tively large thermal displacements for the μ-H atom are consistent with the deformability of the Cr–H–Cr linkage. Despite the fact that it is surrounded by the cryptate molecule, the K^+ ion is not totally screened from interacting with atoms outside its immediate coordination environment. Consequently, whenever a cryptate cation is employed as the counterion for structural studies of polynuclear anions, the potential importance of cation–anion interactions should not be overlooked.

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Registry No. $[K(\text{crypt-222})]^+[Cr_2(CO)_{10}(\mu\text{-}H)]^-$, 75198-25-3; $Cr(CO)_6$, 13007-92-6.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and bond angles, root-mean-square thermal displacements, and observed and calculated structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, and the Istituto di Strutturistica Chimica, Università di Parma, 43100 Parma, Italy

Activation of CO_2-like Molecules: Synthetic and Structural Studies on a η^2-C,N Metal-Bonded Carbodiimide and Its Conversion into a η^2-C,N Metal-Bonded Amidinyl Ligand

MARCO PASQUALI, SANDRO GAMBAROTTA, CARLO FLORIANI,* ANGIOLA CHIESI-VILLA, and CARLO GUASTINI

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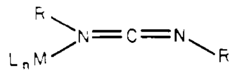
Vanadocene reacts with *p*-tolylcarbodiimide (*p*-TCD) producing a metallaazacyclopropane-like complex $Cp_2V(RN{-}C{=}NR)$ (I) ($R = p\text{-}CH_3C_6H_4$; $Cp = \eta^5\text{-}C_5H_5$; ν_{CN}(Nujol) 1645 cm^{-1}; $\mu_{eff} = 1.76\ \mu_B$ at 293.5 K). The X-ray analysis performed on complex I shows that vanadium is η^5 bonded to the two Cp rings, which are in a bent arrangement, making a cavity in the equatorial plane for the CN_2 unit. The C—N bond distances agree with the presence of a single C—N bond interacting with the metal and a free C=N double bond. Complex I reacts with both O_2 and I_2, releasing *p*-TCD. Coordinated *p*-TCD is converted in a η^2-C,N metal-bonded trialkylamidinyl ligand by the action of CH_3I on complex I. The reaction with CH_3I, followed by the addition of I_2, allowed isolation of $[Cp_2V(R(CH_3)NC{=}NR)]I_3$ (II) ($R = p\text{-}CH_3C_6H_4$; ν_{CN}(Nujol) 1680 cm^{-1}; $\mu_{eff} = 1.78\ \mu_B$ at 293 K). The X-ray analysis showed an overall structure of the cation similar to that of I, with the amidinyl ligand acting as a three-electron-donor ligand and displaying a bonding mode similar to that observed for η^2-C,O acyls and η^2-C,N iminoacyls. The two C–N bond distances within the CN_2 unit have a high double-bond character (1.26 (2) and 1.33 (2) Å), indicating a significant electronic delocalization all over the VCN_2 unit with a carbenoid character for the carbon bonded to the vanadium atom. In both complexes, V–C bond distances (about 2.0 Å) fall in the expected range for a V–C (sp^2) bond. Crystallographic details for complex I: space group $Pna2_1$ (orthorhombic); $a = 14.446$ (3) Å, $b = 14.186$ (2) Å, $c = 20.903$ (4) Å, $V = 4283.7$ Å^3; $Z = 8$; $D_{calcd} = 1.251$ g cm^{-3}. The final R factor was 8.4% for 1439 observed reflections. Crystallographic details for complex II: space group $P2_1/c$ (monoclinic); $a = 14.260$ (6) Å, $b = 19.176$ (5) Å, $c = 10.628$ (4) Å; $\beta = 106.92$ (5)°; $V = 2780.4$ Å^3; $Z = 4$; $D_{calcd} = 1.910$ g cm^{-3}. The final R factor was 6.3% for 2283 observed reflections.

Introduction

The interest in carbodiimide–transition metal chemistry is justified by the nature of carbodiimides, which closely imitate carbon dioxide, as well as by the possibility of modifying their reactivity[1] with the assistance of a metal center.

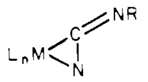
The so far reported results concerning the reaction between carbodiimides and transition-metal complexes have been summarized below.

(i) Carbodiimides have been found to be σ bonded through a nitrogen atom to the metal



in some Pd(II) complexes.[2]

(ii) Carbene-like metals add to one of the C=N bonds, as in



This metal–carbodiimide interaction suggested for $(PPh_3)_2Ni(PhN{=}C{=}NPh)^3$ was structurally proven in $Cp_2V(p\text{-}TCD)$ ($Cp = \eta^5\text{-}C_5H_5$; *p*-TCD = *p*-tolylcarbodiimide), whose synthesis and structure are described in this paper. This is the first structural report on a metal–carbodiimide complex.

(iii) Metal–carbonyl complexes promote the so-called disproportionation of carbodiimides[4-6] to dihydrotrialkylguanidinium dianion, A, being complexed by the metal and

$$2RN{=}C{=}NR + 2e^- \rightarrow \left[RN{-}\overset{\overset{\displaystyle NR}{\|}}{C}{-}NR\right]^{2-} + RNC$$

A

isocyanide. This metal-promoted carbodiimide transformation seems to involve the dimerization of the organic molecule as a key step in a sequence like[6-9]

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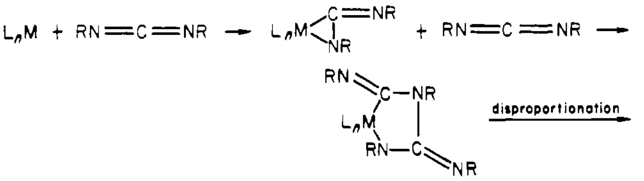
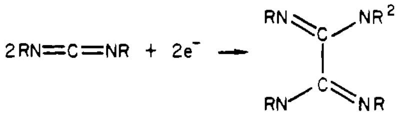


(iv) Two molecules of *p*-tolylcarbodiimide (*p*-TCD) have been reductively coupled to a tetra-*p*-tolyloxalylamidinyl ligand via a C–C bond formation:[10]



R = *p*-MeC_6H_4

An interesting relationship can be found between CO_2 and carbodiimides in their interaction with metal centers. Some of the presented carbodiimide metal-induced transformations occur with CO_2, while others represent a prospect of the CO_2 metal-promoted reactivity.

The present report concerns the synthesis and the structure of a η^2-C,N metal-bonded *p*-tolylcarbodiimide. The alkylation of the coordinated carbodiimide gives a η^2-C,N metal-bonded trialkylamidinyl ligand. This carbodiimide metal-controlled transformation represents a modeling study of carbon dioxide alkylation.

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) was prepared as in the literature.[11] *p*-Tolylcarbodiimide (*p*-TCD) was recrystallized from toluene. IR spectra were measured with a Perkin-Elmer 282 spectrophotometer. Magnetic susceptibility measurements were made with a Faraday balance.

Synthesis of Cp_2V(*p*-TCD). Bis(cyclopentadienyl)vanadium (1.81 g, 10.0 mmol) dissolved in a toluene–hexane mixture (30 mL + 10 mL), reacted with *p*-tolylcarbodiimide (2.22 g, 10.0 mmol) at room temperature. The color of the solution changed suddenly from violet to deep red. The addition of 5 mL of hexane after 2 h induced the crystallization of a deep red solid (65%). Anal. Calcd for Cp_2V-(*p*-TCD), $C_{25}H_{24}N_2V$: C, 74.44; H, 5.96; N, 6.95. Found: C, 74.1; H, 5.83; N, 6.82. ν_{CN}(Nujol) = 1645 cm^{-1}. μ_{eff} = 1.76 μ_B at 293.5 K. Complex I reacts with O_2 both in the solid state and in solution, releasing *p*-TCD, as was indicated by the IR spectrum showing a strong C–N band at 2120 cm^{-1}.

Synthesis of [Cp_2V(*p*-$MeC_6H_4N(Me)C{=}NC_6H_4Me$-*p*)]$I_3$. A toluene (30 mL) solution of Cp_2V(*p*-TCD) (1.0 g, 2.48 mmol) was treated with neat CH_3I (0.25 mL, 4.0 mmol) at room temperature. The solution did not change color. When the solution was heated at 80 °C for 10 min, a red oil was formed. Toluene was completely evaporated, and the residue dissolved in THF (20 mL). When iodine was added (0.67 g, 2.64 mmol), the color of the solution changed from deep red to violet. The addition of toluene (25 mL) precipitated red-maroon crystals of [Cp_2V(*p*-$MeC_6H_4N(Me)C{=}NC_6H_4Me$-*p*)]$I_3$. Anal. Calcd for $C_{26}H_{27}I_3N_2V$: C, 39.05; H, 3.38; I, 47.65; N, 3.50. Found: C, 38.25; H, 3.31; I, 48.1; N, 3.42. ν_{CN}(Nujol) = 1680 cm^{-1}. μ_{eff} = 1.78 μ_B at 298 K.

Reaction of Cp_2V(*p*-TCD) with Iodine. A THF (30 mL) solution of [Cp_2V(*p*-TCD)] (2.25 g, 5.58 mmol) was reacted with a THF (20 mL) solution of I_2 (2.60 g, 10.24 mmol). A brown crystalline solid suddenly formed (70%), while the supernatant green-maroon solution showed a strong C–N band at 2120 cm^{-1}. Anal. Calcd for Cp_2VI_2, $C_{10}H_{10}I_2V$: C, 27.59; H, 2.30; I, 58.39. Found: C, 27.79; H, 2.46; I, 57.90.

Table I. Summary of Crystal Data and Intensity Collection

	$C_{25}H_{24}N_2V$ (I)	$C_{26}H_{27}I_3N_2V$ (II)
a, Å	14.446 (3)	14.260 (6)
b, Å	14.186 (2)	19.176 (5)
c, Å	20.903 (4)	10.628 (4)
α, deg	90	90
β, deg	90	106.92 (5)
γ, deg	90	90
Z	8	4
M_r	403.4	799.2
D_{calcd}, g cm^{-3}	1.251	1.910
space group	$Pna2_1$	$P2_1/c$
radiation	Ni-filtered Cu Kα (λ = 1.541 78 Å)	Nb-filtered Mo Kα (λ = 0.710 69 Å)
μ, mm^{-1}	3.97	3.66
$\mu\bar{r}$	0.5	0.3
scan type	θ–2θ	θ–2θ
scan range	±0.5° from peak center	
scan speed	2.5–10° θ/min	
bkgd	stationary cryst at ±0.5°	
2θ limits, deg	6–110	5–46
criterion for obsn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	1439	2283
unique total data	2776	3867
cryst dimens, mm	0.11 × 0.36 × 0.50	0.10 × 0.26 × 0.45

X-ray Data Collection and Structure Refinement. Complex I.[12] Preliminary examination of the crystals revealed an orthorhombic unit cell. A summary of the crystal data and intensity data collection is given in Table I. Lattice constants came from a least-squares refinement of the 2θ values for 21 reflections having 2θ > 60°.

Data were collected at room temperature on a single-crystal Siemens AED automated diffractometer using a crystal mounted with its [100] axis along the axis of the diffractometer. The crystals were wedged into a thin-walled glass capillary and sealed under nitrogen. The pulse-height discriminator was set to accept 90% of the Cu Kα peak. The intensity of a standard reflection was monitored every 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"[13] was used. The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[14] No correction for absorption was made. The space group $Pna2_1$ was confirmed by structure determination and systematic absences.

The analysis of a three-dimensional Patterson map indicated that the vector distribution could be interpreted either on the basis of the *Pnma* centrosymmetric space group or on the basis of the $Pna2_1$ noncentrosymmetric one, in the first case with the assumption that the two independent vanadium atoms to lie on the mirror plane. The high number of the peaks around the metal centers in the Fourier map, phased on the positions of the two vanadium atoms and computed in the two space groups, indicated the structure to be probably noncentrosymmetric. Nevertheless we tried to solve the structure in the *Pnma* space group. The attempts were unsuccessful, and the centrosymmetric model was abandoned. The impossibility of removing the centrosymmetric distribution of the peaks, imposed by the particular positions of the two independent vanadium atoms, prevented us from solving the structure on the basis of the $Pna2_1$ space group with the use of the heavy-atom technique. Direct methods (MULTAN) were then used, and an *E* map computed with 100 phases having |*E*| > 1.96 yielded the coordinates of the metal atoms and those of a cyclopentadienyl ring. The Fourier map phased on these positions

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Table II. Final Atomic Fractional Coordinates ($\times 10^4$) for Complex I[a]

	molecule A			molecule B		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
V	1152 (2)	2484 (2)	2446 (4)	1131 (2)	2264 (1)	7432 (4)
N(1)	2204 (17)	1778 (17)	1924 (20)	51 (10)	1732 (11)	6877 (8)
N(2)	2983 (13)	1224 (11)	2768 (9)	−833 (11)	1259 (10)	7799 (10)
C(30)	2252 (18)	1685 (16)	2628 (21)	−102 (10)	1638 (9)	7537 (12)
C(1)	687 (9)	4024 (10)	2390 (15)	1284 (15)	3631 (15)	8014 (8)
C(2)	1297 (9)	3897 (10)	1864 (15)	1782 (15)	3721 (15)	7432 (8)
C(3)	2184 (9)	3664 (10)	2111 (15)	1136 (15)	3679 (15)	6920 (8)
C(4)	2122 (9)	3647 (10)	2789 (15)	239 (15)	3563 (15)	7187 (8)
C(5)	1196 (9)	3869 (10)	2961 (15)	330 (15)	3534 (15)	7863 (8)
C(6)	−188 (16)	2102 (11)	1973 (13)	1827 (18)	1044 (18)	7026 (11)
C(7)	−390 (16)	2376 (11)	2611 (13)	2495 (18)	1764 (18)	7123 (11)
C(8)	23 (16)	1708 (11)	3029 (13)	2621 (18)	1875 (18)	7793 (11)
C(9)	480 (16)	1021 (11)	2649 (13)	2031 (18)	1224 (18)	8109 (11)
C(10)	349 (16)	1264 (11)	1996 (13)	1540 (18)	710 (18)	7635 (11)
C(11)	2580 (14)	1554 (11)	1324 (9)	−294 (11)	1452 (11)	6331 (8)
C(12)	3384 (14)	1010 (11)	1323 (9)	−1134 (11)	969 (11)	6305 (8)
C(13)	3837 (14)	818 (11)	748 (9)	−1516 (11)	726 (11)	5714 (8)
C(14)	3485 (14)	1170 (11)	174 (9)	−1057 (11)	967 (11)	5150 (8)
C(15)	2681 (14)	1715 (11)	175 (9)	−217 (11)	1451 (11)	5176 (8)
C(16)	2229 (14)	1907 (11)	750 (9)	164 (11)	1693 (11)	5767 (8)
C(17)	3694 (22)	1083 (25)	−540 (18)	−1301 (20)	688 (27)	4460 (18)
C(21)	2973 (14)	1318 (12)	3526 (10)	−822 (9)	1242 (10)	8508 (10)
C(22)	3736 (14)	800 (12)	3733 (10)	−1572 (9)	755 (10)	8768 (10)
C(23)	3963 (14)	778 (12)	4382 (10)	−1642 (9)	641 (10)	9429 (10)
C(24)	3426 (14)	1273 (12)	4823 (10)	−963 (9)	1014 (10)	9830 (10)
C(25)	2662 (14)	1791 (12)	4615 (10)	−213 (9)	1501 (10)	9570 (10)
C(26)	2436 (14)	1814 (12)	3967 (10)	−143 (9)	1615 (10)	8908 (10)
C(27)	3928 (32)	1121 (35)	5459 (23)	−1240 (26)	789 (26)	10541 (14)
H(1)	−46	4212	2373	1637	3637	8423
H(2)	1024	3894	1342	2516	3788	7293
H(3)	2738	3473	1756	1238	3705	6360
H(4)	2726	3530	3042	−432	3502	6912
H(5)	1005	3987	3423	−185	3460	8187
H(6)	−444	2515	1593	1602	746	6611
H(7)	−758	2959	2825	2858	2129	6757
H(8)	67	1647	3558	3096	2419	8018
H(9)	890	392	2780	1987	1216	8651
H(10)	575	928	1565	1063	182	7782
H(12)	3634	797	1776	−1487	718	6716
H(13)	4461	378	779	−2138	263	5666
H(15)	2460	1925	−314	109	1662	4722
H(16)	1633	2344	683	760	2117	5772
H(22)	4179	395	3439	−2145	481	8517
H(23)	4569	406	4592	−2198	343	9696
H(25)	2213	2158	4965	390	1809	9831
H(26)	1823	2147	3812	443	1947	8651

[a] Estimated standard deviations in parentheses.

showed a partial releasing of centrosymmetry and gave the coordinates of some atoms of *p*-TCD ligands. The remaining nonhydrogen atoms of the two independent molecules were located by five successive Fourier difference syntheses. Refinement was carried out isotropically down to $R = 0.17$ by using full-matrix least squares[15] and a rigid-body constraint for the Cp and Ph rings. As refinement proceeded, it became evident that many of the parameters were oscillating. This prompted us to examine the possibility that the two unique molecules might be crystallographically related, especially since they are essentially identical and related by a pseudo *c* glide plane passing through the two independent vanadium atoms and perpendicular to [100] (see Figure 1). Reexamination of the row data, axial photos, and cell constants[16] indicated that no higher symmetry existed and supported our choice of unit cell. We concluded that the presence of the pseudosymmetry element caused complications in the final stages of refinement. Inclusion of anisotropic parameters tended to make the thermal ellipsoids non positive definite for some carbon atoms. These were then refined isotropically. After introduction of the cyclopentadienyl and phenyl hydrogen atoms[17] in calculated positions as fixed contributors, refinement was stopped at $R = 0.084$. An electron density synthesis for the final rigid-group model showed no unusual features with no peaks above the general background. This model was considered satisfactory, although poorly refined, in view of the large number of variables with respect to the number of observations and in view of the high correlations between the two pseudosymmetry-related molecules. The effects of anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. During the final stage of refinement, no parameter shifted by more than 1.5σ. The function minimized during least-squares refinement was $\sum w|\Delta F|^2$. A value of 0.003 for g was used in the calculation of the weight, w ($w^{-1} = \sigma_{F_o}{}^2 + |g|F_o{}^2$). Final atomic coordinates are given in Table II. Thermal parameters are reported in Table VI.[18]

Complex II. Preliminary examination of the crystals revealed a monoclinic unit cell. A summary of the crystal data and intensity data collection is given in Table I. The unit cell parameters were obtained from a least-squares refinement of the 2θ values of 20

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(15) Atomic form factors were from: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321 (for nitrogen and carbon); "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99 (for vanadium and iodine).

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(17) Scattering factors for hydrogen atoms were taken from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(18) See paragraph at the end of the paper regarding supplementary material.

Table III. Final Atomic Fractional Coordinates ($\times 10^4$) for Complex II[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
V	2684 (2)	729 (2)	637 (3)	C(21)	3125 (10)	−1387 (8)	−712 (16)
I(1)	−254 (1)	863 (1)	3326 (1)	C(22)	3688 (12)	−1590 (9)	531 (15)
I(2)	1707 (1)	1127 (1)	4889 (1)	C(23)	3934 (11)	−2269 (10)	779 (14)
I(3)	3743 (1)	1417 (1)	6488 (1)	C(24)	3652 (11)	−2808 (9)	−171 (16)
N(1)	2365 (9)	−295 (7)	837 (12)	C(25)	3091 (11)	−2575 (9)	−1400 (15)
N(2)	2892 (9)	−674 (7)	−1000 (12)	C(26)	2839 (11)	−1898 (10)	−1657 (16)
C(30)	2688 (11)	−238 (8)	−142 (16)	C(27)	3912 (14)	−3544 (9)	99 (19)
C(31)	3087 (12)	−356 (9)	−2181 (16)	H(1)	1172	1368	1658
C(1)	1357 (24)	1337 (22)	723 (24)	H(2)	2160	2242	589
C(2)	1842 (18)	1744 (10)	140 (30)	H(3)	2257	1660	−1660
C(3)	1870 (18)	1433 (17)	−992 (24)	H(4)	1312	468	−1977
C(4)	1378 (21)	822 (14)	−1121 (35)	H(5)	559	289	−84
C(5)	1038 (18)	757 (20)	−105 (50)	H(6)	3792	2086	1140
C(6)	3887 (25)	1531 (16)	1387 (62)	H(7)	4419	1055	−184
C(7)	4236 (19)	994 (32)	749 (23)	H(8)	4619	−50	1223
C(8)	4285 (17)	431 (15)	1502 (58)	H(9)	3887	100	3108
C(9)	3934 (27)	554 (32)	2464 (36)	H(10)	3396	1396	3246
C(10)	3690 (22)	1182 (35)	2470 (47)	H(12)	1514	−1483	−170
C(11)	1874 (11)	−773 (8)	1415 (14)	H(13)	589	−2287	905
C(12)	1441 (11)	−1352 (9)	804 (14)	H(15)	1158	−883	4178
C(13)	918 (11)	−1807 (9)	1405 (15)	H(16)	2053	−84	3110
C(14)	808 (12)	−1645 (9)	2643 (15)	H(22)	3940	−1197	1307
C(15)	1235 (14)	−1031 (10)	3218 (16)	H(23)	4358	−2421	1786
C(16)	1747 (12)	−581 (8)	2634 (15)	H(25)	2844	−2963	−2185
C(17)	285 (15)	−2141 (9)	3306 (19)	H(26)	2403	−1745	−2667

[a] Estimated standard deviations in parentheses.

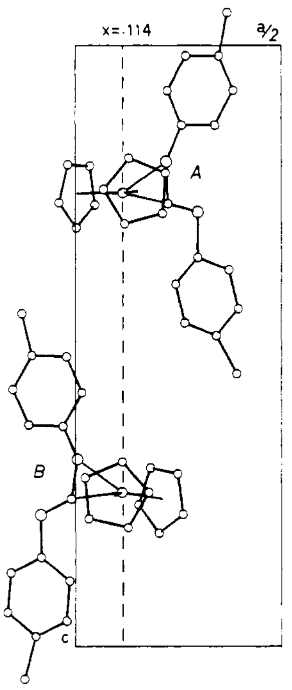


Figure 1. Projection on (010) showing the two crystallographically independent molecules related by the pseudo *c* glide in complex I.

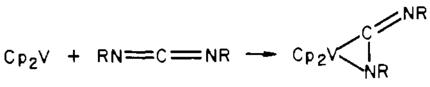
reflections ($2\theta > 30°$). Data collection and data reduction techniques have been described above.[12] No corrections for absorption were made.

The structure was solved by the usual heavy-atom method. From the three-dimensional Patterson synthesis, approximate coordinates were obtained for the three independent iodine atoms in general positions. Two successive Fourier syntheses established the coordinates of the remaining nonhydrogen atoms. Refinement was by full-matrix least squares first isotropically down to $R = 0.17$ and then anisotropically for iodine and vanadium down to $R = 0.077$. An improvement to $R = 0.065$ was obtained with the anisotropic refinement of all the atoms. The hydrogen atoms were included in idealized positions as fixed contributors with isotropic thermal parameters equal to those of the carbon atoms to which they are bonded. The subsequent refinement of the nonhydrogen atoms stopped at $R = 0.063$. The final difference map showed several peaks of height 0.6–1.4 e Å^{-3} in the environment of the I_3^- ion. In the other regions the height of the most important peaks was about 0.4 e Å^{-3}. The effects of anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. During the final stage of refinement, no parameter shifted by more than 0.4σ.

The function minimized was $\sum w|\Delta F|^2$. A value of 0.003 for *g* was used in the calculation of *w*. Final atomic coordinates are given in Table III. Thermal parameters are reported in Table VII.[18]

Results and Discussion

Vanadocene, Cp_2V (Cp = η^5-C_5H_5), reacts readily with *p*-tolylcarbodiimide (*p*-TCD) dissolved in toluene, giving a red-brown solution from which the addition of hexane induces the crystallization of I. Complex I, which is very sensitive to oxygen, releases *p*-TCD. The magnetic moment of 1.76 μ_B at 293.5 K as well as the IR spectrum justifies the formulation given for I. The drastic lowering of the C=N stretching vibration from 2120 cm^{-1} (free *p*-TCD) to 1645 cm^{-1} indicates that the cumulene structure is no longer present. Analogous lowering was observed for $(PPh_3)_2Ni$-(PhN=C—NPh), whose C=N band is at 1660 cm^{-1}. The X-ray structure analysis confirmed the reported formulation.

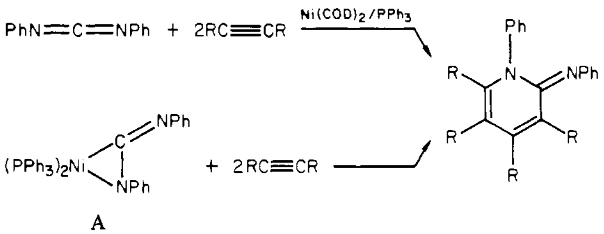


(1)

I

$R = p\text{-}CH_3C_6H_4$

The possibility of modifying the carbodiimide reactivity with the assistance of a metal center deserves much attention. On this subject, we note that complex I is the intermediate which, adding a further carbodiimide, gives the metallacycle preceding the carbodiimide's disproportionation (see Introduction). A related process is the recently reported cocyclization of diphenylcarbodiimide with acetylenes[19]



A

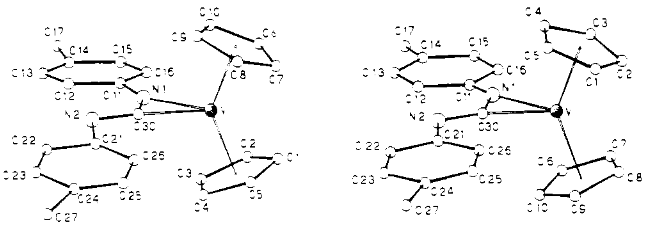


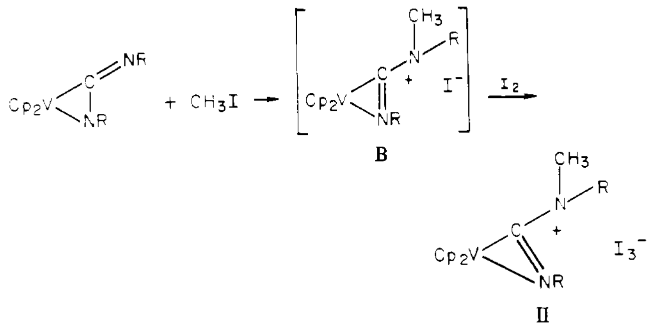
Figure 2. View of the molecular shape of the two crystallographically independent molecules $Cp_2V(p\text{-TCD})$.

which involves in a first step the formation of A followed by the reaction with acetylenes. This reactivity bears relevance to incorporating CO_2 in unsaturated organic substrates.[20]

Moreover, various kinds of cycloadditions to the uncomplexed C=N bond can be devised. This application requires, however, restoring the starting C=N bond from the coordinated C—N unit. With regard to this, we found that complex I reacts with I_2 giving the starting *p*-TCD and Cp_2VI_2.[21]

The alkylation of the η^2-C,N-bonded *p*-TCD, here reported, represents a model study for converting CO_2 into the corresponding η^2-C,O metal-bonded formato esters. This reaction, which finds rather wide application for transforming coordinated CS_2 into coordinated methoxy dithioesters,[22,23] has never been applied to other CO_2-like molecules.

A toluene solution of I reacts at 80 °C with CH_3I, giving a red oil which was dissolved in THF and reacted with iodine.



$R = p\text{-}CH_3C_6H_4$

II was isolated as red-brown crystals (1.78 μ_B at 298 K; ν_{CN}(Nujol) 1680 cm^{-1}). Although the isolation of B was not realized, its existence is proposed on the basis of the nature of II and of the sequence observed in the alkylation of coordinated CS_2.[23] Complex II represents the first complex containing an amidinyl ligand. Should this alkylation be accomplished on CO_2, this could produce η^2-C,O metal-bonded formato esters. The structures of I and II greatly help in understanding the carbodiimide and amidinyl ligand bonding modes and the related interconversion.

Description of the Structures of I and II

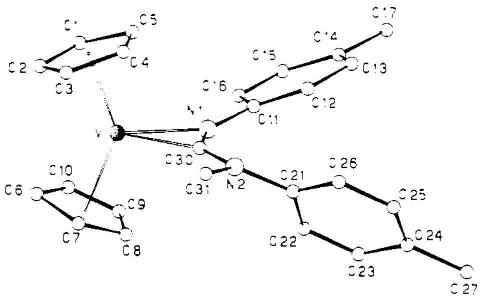


Figure 3. View of the molecular structure of $[Cp_2V(p\text{-}CH_3C_6H_4N\text{-}(CH_3)C{=}NC_6H_4CH_3\text{-}p)]^+$ in complex II.

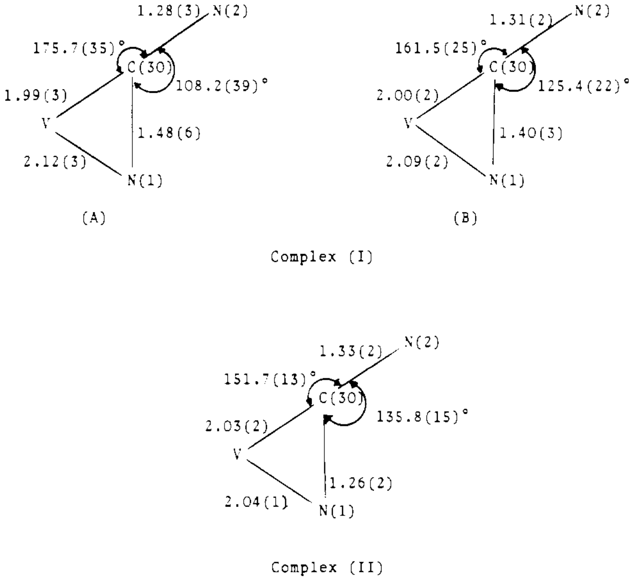


Figure 4.

In the asymmetric unit of complex I there are two crystallographically independent molecules (Figure 1), $Cp_2V(p\text{-TCD})$, whose geometries are not significantly different (Figure 2). The crystals of II are built up by monomeric cations $[Cp_2V(p\text{-}MeC_6H_4N{=}C{-}N(Me)C_6H_4Me\text{-}p)]^+$ (Figure 3) and I_3^- anions separated by the usual van der Waals interactions. In both cases the two Cp rings, which are η^5 bonded to vanadium, make a cavity in the equatorial plane for the accommodation of the carbodiimide ligand, η^2-C,N bonded to the metal. The nonbonded nitrogen lies in the plane of the VCN unit in both complexes (Table VIII). The reciprocal orientation of the Cp rings is staggered for molecule A in I and midway (neither staggered nor eclipsed) for molecule B in complex II; Cp–V–Cp angles are 140.0 (10) and 138.9 (18)° in I and II, respectively. V–C(Cp) and V–Cp(centroid) distances (Tables IV and V) fall in the usual range.[21,23,24] In II, the C(Cp)–C(Cp) ring distances, which are shorter than those usually found (1.43 Å),[25] are influenced by thermal motion or disorder by which cyclopentadienyls are affected, as indicated by the high values of the anisotropic thermal parameters of the ring carbon atoms.

In spite of the poor reliability of the structure of I, some interesting comparisons can be done between $M(CN_2)$ units of the two complexes. The most relevant structural parameters (Tables IV and V) are associated with these parts in complexes (Figure 4). The same trend of distorted trigonal angles around C(30) is observed in both complexes.

The C(30)–N(1) and C(30)–N(2) distances in I are different, although the high values of esd's make the comparison uncertain, and approximate closely a single and a double bond,

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Table IV. Bond Distances (Å) and Bond Angles (Deg) in Complex I,[a] with Estimated Standard Deviations in Parentheses

	mol A	mol B		mol A	mol B
V–C(1)	2.29 (2)	2.30 (2)	V–C(6)	2.24 (2)	2.17 (3)
V–C(2)	2.35 (2)	2.27 (2)	V–C(7)	2.26 (2)	2.19 (3)
V–C(3)	2.35 (2)	2.27 (2)	V–C(8)	2.32 (2)	2.35 (3)
V–C(4)	2.28 (2)	2.30 (2)	V–C(9)	2.33 (2)	2.42 (3)
V–C(5)	2.24 (2)	2.32 (2)	V–C(10)	2.29 (2)	2.32 (3)
average	2.30 (3)	2.29 (1)	average	2.29 (2)	2.29 (5)
V–Cp(1)	1.96 (2)	1.95 (2)	C(30)–N(2)	1.28 (3)	1.31 (2)
V–Cp(2)	1.94 (2)	1.95 (3)	N(1)–C(11)	1.40 (4)	1.31 (2)
V–N(1)	2.12 (3)	2.09 (2)	N(2)–C(21)	1.59 (3)	1.48 (3)
V–C(30)	1.99 (3)	2.00 (2)	C(14)–C(17)	1.53 (4)	1.54 (4)
C(30)–N(1)	1.48 (6)	1.40 (3)	C(24)–C(27)	1.53 (5)	1.57 (4)
	mol A	mol B		mol A	mol B
C(1)–V–C(2)	35.6 (9)	36.2 (7)	C(6)–V–C(7)	36.8 (9)	38.0 (10)
C(2)–V–C(3)	35.2 (6)	36.4 (7)	C(7)–V–C(8)	36.2 (7)	36.3 (9)
C(3)–V–C(4)	35.7 (11)	36.1 (7)	C(8)–V–C(9)	35.6 (6)	34.6 (9)
C(4)–V–C(5)	36.6 (5)	35.7 (7)	C(9)–V–C(10)	35.8 (8)	34.8 (8)
C(5)–V–C(1)	36.5 (7)	35.8 (7)	C(10)–V–C(6)	36.6 (7)	36.7 (9)
average	36.0 (6)	36.0 (3)	average	36.1 (4)	35.9 (7)
N(1)–V–C(30)	42.0 (12)	40.1 (6)	N(1)–C(30)–N(2)	108.2 (39)	125.4 (22)
N(1)–V–Cp(1)	105.2 (8)	106.9 (8)	C(30)–N(2)–C(21)	100.3 (23)	114.7 (15)
N(1)–V–Cp(2)	108.4 (8)	110.7 (9)	N(1)–C(11)–C(12)	116.7 (19)	121.0 (16)
C(30)–V–Cp(1)	110.7 (8)	108.5 (7)	N(1)–C(11)–C(16)	123.1 (19)	118.9 (15)
C(30)–V–Cp(2)	108.8 (8)	108.9 (8)	N(2)–C(21)–C(22)	105.0 (16)	112.9 (15)
Cp(1)–V–Cp(2)	140.0 (7)	140.0 (10)	N(2)–C(21)–C(26)	135.0 (17)	127.0 (15)
V–N(1)–C(30)	64.2 (15)	66.8 (10)	C(13)–C(14)–C(17)	137.7 (20)	128.4 (18)
V–N(1)–C(11)	147.5 (19)	151.7 (13)	C(15)–C(14)–C(17)	102.2 (19)	111.3 (18)
C(11)–N(1)–C(30)	148.3 (23)	140.3 (15)	C(23)–C(24)–C(27)	103.9 (23)	108.2 (17)
V–C(30)–N(1)	73.8 (15)	73.1 (10)	C(25)–C(24)–C(27)	136.1 (24)	131.8 (17)
V–C(30)–N(2)	175.7 (35)	161.5 (25)			

[a] Cp(1) and Cp(2) are referred to the centroids of the rings C(1)–C(5) and C(6)–C(10), respectively. All the average values were calculated by using the formulas

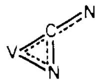
$$x_m = \frac{\Sigma w_i x_i}{\Sigma w_i} \qquad \left[\sigma_m = \frac{1}{N-1}\left(\frac{\Sigma w_i x_i^2}{\Sigma w_i} - x_m^2\right) + \frac{1}{\Sigma w_i}\right]^{1/2} \qquad w_i = \sigma_i^{-2}$$

where x_i are the individual observations and σ_i are their standard deviations.

Table V. Bond Distances (Å) and Bond Angles (Deg), with Estimated Standard Deviations in Parentheses, in Complex II

V–C(1)	2.25 (4)	V–C(6)	2.27 (4)	C(1)–C(2)	1.31 (4)	C(6)–C(7)	1.40 (6)
V–C(2)	2.27 (2)	V–C(7)	2.24 (3)	C(2)–C(3)	1.35 (4)	C(7)–C(8)	1.33 (7)
V–C(3)	2.24 (3)	V–C(8)	2.27 (4)	C(3)–C(4)	1.35 (4)	C(8)–C(9)	1.28 (6)
V–C(4)	2.23 (3)	V–C(9)	2.25 (4)	C(4)–C(5)	1.31 (6)	C(9)–C(10)	1.25 (9)
V–C(5)	2.25 (3)	V–C(10)	2.23 (5)	C(5)–C(1)	1.41 (6)	C(10)–C(6)	1.43 (7)
average	2.25 (2)	average	2.25 (2)	average	1.34 (3)	average	1.35 (5)
V–Cp(1)	1.93 (3)	C(30)–N(2)	1.33 (2)	C(11)–C(12)	1.34 (2)	C(21)–C(22)	1.39 (2)
V–Cp(2)	1.94 (4)	N(1)–C(11)	1.40 (2)	C(12)–C(13)	1.42 (2)	C(22)–C(23)	1.35 (3)
V–N(1)	2.04 (1)	N(2)–C(21)	1.42 (2)	C(13)–C(14)	1.40 (2)	C(23)–C(24)	1.42 (2)
V–C(30)	2.03 (2)	N(2)–C(31)	1.49 (2)	C(14)–C(15)	1.38 (3)	C(24)–C(25)	1.39 (2)
C(30)–N(1)	1.26 (2)	C(14)–C(17)	1.50 (3)	C(15)–C(16)	1.39 (3)	C(25)–C(26)	1.35 (3)
I(1)–I(2)	2.852 (3)	C(24)–C(27)	1.47 (2)	C(16)–C(11)	1.41 (2)	C(26)–C(21)	1.38 (2)
I(2)–I(3)	2.959 (3)			average	1.39 (2)	average	1.39 (1)
C(1)–V–C(2)	33.8 (12)	C(6)–V–C(7)	36.2 (17)	C(2)–C(1)–C(5)	107.1 (28)	C(7)–C(6)–C(10)	103.1 (37)
C(2)–V–C(3)	35.0 (11)	C(7)–V–C(8)	34.4 (16)	C(1)–C(2)–C(3)	108.3 (25)	C(6)–C(7)–C(8)	105.6 (33)
C(3)–V–C(4)	35.3 (10)	C(8)–V–C(9)	33.0 (17)	C(2)–C(3)–C(4)	108.9 (25)	C(7)–C(8)–C(9)	111.4 (38)
C(4)–V–C(5)	34.1 (15)	C(9)–V–C(10)	32.5 (22)	C(3)–C(4)–C(5)	107.7 (30)	C(8)–C(9)–C(10)	110.7 (45)
C(5)–V–C(1)	36.5 (14)	C(10)–V–C(6)	37.0 (20)	C(4)–C(5)–C(1)	108.0 (30)	C(9)–C(10)–C(6)	109.0 (40)
average	35.0 (7)	average	34.7 (11)	average	108.1 (12)	average	107.5 (23)
N(1)–V–C(30)	36.0 (6)	C(30)–N(2)–C(21)	122.8 (13)	C(12)–C(11)–C(16)	119.8 (15)	C(22)–C(21)–C(26)	117.5 (15)
N(1)–V–Cp(1)	109.3 (10)	C(30)–N(2)–C(31)	116.8 (13)	C(11)–C(12)–C(13)	121.3 (14)	C(21)–C(22)–C(23)	120.0 (15)
N(1)–V–Cp(2)	110.2 (15)	C(31)–N(2)–C(21)	119.1 (13)	C(12)–C(13)–C(14)	120.2 (15)	C(22)–C(23)–C(24)	123.9 (14)
C(30)–V–Cp(1)	110.3 (11)	N(1)–C(11)–C(12)	123.2 (14)	C(13)–C(14)–C(15)	116.6 (16)	C(23)–C(24)–C(25)	113.6 (15)
C(30)–V–Cp(2)	108.1 (15)	N(1)–C(11)–C(16)	116.6 (13)	C(14)–C(15)–C(16)	123.6 (16)	C(24)–C(25)–C(26)	122.9 (16)
Cp(1)–V–Cp(2)	138.9 (18)	N(2)–C(21)–C(22)	120.7 (14)	C(15)–C(16)–C(11)	118.3 (15)	C(25)–C(26)–C(21)	122.0 (15)
V–N(1)–C(30)	71.6 (9)	N(2)–C(21)–C(26)	121.8 (15)	average	119.2 (26)	average	119.7 (29)
V–N(1)–C(11)	146.2 (11)	C(13)–C(14)–C(17)	120.3 (15)				
C(11)–N(1)–C(30)	140.3 (14)	C(15)–C(14)–C(17)	123.1 (15)				
V–C(30)–N(1)	72.4 (10)	C(23)–C(24)–C(27)	124.0 (15)				
V–C(30)–N(2)	151.7 (13)	C(25)–C(24)–C(27)	122.4 (16)				
N(1)–C(30)–N(2)	135.8 (15)						
I(1)–I(2)–I(3)	179.2 (1)						

respectively. In II both C–N distances have a high double-bond character. The unhybridized p orbital on C(30) in II may have some interaction with the two nitrogen atoms and the metal, so that considerable electronic delocalization occurs over the three atoms. This is the pattern observed in many carbenoid complexes and supports the carbenoid nature of C(30).



The C=N stretching frequencies of I and II parallel the structural data, indicating an increasing C=N double-bond character of the C(30)–N(1) unit passing from I to II. This and other features of the η^2-C,N-bonded amidinyl are highly reminiscent of η^2-C,O-bonded acyls[26] and η^2-C,N-bonded iminoacyls.[27] Amidinyl ligands in this form, like the ligands cited above, can be viewed as three-electron donors.

V–C(30) bond distances fall in the range of the very few V–C (sp^2) distances so far reported.[24] The counteranion I_3^- has the usual structural features (Table V)[28] and does not interact significantly with the macrocation, the shortest contact distance being 3.87 (13) Å [I(1)···N(2) $(\bar{x}, \bar{y}, \bar{z})$].

Conclusions

Besides the structural models for metal-bonded CO_2 and carboxylato esters, the present report describes the alkylation of a coordinated carbodiimide viewed as a reaction which can be considered a modeling study for the alkylation of metal-bonded CO_2. Moreover, vanadocene can be proposed as a blocking agent for one double bond of a cumulene, so that it may promote a new kind of reactivity for the coordinated molecule.

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Registry No. I, 75102-51-1; II, 75102-53-3; Cp_2VI_2, 75102-54-4; Cp_2V, 1277-47-0; CH_3I, 74-88-4.

Supplementary Material Available: Listings of structure factor amplitudes for complexes I and II, anisotropic thermal parameters (Tables VI and VII), and least-squares planes (Table VIII) (32 pages). Ordering information is given on any current masthead page.

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The Molybdenum–Molybdenum Triple Bond. 7.[1] Bis(1,3-di-*p*-tolyltriazenido)tetrakis(dimethylamido)dimolybdenum

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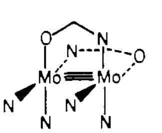
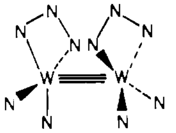
$Mo_2(NMe_2)_6$ reacts in hydrocarbon solvents with 1,3-di-*p*-tolyltriazine, $C_7H_8NNNHC_7H_8$, to give the title compound, $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$, as a red, crystalline solid. An X-ray study shows that in the solid state each molybdenum atom is coordinated to four nitrogen atoms which lie in a plane; there is an unbridged molybdenum-to-molybdenum triple bond with a Mo–Mo distance of 2.212 (1) Å, and the molecule has crystallographically imposed C_2 symmetry. Variable-temperature ^{1}H NMR spectra recorded at 220 MHz support the view that this form of the molecule is present in solution. These observations are compared with other findings in dimolybdenum and ditungsten chemistry. Crystal data for $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ are $a = 27.529$ (7) Å, $b = 8.728$ (2) Å, $c = 18.294$ (4) Å, $\beta = 58.34$ (1)°, $V = 3741.58$ Å^3, $Z = 4$, $d_{calcd} = 1.45$ g cm^{-3}, and space group $C2/c$.

Introduction

Previously we have shown that 1,3-diphenyltriazine and $W_2(NMe_2)_6$ react to give $W_2(NMe_2)_4(PhN_3Ph)_2$[2] and $Mo_2(NMe_2)_6$ and 2-hydroxy-6-methylpyridine react to give $Mo_2(NMe_2)_4(C_6H_6NO)_2$.[1] In both reactions, the replacement of two dimethylamido groups is accomplished by an increase in coordination number of the metal, since the triazenido and pyridine ligands act as bidentate ligands. However, the molybdenum and tungsten compounds adopt bridged and unbridged structures, respectively, as shown in **1** and **2**. The preference for the bridged or nonbridged structure could be determined by the subtle differences that exist within the coordination chemistry of molybdenum and tungsten. For example, in closely related compounds containing metal-to-metal triple bonds, the Mo-to-Mo distance is shorter by ca. 0.08 Å than the W-to-W distance, and the triazenido ligand is known to bridge the molybdenum-to-molybdenum quadruple bond in the compound $Mo_2(PhN_3Ph)_4$ which has a Mo-to-Mo distance of 2.083 (2) Å.[3] As part of our continuing program which is aimed at establishing the coordination chemistry surrounding the $(M{\equiv}M)^{6+}$ moiety (M = Mo, W), we decided to prepare and structurally characterize the related pair of molybdenum and tungsten compounds. We report here the preparation and characterization of $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$.



1



2

Results

Synthesis. In hydrocarbon solvents, $Mo_2(NMe_2)_6$ and 1,3-di-*p*-tolyltriazine react upon mixing at room temperature

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[1] Part 6: M. H. Chisholm, J. C. Huffman, K. Folting, and I. P. Rothwell, submitted for publication in *Inorg. Chem.*

[2] M. H. Chisholm, J. C. Huffman, and R. L. Kelly, *Inorg. Chem.*, **18**, 3554 (1979).

[3] F. A. Cotton, G. W. Rice, and J. C. Sekutowski, *Inorg. Chem.*, **18**, 1143 (1979).

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