)	3158 (4)	6227 (3)				
C(31)	443 (2)	3584 (5)	7500 (–)				
C(32)	142 (2)	3710 (4)	8359 (4)				
C(33)	–423 (2)	4029 (6)	8355 (8)				
C(34)	–716 (4)	4173 (1)	7500 (–)				

Table IV. Bond Distances[a] (Å) and Angles (Deg), with Estimated Standard Deviations in Parentheses, for $[V(C_5H_5)_2(Ph_2C_2O)]$

Distances

V–C(1)	2.259 (7)	V–C(6)	2.259 (6)	C(1)–C(2)	1.346 (11)	C(6)–C(7)	1.395 (9)
V–C(2)	2.255 (7)	V–C(7)	2.261 (6)	C(1)–C(5)	1.332 (10)	C(6)–C(10)	1.369 (9)
V–C(3)	2.264 (8)	V–C(8)	2.288 (5)	C(2)–C(3)	1.357 (13)	C(7)–C(8)	1.382 (9)
V–C(4)	2.255 (7)	V–C(9)	2.282 (7)	C(3)–C(4)	1.374 (12)	C(8)–C(9)	1.378 (9)
V–C(5)	2.260 (8)	V–C(10)	2.276 (6)	C(4)–C(5)	1.390 (12)	C(9)–C(10)	1.377 (9)
av[b]	2.258 (4)	av	2.274 (6)	av	1.357 (12)	av	1.380 (6)
V–O	2.020 (4)	O–C(11)	1.290 (6)	C(21)–C(22)	1.400 (7)	C(31)–C(32)	1.399 (7)
V–C(11)	2.013 (6)	C(11)–C(12)	1.340 (7)	C(21)–C(26)	1.381 (7)	C(31)–C(36)	1.393 (7)
V–Cp(1)	1.940 (8)	C(12)–C(21)	1.486 (7)	C(22)–C(23)	1.373 (8)	C(32)–C(33)	1.370 (8)
V–Cp(2)	1.946 (6)	C(12)–C(31)	1.476 (5)	C(23)–C(24)	1.372 (8)	C(33)–C(34)	1.381 (8)
				C(24)–C(25)	1.357 (8)	C(34)–C(35)	1.355 (8)
				C(25)–C(26)	1.377 (8)	C(35)–C(36)	1.378 (8)
				av	1.378 (7)	av	1.381 (7)

Angles

C(1)-V–C(2)	34.7 (3)	C(6)-V–C(7)	36.0 (2)	C(11)-V–O	37.3 (2)
C(1)-V–C(5)	34.3 (3)	C(6)-V–C(10)	35.1 (2)	Cp(1)-V–Cp(2)	139.4 (3)
C(2)-V–C(3)	35.0 (3)	C(7)-V–C(8)	35.4 (2)	Cp(1)-V–O	110.0 (3)
C(3)-V–C(4)	35.4 (3)	C(8)-V–C(9)	35.1 (2)	Cp(1)-V–C(11)	108.7 (3)
C(4)-V–C(5)	35.9 (3)	C(9)-V–C(10)	35.2 (2)	Cp(2)-V–O	109.3 (2)
av	35.1 (3)	av	35.4 (2)	Cp(2)-V–C(11)	108.4 (2)
V-O–C(11)	71.0 (3)	C(1)–C(2)–C(3)	108.5 (7)	C(6)–C(7)–C(8)	108.5 (5)
V–C(11)–O	71.6 (3)	C(2)–C(3)–C(4)	107.5 (7)	C(7)–C(8)–C(9)	106.4 (6)
V–C(11)–C(12)	152.0 (4)	C(3)–C(4)–C(5)	106.9 (6)	C(8)–C(9)–C(10)	109.7 (6)
O–C(11)–C(12)	135.9 (5)	C(4)–C(5)–C(1)	107.6 (7)	C(9)–C(10)–C(6)	107.5 (6)
		C(5)–C(1)–C(2)	109.5 (7)	C(10)–C(6)–C(7)	107.8 (6)
		av	107.9 (6)	av	108.0 (6)
C(11)–C(12)–C(21)	117.9 (4)	C(21)–C(22)–C(23)	120.6 (5)	C(31)–C(32)–C(33)	120.4 (5)
C(11)–C(12)–C(31)	124.4 (4)	C(22)–C(23)–C(24)	120.3 (5)	C(32)–C(33)–C(34)	121.9 (5)
C(21)–C(12)–C(31)	117.6 (4)	C(23)–C(24)–C(25)	120.1 (5)	C(33)–C(34)–C(35)	118.3 (5)
C(12)–C(21)–C(22)	121.8 (4)	C(24)–C(25)–C(26)	120.1 (5)	C(34)–C(35)–C(36)	120.8 (5)
C(12)–C(21)–C(26)	120.7 (4)	C(25)–C(26)–C(21)	121.4 (5)	C(35)–C(36)–C(31)	121.9 (4)
C(12)–C(31)–C(32)	122.8 (4)	C(26)–C(21)–C(22)	117.5 (5)	C(36)–C(31)–C(32)	116.6 (4)
C(12)–C(31)–C(36)	120.7 (4)	av	120.0 (6)	av	119.9 (9)

[a] The C-H distances range from 0.80 (6) to 1.03 (6) Å. [b] All the average values have been calculated by using the formulas

$$x_m = \frac{\Sigma w_i x_i}{\Sigma w_i} \qquad w_i = \sigma_i^{-2} \qquad \sigma_m = \left[\frac{1}{N-1}\left(\frac{\Sigma w_i x_i^2}{\Sigma w_i} - x_m^2\right) + \frac{1}{\Sigma w_i}\right]^{1/2}$$

in C–O bond distance is observed for the vanadium complex vs. the titanium analogue. Therefore C–O maintains a preeminent character of a double bond. This suggests a metal-promoted reduction of the ligand in the case of vanadium occurring at a lesser extent than in the titanium complex. This agrees with a more electron-donating ability of the Cp_2Ti vs. the Cp_2V unit. The most astonishing feature is the long-range metal-induced weakening of the C═C bond, which has the same value as in the η^2-C,C bonded DPK. This static feature

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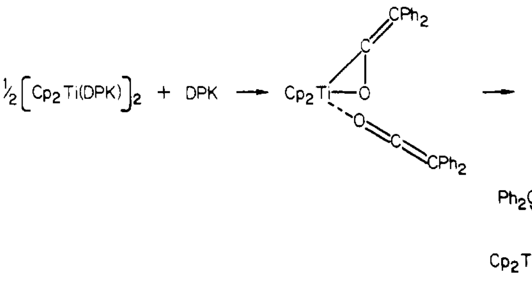
agrees with the possible C=C bond breaking in ketenes, which can be potentially considered as a source of carbenes.[21] Moreover, this would be a structural model for the precursor of a vinylidene ligand in complexes formed in reaction between metal carbonyls and ketenes.[22]

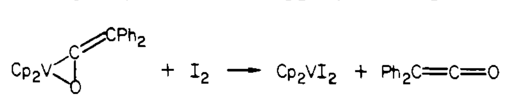
The fundamental difference between the Cp_2V and Cp_2Ti unit chemistries resides mainly in the presence of one empty orbital on titanium, which is occupied by one electron in vanadium(IV).[23] The presence of one empty orbital on titanium would promote the coordination of a further oxygen donor atom, belonging either to a complex molecule or to a free DPK. Therefore the titanium-promoted dimerization of DPK can be depicted as



This titanium-promoted dimerization occurs with other functional groups such as –C≡C– (diphenylacetylene),[24] >C=O (diethyl ketomalonate)[25] and >C=N– (p-tolylcarbodiimide),[25] which are reductively coupled to form metallacycle derivatives. With the same functional groups, vanadocene forms 1:1 adducts only.[19,26] On the other hand, it is very well-known that $Cp_2Ti(CO)_2$ undergoes two-electron oxidative addition,[27,28] while vanadocene prefers one-electron oxidative addition reactions.[28,29]

Complex II represents a model compound for studying the C=C bond reactivity in ketenes when C–O is blocked by coordination to the metal and the cumulene structure is no longer present. The utilization of complex II in this sense requires a simple method for restoring the original C=O function.

Complex II in THF, toluene, or acetone reacts with iodine, giving free diphenylketene and Cp_2VI_2, as in eq 2. The use

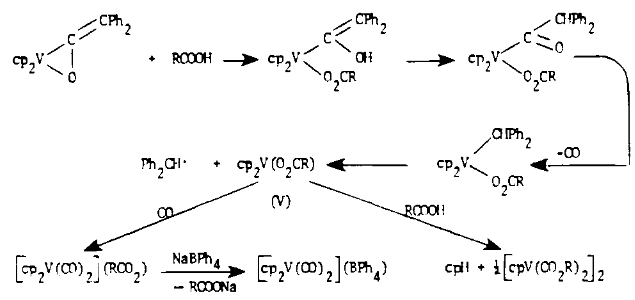


(2)

III

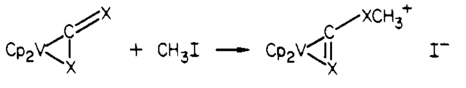
of oxygen does not allow an easy identification of the inorganic part coming from the reaction. In both cases, however, DPK is recovered unchanged. III may contain sometimes small amounts of solvent. The magnetic moment of 1.81 μ_B at 293 K confirms the oxidation state (+4) for vanadium. The isolation of III, which was not so far reported, is relevant to the proposed influence on the chemistry of the Cp_2V unit of the vanadium atomic radius, which might not accommodate two bulky ligands.[18,30]

Scheme I



R = H, CH_3.

Symmetric cumulenes such as carbon disulfide[31] and p-tolylcarbodiimide[26] bonded to vanadocene have been alkylated as reported in eq 3. Even under more drastic conditions, complex II does not react with CH_3I.

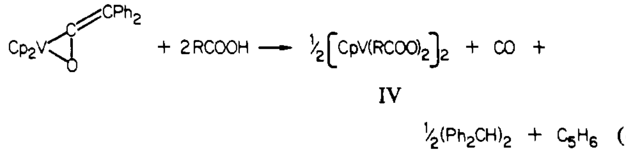


(3)

X = S, NR

The reaction of the C,O coordinated DPK with protic acids emphasizes the metal-induced change on the reactivity of a coordinated vs. a free organic molecule.

When a suspension of II is reacted with CH_3COOH or HCOOH, evolution of carbon monoxide (1 mol/g-atom of vanadium) and $(Ph_2CH)_2$ formation are observed (see eq 4).



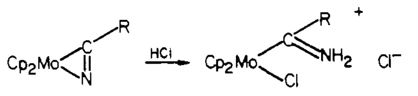
IV

(4)

R = H, CH_3

Vanadium was transformed by the action of RCOOH in complexes IV.[32] This result agrees with the observation that carboxylic acids react with Cp_2V derivatives, causing the hydrolytic splitting of one Cp ring.[32] It must be pointed out, however, that vanadium is recovered as $[CpV(HCOO)_2]_2$ only if carbon monoxide is continuously removed in reaction 4. If reaction 4 is carried out in toluene with an excess of HCOOH in a carbon monoxide atmosphere, a fast absorption of 1 mol of CO occurs and vanadium is transformed into $Cp_2V(CO)_2^+$, which was isolated as tetraphenylborate derivative.[8]

All the experimental data cited above can be accommodated in Scheme I. The protonation of the coordinated DPK is parallel to that occurring on a nitrile π bonded to molybdenocene[33] (eq 5). The decarbonylation of an acyl intermediate[34]



(5)

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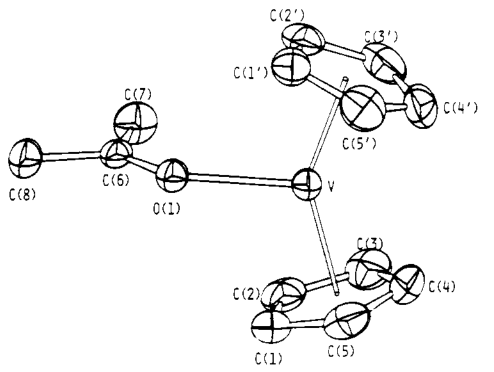
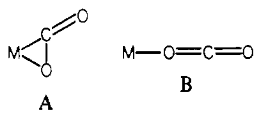
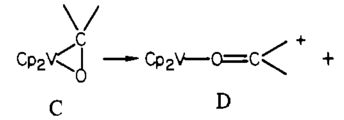


Figure 3. An ORTEP drawing of the cation $[Cp_2V(acetone)]^+$ displaying the thermal ellipsoids at 30% probability and showing the numbering scheme. Primes signify x, y, $^1/_2 - z$.

and the instability of a Cp_2V–alkyl derivative, when vanadium is in the +4 oxidation state,[30] are rather expected results. $[Cp_2V(HCOO)]$ in the presence of an excess of HCOOH acting as ionizing agent can be carbonylated to $[Cp_2V(CO)_2]^+$,[8] or, in the absence of CO, formic acid causes the splitting of one Cp ring, giving $[CpV(HCOO)_2]_2$. The following bonding modes have been found (A) or proposed (B)

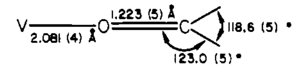


for CO_2 binding basic and acid metals, respectively.[35] Both are exemplified by carbonylic groups bonded to the Cp_2V unit. The first one is present in complex II, while the other one is shown in the structure of $[Cp_2V(acetone)](BPh_4)$.[8] The change in the oxidation state of vanadium, V(II) → V(III), causes the change from a η^2-C,O to a η^1-O bonded carbonylic group:



A coordination like D is usually found around vanadium in Cp_2V–L^+ derivatives, when weak π-acceptor ligands are present.

Description of the Structure of $[Cp_2V(acetone)](BPh_4)$. The crystals consist of $[Cp_2V(acetone)]^+$ cations (Figure 3) and BPh_4^- anions, both having a *Cm* symmetry, separated by the usual van der Waals contacts. The two Cp rings, eclipsed for crystallographic requirements, are η^5 bonded to the metal and bent away to make a cavity on the crystallographic plane for the acetone molecule. The Cp–V–Cp angle, which usually falls in the range 138–140° for Cp_2V derivatives including Cp_2VCl,[16] is unusually high (144°). V–C, V–Cp(⊥), and C–C bonds within the planar Cp rings fall in the usual range. The most relevant structural parameters concern the V–acetone unit:



The V···C(6) distance (3.089 (5) Å) indicates that acetone is O bonded to the metal. The angle values around O and C(6) approximate sp^2 geometries (Table V). The double-bond character C═O is only slightly affected upon coordination. As expected, the IR spectrum shows a lowering of the C═O band at 1660 cm^{-1}. The vanadium–oxygen bond distance compares well with that found in II.

Table V. Bond Distances[a] (Å) and Angles (Deg), with Estimated Standard Deviations in Parentheses, for $[V(C_5H_5)_2(Me_2CO)]BPh_4$

	Distances		
V–C(1)	2.271 (5)	B–C(11)	1.646 (7)
V–C(2)	2.261 (5)	B–C(21)	1.644 (5)
V–C(3)	2.265 (6)	B–C(31)	1.651 (7)
V–C(4)	2.251 (7)	C(11)–C(12)	1.387 (5)
V–C(5)	2.277 (7)	C(12)–C(13)	1.402 (5)
av	2.265 (4)	C(13)–C(14)	1.372 (5)
V–Cp(1)	1.934 (6)	C(21)–C(22)	1.407 (5)
V–O(1)	2.081 (4)	C(22)–C(23)	1.383 (6)
C(6)–O(1)	1.223 (5)	C(23)–C(24)	1.365 (7)
C(6)–C(7)	1.464 (10)	C(24)–C(25)	1.379 (7)
C(6)–C(8)	1.492 (10)	C(25)–C(26)	1.384 (7)
		C(26)–C(21)	1.393 (6)
C(1)–C(2)	1.381 (8)	C(31)–C(32)	1.385 (6)
C(2)–C(3)	1.386 (8)	C(32)–C(33)	1.389 (7)
C(3)–C(4)	1.380 (10)	C(33)–C(34)	1.372 (11)
C(4)–C(5)	1.400 (10)		
C(5)–C(1)	1.375 (9)		
av	1.384 (5)		
	Angles		
C(1)–V–C(2)	35.5 (2)	C(5)–C(1)–C(2)	109.0 (5)
C(2)–V–C(3)	35.7 (2)	C(1)–C(2)–C(3)	108.3 (5)
C(3)–V–C(4)	35.6 (3)	C(2)–C(3)–C(4)	107.0 (5)
C(4)–V–C(5)	36.0 (3)	C(3)–C(4)–C(5)	109.1 (6)
C(5)–V–C(1)	35.2 (2)	C(4)–C(5)–C(1)	106.6 (6)
av	35.5 (1)	av	108.0 (3)
Cp(1)–V–Cp(1′)	144.4 (3)	O(1)–C(6)–C(7)	123.0 (5)
Cp(1)–V–O(1)	107.7 (2)	O(1)–C(6)–C(8)	118.4 (5)
V–O(1)–C(6)	136.8 (4)	C(7)–C(6)–C(8)	118.6 (5)
C(11)–B–C(21)	111.9 (3)	C(13)–C(14)–C(13′)	119.8 (5)
C(11)–B–C(31)	103.5 (4)	C(32)–C(31)–C(32′)	116.2 (5)
C(21)–B–C(31)	112.7 (3)	C(31)–C(32)–C(33)	121.6 (6)
C(21)–B–C(21′)	104.4 (3)	C(32)–C(33)–C(34)	121.7 (8)
B–C(11)–C(12)	121.7 (3)	C(33)–C(34)–C(33′)	117.1 (8)
B–C(21)–C(22)	123.8 (4)	C(26)–C(21)–C(22)	114.8 (3)
B–C(21)–C(26)	121.2 (3)	C(21)–C(22)–C(23)	122.3 (4)
B–C(31)–C(32)	121.8 (3)	C(22)–C(23)–C(24)	120.9 (4)
C(12)–C(11)–C(12′)	116.4 (4)	C(23)–C(24)–C(25)	118.9 (4)
C(11)–C(12)–C(13)	122.1 (4)	C(24)–C(25)–C(26)	120.0 (4)
C(12)–C(13)–C(14)	119.7 (4)	C(25)–C(26)–C(21)	123.2 (4)

[a] The C–H distances range from 0.85 to 1.23 Å. [b] A prime indicates x, y, $^1/_2 - z$.

It must be recalled that the structure described above is the first example of a wide class of d^2 paramagnetic complexes, $[Cp_2V–X]^+$.

All the complexes reported in this paper can be related both structurally and chemically to some intermediates believed to form in the reaction between a metal center and carbon dioxide.

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Registry No. I, 1277-47-0; II, 76173-79-0; III, 75102-54-4; IV, R = Me, 11077-92-2; IV, R = H, 39366-49-9; $[Cp_2V(Me_2CO)]BPh_4$, 60686-18-2; $(Ph_2CH)_2$, 632-50-8.

Supplementary Material Available: Listings of observed and calculated structure factors, equations of least-squares planes (Table VI), and thermal parameters (Tables VII and VIII) (24 pages). Ordering information is given on any current masthead page.

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