Reactions of Nitrogen Monoxide and Dioxygen with Bis(pentamethylcyclopentadienyl)vanadium Dihalides: Preparation and Structures of Oxo Derivatives of (Pentamethylcyclopentadienyl)vanadium

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Reaction of $Cp*_2VCl_2$ ($Cp* = \eta^5$-$C_5(CH_3)_5$) with NO gave green $Cp*VCl_2(O)$ (I) as the major and brown $[Cp*VCl(\mu$-$O)]_4$ (II) as the minor product. The structures of I and II have been determined by X-ray diffraction. I is a monomeric complex of vanadium(V) containing a V=O bond ($\nu(V$—$O) = 965$ cm^{-1}; $r(V$—$O)$ 1.576 (8) Å). II is antiferromagnetic and has an almost planar eight-membered $[V(\mu$-$O)]_4$ ring with the $Cp*$ and Cl ligands alternating above and below the plane; $r(V$—$O)$ is 1.800 (2) Å. I and II were also obtained in low yield from the reaction between $Cp*_2VCl_2$ and O_2, which was very slow. Reaction of $Cp*_2VI_2$ with NO gave $[Cp*_2V(NO)]_2I_8$, in which two $Cp*_2VI(NO)$ units are linked together by three iodine molecules. The spectral properties of $[Cp*_2V(NO)]_2I_8$ are very similar to those of $Cp*_2VI(NO)$ published previously. There was no reaction between $Cp*_2VI_2$ and N_2O, but O_2 gave two products, depending on the ratio of the reactants. With a $Cp*_2VI_2$:O_2 ratio of 2:1 the product was green $[Cp*VI(O)]_2(\mu$-$O)$, a vanadium(V) complex with $\nu(V$=$O)$ at 955 cm^{-1}. With a $Cp*_2VI_2$:O_2 ratio of 4:1 the yellow, paramagnetic, vanadium(IV) complex $[Cp*VI_2]_2(\mu$-$O)$ (III) was obtained. The structure of III has been determined by X-ray diffraction. It has a crystallographically imposed linear and symmetrical V-O-V bridge ($r(V$-$O) = 1.765$ (1) Å).

Introduction

Organometallic oxo complexes are of considerable interest because they combine a very hard ligand, oxygen, with organic ligands which are usually regarded as soft. A variety of oxygen-bridged derivatives of CpTi (Cp = η^5-C_5H_5) have been known for some time; an example is $[CpTiCl_2]_2(\mu$-$O)$.[1,2] Recently clusters containing oxygen atoms have been characterized, for example, $Cp_5V_5O_6$[3,4] and $Cp_{14}V_{16}O_{24}$;[5] one such cluster, $Cp_4Cr_4O_4$, was also known earlier.[4,6] The first examples of organometallic compounds containing M=O terminal units appear to be $CpVX_2(O)$ (X = Cl, Br) described by Fischer and Vigoureux[7,8] and those of molybdenum described by Cousins and Green,[9] the structure of one of which, cis-[CpMo-

(O)]$_2(\mu$-$O)_2$, was later proved by X-ray diffraction.[10] The analogous trans-$[Cp*Cr(O)]_2(\mu$-$O)_2$ ($Cp* = \eta^5$-$C_5(CH_3)_5$) has been characterized recently.[11] A most interesting development is the preparation of a monomeric organometallic complex containing three M=O bonds, namely, $Cp*Re(O)_3$,[12,13] along with several derivatives and reaction products.[14,15]

All of the above oxo complexes contain Cp or $Cp*$ as the organic ligand. These ligands are known to stabilize metals in higher formal oxidation states than other organic ligands. Alkyl ligands are also able to do this,[16] and a variety of alkyl–oxo complexes of V, Nb, Ta, W, and Re, including $[V(CH_2Si(CH_3)_3)_3(O)]$, $(CH_3)ReO_3$, and $(CH_3)_3ReO_2$, and mixed alkyl–cyclopentadienyl–oxo complexes such as

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$Cp_2Nb(CH_3)(O)$ have been prepared, principally by Wilkinson and co-workers.[16-20]

We have found that nitrogen oxides are efficient and clean sources of oxygen atoms, and organometallic oxo complexes can be readily prepared by using them. Nitrogen oxides such as N_2O or $(CH_3)_3NO$ usually produce clusters;[3-5,21] nitrogen monoxide (NO) produces nitrosyls,[22,23] but these often decompose to give oxo complexes.[23-26] Insertion reactions of NO with metal alkyls which lead to oxo complexes have been reported by Wilkinson,[18] and a recent discovery is that $[Cp(CO)_2W(O=C(CH_3)$ $CH=CH)]$ and NO give a mixture of $[CpW(C_2H_4)(CH_3)(O)]$ and $[CpW(C_2H_4)(C(O)CH_3)(O)]$.[27] Dioxygen has generally not given tractable products, although in a few cases the oxidation is clean.[28] We have extended our previously reported investigations of the reactions of derivatives of Cp_2V and $Cp*_2V$ with NO, N_2O, and O_2[4,22,23,29] to $Cp*_2VCl_2$ and $Cp*_2VI_2$, with the interesting results presented here.

Experimental Section

General Data. All experiments were carried out under argon or vacuum using standard vacuum line techniques. Solvents were predried, stored over methyllithium, and distilled under vacuum. The complexes $Cp*_2VCl_2$ and $Cp*VCl_3$ were prepared analogously to Cp_2VCl_2[30] and $CpVCl_3$,[31] respectively; the yield of $Cp*VCl_3$ was very low even when the highly exothermic reaction between $Cp*_2VCl_2$ and $SOCl_2$ was conducted at 0 °C for short reaction times (2 h). $Cp*_2VI_2$ was prepared by the literature method.[32] Nitrogen monoxide (99%) was purified by passage through silica gel at -78 °C, N_2O and O_2 were used as received, and all other chemicals were reagent grade. Volumes of gaseous reactants and products were measured by using manometers and calibrated bulbs; gaseous products were separated by a Toepler pump with traps at different temperatures and a Cu/CuO bed at 300 °C. Instruments used were a Perkin-Elmer 683 infrared spectrophotometer (spectra measured as Nujol or Fluorolube mulls between KBr plates), a locally modified version of the Varian E4 ESR spectrometer, and a Varian XL-200 NMR spectrometer. Magnetic moments were determined by the Faraday method. Microanalyses were by Beller Laboratorium, Göttingen, West Germany.

Reaction of Bis(pentamethylcyclopentadienyl)dichlorovanadium with Nitrogen Monoxide: (Pentamethylcyclopentadienyl)oxodichlorovanadium, $(\eta-C_5(CH_3)_5)VCl_2(O)$ (I), and cyclo-Tetrakis((μ-oxo)chloro(pentamethylcyclopentadienyl)vanadium), $[(\eta-C_5(CH_3)_5VCl(\mu-O)]_4$ (II). A suspension of $Cp*_2VCl_2$ (0.67 g, 1.70 mmol) in toluene (50 cm³) was incubated under NO (1.5 mmol) for 24 h. During this time

the yellow-green suspension turned to a bright green solution still containing some unreacted starting material. This was removed by filtration, and then the solvent was removed under vacuum. The residue was sublimed under vacuum at 70 °C, giving initially 0.15 g of green $Cp*VCl_2(O)$. A second sublimation of the residue gave a further 0.07 g of product for a total yield of 59% based on the $Cp*_2VCl_2$ which actually reacted or 32% based on the initial amount of $Cp*_2VCl_2$. Anal. Calcd for $C_{10}H_{15}Cl_2OV$: C, 44.0; H, 5.6; V, 18.6. Found: C, 43.5% H, 5.6; V, 18.1. IR: 965 cm⁻¹ (vs, $\nu(V=O)$). NMR: ¹H, 1.81 ppm (s); ¹³C, 133.64 (s, $C_5(CH_3)_5$), 13.31 ppm (s, $C_5(CH_3)_5$). Mass spectrum: m/e 272 ($[Cp*V^{35}Cl_2(O)]^+$); 237 ($[Cp*V^{35}Cl(O)]^+$). There was also a peak at m/e 493 ($[Cp*_2V_2^{35}Cl_3O]^+$). The intensity ratio of 272:493 was approximately 7:1.

After sublimation of $Cp*VCl_2(O)$ there remained a brown residue. This was dissolved in toluene and filtered, and hexane was layered onto the filtrate. On setting aside, brown crystals of $[Cp*VCl(\mu-O)]_4$ precipitated; yield, 0.03 g (8% based on the $Cp*_2VCl_2$ which actually reacted and 4.5% based on the initial amount of $Cp*_2VCl_2$). Anal. Calcd for $C_{40}H_{60}Cl_4O_4V_4$: C, 50.5; H, 6.4; Cl, 14.9; V, 21.4. Found: C, 48.7; H, 6.2; Cl, 15.6; V, 20.1. The analysis is not completely satisfactory, probably due to the presence of residual $Cp*VCl_2(O)$ and/or $[Cp*VCl_2]_2O$ in the sample. Because of the low yield of $[Cp*VCl(\mu-O)]_4$ repeated recrystallisation was difficult to perform. NMR: ¹H, 10.4 ppm (vw, br). The compound was ESR silent down to -170 °C but had a bulk magnetic susceptibility of 2.27 μB at 20 °C (corrected for ligand diamagnetism). The susceptibility was field dependent, indicating antiferromagnetism.

Reaction of (Pentamethylcyclopentadienyl)trichlorovanadium with Nitrogen Monoxide. A solution of $Cp*VCl_3$ (0.20 g, 0.70 mmol) in toluene (50 cm³) was incubated under NO (0.70 mmol) for 5 days, during which time the dark purple solution changed to green. The solvent was removed in vacuo and the residue sublimed at 70 °C under vacuum to give green $Cp*VCl_2(O)$ (0.05 g, 26%). The physical and chemical properties of the product were identical with those described above. The residue remaining after sublimation was intractable.

Reaction of Bis(pentamethylcyclopentadienyl)dichlorovanadium with Dioxygen: $(\eta-C_5(CH_3)_5)VCl_2(O)$ (I) and $[(\eta-C_5(CH_3)_5)VCl(\mu-O)]_4$ (II). A suspension of $Cp*_2VCl_2$ (0.73 g, 1.86 mmol) in toluene (50 cm³) was incubated under O_2 (0.93 mmol) for 7 days, during which time the solution turned bright green. Unreacted starting material was removed by filtration and the solvent distilled off under vacuum. Sublimation at 70 °C under vacuum gave green $Cp*VCl_2(O)$ (0.02 g, 19% based on the $Cp*_2VCl_2$ which actually reacted or 3.8% based on the initial amount of $Cp*_2VCl_2$). The physical and chemical properties of the product were the same as those of $Cp*VCl_2(O)$ obtained from the reaction between $Cp*_2VCl_2$ and NO described above.

After sublimation there remained a brown residue, presumed to contain $[Cp*VCl(\mu-O)]_4$, but the quantity was insufficient for workup.

Reaction of Bis(pentamethylcyclopentadienyl)diiodovanadium with Nitrogen Monoxide: Bis(bis(pentamethylcyclopentadienyl)nitrosylvanadium) Octaiodide, $[(\eta-C_5(CH_3)_5)_2V(NO)]_2I_8$. A suspension of $Cp*_2VI_2$ (0.93 g, 1.61 mmol) in toluene (75 cm³) was incubated under NO (1.60 mmol) for 30 h. The maroon suspension slowly turned to brick-red with no gas evolution. The very air-sensitive solid was separated by filtration and recrystallized from either thf/ether or CH_2Cl_2/hexane; yield of brick-red $[Cp*_2V(NO)]_2I_8$, 0.33 g (47%). Anal. Calcd for $C_{40}H_{60}I_8N_2O_2V_2$: C, 28.0; H, 3.5; I, 59.1; N, 1.6; V, 5.9. Found: C, 28.5; H, 3.6; I, 59.0; N, 1.8; V, 5.7. Infrared spectrum: $\nu(NO)$ 1760 cm⁻¹ (vs) in Nujol or Fluorolube; 1743 cm⁻¹ in thf solution. ESR spectrum (20 °C): 24 lines, g_{iso} = 1.9943, $A_{iso}(^{51}V)$ = 12.37 G, $A_{iso}(^{14}N)$ = 4.12 G. NMR: ¹H, $\delta(CH_3)$ 5.37 (w, br s). Mass spectrum: m/e 254 (I_2^+), all other peaks very weak; nonconducting in CH_2Cl_2.

Reaction of Bis(pentamethylcyclopentadienyl)diiodovanadium with Dioxygen: (μ-Oxo)bis((pentamethylcyclopentadienyl)diiodovanadium), $[(\eta-C_5(CH_3)_5)VI_2]_2(\mu-O)$ (III). A suspension of $Cp*_2VI_2$ (0.93 g, 1.60 mmol) in toluene (75 cm³) was incubated under O_2 (0.4 mmol) with vigorous stirring for 12 h. During this time the suspension turned from maroon to yellow-brown. The air-sensitive yellow-brown precipitate of

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Table I. Crystal and Refinement Data for I–III

	I	II	III
constitutn	$C_{10}H_{15}Cl_2OV$	$C_{40}H_{60}Cl_4O_4V_4$	$C_{20}H_{30}I_4V_2$
M_r	273.09	950.56	895.96
a, Å	6.439 (1)	16.568 (3)	20.417 (9)
b, Å	8.598 (1)	16.568 (3)	8.527 (2)
c, Å	11.217 (1)	9.005 (1)	15.757 (6)
α, deg	84.75 (1)	90	90
β, deg	87.61 (1)	90	106.33 (3)
γ, deg	89.33 (1)	90	90
V, Å³	617.8	2471.9	2632.6
Z	2	2	4
D_{calcd}, Mg m⁻³	1.47	1.28	2.26
λ (X-ray wavelength), Å	0.710 73	0.710 73	0.710 73
class	triclinic	tetragonal	monoclinic
space group	$P\bar{1}$	$I\bar{4}2m$	$C2/c$
μ (absorptn coeff), cm⁻¹	11.30	9.24	53.24
absorptn correct	yes; empirical[b]	no	yes; empirical[b]
temp, °C	20	20	20
scan type	ω–2θ	ω–2θ	ω–2θ
2θ(max), deg	45	50	50
max no. of independent reflctns	1625	662	2311
no. of observed	640	497	1777
observn criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of parameters refined	77	67	124
R (= $\sum\Delta|F|/\sum|F|$)	0.057	0.067	0.048
R_w (= $(\sum w(\Delta F)^2/\sum wF^2)^{1/2}$)	0.056	0.070	0.053
max residual intensity, e Å⁻³	0.30	1.04	1.18
min residual intensity, e Å⁻³	−0.34	−0.51	−1.47

[a] I, $[(\eta\text{-}C_5(CH_3)_5)VCl_2(O)]$; II, $[(\eta\text{-}C_5(CH_3)_5)VCl(\mu\text{-}O)]_4$; III, $[(\eta\text{-}C_5(CH_3)_5VI_2]_2(\mu\text{-}O)$. [b] See ref 54.

[Cp*VI₂]₂(μ-O) was collected by filtration and recrystallizated from toluene/hexane (yield, 0.70 g (61%)). Anal. Calcd for $C_{20}H_{30}I_4OV_2$: C, 26.8; H, 3.4. Found: C, 26.5; H, 3.4. NMR: ¹H, 13.0 ppm (v, br s). The complex was ESR silent at 20 and −170 °C. The spectroscopy showed that the product was always contaminated with Cp*₂VI₂ and [Cp*VI(O)]₂(μ-O). Attempts to purify the product further only lead to an increase in one or the other impurity.

Reaction of Bis(pentamethylcyclopentadienyl)diiodovanadium with Dioxygen: (μ-Oxo)bis((pentamethylcyclopentadienyl)oxoiodovanadium), $[(\eta\text{-}C_5(CH_3)_5)VI(O)]_2(\mu\text{-}O)$. A suspension of Cp*₂VI₂ (1.10 g, 1.91 mmol) in toluene (75 cm³) was incubated with O₂ (0.95 mmol) for 12 h. The maroon suspension turned to a green solution which, on setting aside, deposited dark green microcrystalline [Cp*VI(O)]₂(μ-O), yield, 0.95 g (74%). Anal. Calcd for $C_{20}H_{30}I_2O_3V_2$: C, 35.6; H, 4.5. Found: C, 35.8; H, 4.5. The IR of the solid (Nujol mull) showed an intense band at 955 cm⁻¹ (ν(V=O)) with a shoulder at 942 cm⁻¹. The complex was diamagnetic.

Collection and Reduction of X-ray Data for I–III. Crystals of I were obtained by setting aside a toluene solution at room temperature for 5 weeks. Crystals of II were obtained by extracting the residue after sublimation of I (see above) with toluene and layering the toluene extract with hexane. Crystals formed after about 5 weeks at room temperature. Crystals of III were obtained by layering hexane onto a toluene solution and setting aside for several weeks. In all cases the crystals were coated with air-free "Apiezon" grease and mounted in sealed tubes under argon. The symmetry class and space group were determined by using precession photographs and the diffractometer. Data for I and II were collected on a Nonius CAD4 and for III on a Picker FACS-1 computer-controlled diffractometer. During the data collection of II a reduction of 20% in the intensity of the three standard reflections was noted, and this was corrected for by using a smoothed curve to describe the variation in the standards. Because of this drop in intensity no absorption correction was applied to II. The crystal of I was very small, and as a consequence of this only 40% of the available reflections were judged as observed. Crystal data for I–III are collected in Table I.

Structure Solution and Refinement of I–III. Preliminary positions for the vanadium and/or iodine atoms were found by using the MULTAN-80 package.[33] The positions of the atoms

Table II. Positional Parameters of the Non-Hydrogen Atoms of I

atom[a]	x	y	z
V	1.0577 (4)[b]	0.7277 (3)	0.2132 (2)
Cl(1)	1.2107 (6)	0.4943 (4)	0.2468 (3)
Cl(2)	1.2118 (7)	0.8777 (5)	0.3328 (4)
O	1.1460 (14)	0.7858 (10)	0.0839 (8)
C(1)	0.753 (2)	0.603 (1)	0.315 (1)
C(11)	0.749 (2)	0.455 (1)	0.397 (1)
C(2)	0.753 (2)	0.756 (1)	0.344 (1)
C(21)	0.746 (2)	0.812 (2)	0.467 (1)
C(3)	0.747 (2)	0.854 (1)	0.235 (1)
C(31)	0.737 (2)	1.031 (1)	0.226 (1)
C(4)	0.738 (2)	0.762 (1)	0.135 (1)
C(41)	0.714 (2)	0.821 (1)	0.008 (1)
C(5)	0.750 (2)	0.603 (1)	0.185 (1)
C(51)	0.740 (2)	0.465 (1)	0.115 (1)

[a] For numbering scheme see Figure 1. [b] Estimated standard deviations are given in parentheses.

so found were used in the phasing of a Fourier synthesis and the positions of all non-hydrogen atoms determined by successive Fourier, difference Fourier, and least squares refinement techniques. The structures were refined by standard least-squares techniques, minimizing the function $\sum w(\Delta F)^2$ with a weighting scheme of the form $w = 1/(\sigma(F)^2 + kF^2)$ with σ based on counting statistics. Scattering factors were taken from ref 34 and were corrected for both the real and the imaginary parts of the anomalous dispersion where appropriate. The hydrogen atoms were included with positions calculated by using sp³ hybridization at the C atom, a fixed C–H distance of 0.96 Å, and fixed thermal parameters. Final refinement of II and III was with non-hydrogen atoms anisotropic. In the case of I it was found that refining the 10 C atoms of the C₅(CH₃)₅ ring anisotropically produced no statistically significant decrease in the R value. Therefore in this structure the C atoms were isotropically refined. The SHELX-76[35] program package was used for the refinements; diagrams are by ORTEP-II.[36]

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Table III. Positional Parameters of the Non-Hydrogen Atoms of II

atom[a]	x	y	z
V	0.1077 (1)[b]	0.1077 (1)	0.0052 (3)
Cl	0.1406 (2)	0.1406 (2)	0.7653 (4)
O	0.1217 (5)	0.0	0.0
C(1)	0.1324 (6)	0.1324 (6)	0.2473 (15)
C(11)	0.0863 (8)	0.0863 (8)	0.3659 (17)
C(2)	0.1102 (7)	0.2072 (6)	0.1863 (10)
C(22)	0.0374 (8)	0.2564 (9)	0.2294 (22)
C(3)	0.2303 (7)	0.1683 (6)	0.0794 (13)
C(33)	0.3079 (7)	0.1709 (8)	0.0011 (24)

[a] For numbering scheme see Figure 2. [b] Estimated standard deviations are given in parentheses.

Table IV. Positional Parameters for the Non-Hydrogen Atoms of III

atom[a]	x	y	z
V	0.1637 (1)[b]	0.3096 (1)	-0.0314 (1)
I(1)	0.1215 (1)	0.1448 (1)	0.0831 (1)
I(2)	0.1800 (1)	0.5832 (1)	0.0466 (1)
O	0.25	0.25	0.0
C(1)	0.4008 (4)	0.3306 (9)	0.1489 (5)
C(2)	0.4493 (4)	0.2287 (11)	0.1272 (5)
C(3)	0.4303 (4)	0.0744 (9)	0.1371 (5)
C(4)	0.3705 (4)	0.0760 (9)	0.1674 (5)
C(5)	0.3539 (4)	0.2355 (9)	0.1773 (5)
C(6)	0.4009 (6)	0.5061 (11)	0.1501 (6)
C(7)	0.5115 (4)	0.2817 (14)	0.1059 (7)
C(8)	0.4705 (5)	-0.0640 (11)	0.1278 (6)
C(9)	0.3342 (5)	-0.0606 (11)	0.1918 (6)
C(10)	0.3003 (4)	0.2914 (12)	0.2161 (5)

[a] For numbering scheme see Figure 3. [b] Estimated standard deviations are given in parentheses.

Table V. Important Distances (Å) and Angles (deg) in Cp*VCl₂(O) (I)

		1		
V–O	1.576 (8)[a]	Cl(1)–V–Cl(2)	104.6 (2)
V–Cl(1)[b]	2.233 (5)	Cl(1)–V–Cp*	102.6 (4)
V–Cl(2)	2.215 (5)	Cl(1)–V–Cp*	114.9
V–Cp*[c]	1.999	Cl(2)–V–O	104.3 (4)
		Cl(2)–V–Cp*	115.8
		O–V–Cp*	113.2

[a] Estimated standard deviations are given in parentheses. [b] For numbering scheme see Figure 1. [c] Cp* is the center of the $C_5(CH_3)_5$ ring.

Table VI. Important Distances (Å) and Angles (deg) in [Cp*VCl(μ-O)]₄ (II)

V–Cl	2.294 (5)[a]	V–O–V	165.1 (5)
V–O	1.800 (2)	O–V–O	104.8 (2)
V–Cp*[b]	1.984	O–V–Cl	100.4 (1)
V–V	3.569 (4)	O–V–Cp*	135.4
		Cl–V–Cp*	116.0

[a] Estimated standard deviations are given in parentheses. [b] Cp* is the center of the $C_5(CH_3)_5$ ring.

Details of the final refinements are given in Table I. The positional parameters for the non-hydrogen atoms of I, II, and III are given in Tables II, III, and IV, respectively. Important distances and angles derived from these positions are given in Tables V–VII. Tables of hydrogen atoms positions, thermal parameters, equations of some mean planes, comprehensive lists of bond distances and angles, and tables of $|F_o|$ and $|F_c|$ are available as supplementary material.

Results and Discussion

Reaction of Cp*₂VCl₂ with NO: Formation of Cp*VCl₂(O) and [Cp*VCl(μ-O)]₄. On incubation with NO a yellow-green suspension of Cp*₂VCl₂ in toluene changed to a bright green solution over 24 h. The major

Table VII. Important Distances (Å) and Angles (deg) in [Cp*VI₂]₂O (III)

V–I(1)[a]	2.618 (2)[b]	V–O–V	180.0
V–I(2)	2.614 (1)	O–V–I(1)	98.6 (1)
V–O	1.765 (1)	O–V–I(2)	98.1 (1)
V–Cp*[c]	1.976	O–V–Cp*	112.6
		I(1)–V–I(2)	100.3 (1)
		I(1)–V–Cp*	99.5
		I(2)–V–Cp*	100.0

[a] For numbering scheme see Figure 3. [b] Estimated standard deviations are given in parentheses. [c] Cp* is the center of the $C_5(C-H_3)_5$ ring.
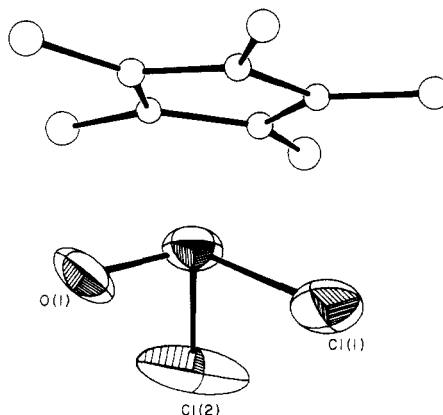
Figure 1. Geometry of Cp*VCl₂(O).

product (59%) of the reaction, which was isolated by sublimation, was bright green Cp*VCl₂(O) (I). A minor product (8%) isolated from the residue after sublimation of Cp* VCl₂(O) was brown [Cp*VCl(μ-O)]₄ (II).

The mass spectrum of the reaction product showed traces of [Cp*VCl₂]₂O and its fragment ions. Since N₂O was evolved during the reaction, two nitrosyl ligands must combine. This is only possible if a Cp* ligand is lost on coordination of NO since Cp*₂VCl₂ is already a 17-electron complex. Coupling of the nitrosyls must be rapid since no nitrosyl complex could be detected during the reaction, even at -70 °C and with very short reaction times. The most reasonable routes from Cp*₂VCl₂ to Cp*VCl₂(O) are either direct, eq 1, or in two steps via the intermediacy of

$$Cp^*_2VCl_2 + 2NO \rightarrow Cp^*VCl_2(O) + N_2O + \text{``Cp*''} \quad (1)$$

[Cp*VCl₂]₂O, eq 2 and 3. On the other hand, the for-

$$2Cp^*_2VCl_2 + 2NO \rightarrow [Cp^*VCl_2]_2O + N_2O + 2 \text{ ``Cp*''} \quad (2)$$

$$[Cp^*VCl_2]_2O + 2NO \rightarrow Cp^*VCl_2(O) + N_2O \quad (3)$$

mation of [Cp*VCl(μ-O)]₄ from Cp*₂VCl₂ is very difficult to explain; II contains vanadium(IV), the same oxidation state as in Cp*₂VCl₂, but it has one less chloride ligand. Reactions such as those of eq 4 or 5 are improbable because

$$4Cp^*_2VCl_2 + 8NO \rightarrow$$
$$[Cp^*VCl(\mu\text{-}O)]_4 + 4N_2O + 4Cp^*Cl \quad (4)$$

$$2[Cp^*VCl_2]_2O + 4NO \rightarrow$$
$$[Cp^*VCl(\mu\text{-}O)]_4 + 2N_2O + 2Cl_2 \quad (5)$$
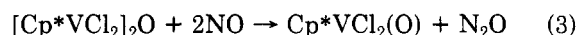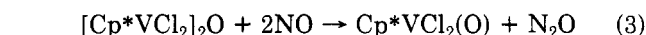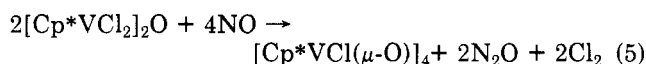
neither Cp*Cl nor Cl₂ could be generated by the mild oxidant NO. The only reasonable possibility is disproportionation of [Cp*VCl₂]₂O (eq 6). We have definitely

$$4[Cp^*VCl_2]_2O \rightarrow 4Cp^*VCl_3 + [Cp^*VCl(\mu\text{-}O)]_4 \quad (6)$$

identified only I, II, and [Cp*VCl₂]₂O as products of the reaction of NO with Cp*₂VCl₂. However we were able to show by an independent reaction that NO oxidized Cp*VCl₃. The reaction was very slow and gave a low yield

of Cp*VCl$_2$(O) among other unidentified products.

Monomeric, air-stable I is an organometallic vanadium complex containing the V=O unit. It has a piano-stool configuration (see Figure 1 and Table V), is formally a complex of vanadium(V), and is diamagnetic as expected. It is analogous to CpVCl$_2$(O)[7,8,37] and to the recently prepared Cp*ReBr$_2$(O).[14] We did not observe Cp*V(O)$_2$, which would be the analogue of Cp*Re(O)$_3$,[12,13] though CpV(O)$_2$, stabilized by two N(CH$_3$)$_3$ ligands, does occur as a bridging unit in (Cp$_5$V$_6$O$_8$)$_2$(CpV(O)$_2$(N(CH$_3$)$_3$)$_2$).[5] In I ν(V=O) occurs at 965 cm^{-1}, and the V—O distance is 1.576 (8) Å. In [V(CH$_2$Si(CH$_3$)$_3$)$_3$(O)] ν(V=O) is at 988 cm^{-1};[16] other complexes with a single V^V=O unit show ν(V=O) at 970 cm^{-1}.[38,39] No other organometallic complex containing a V=O unit has been structurally characterized but the V—O distance found here is extremely close to values recently reported for a single V^V=O unit in inorganic complexes (1.586 (3), 1.599 (3) Å;[39] 1.587 (6) Å[40]). These distances are shorter than the 1.62–1.66 Å found in complexes containing V^V(O)$_2$, i.e., with two V=O units.[38,41,42] The V–Cl distances in I are 2.233 (5) and 2.215 (5) Å: we have been unable to find a chloro complex of vanadium(V) with a coordination number of six with which this distance can be compared. However, V–Cl in [VCl$_4$(O)]$^-$ is 2.256 (2) Å.[43] As usual in complexes containing η^5-C$_5$(CH$_3$)$_5$ ligands, the CH$_3$ groups are displaced from the plane of the C$_5$ ring in the direction away from the vanadium. The displacement averages 0.071 Å in I, 0.098 Å in II, and 0.103 Å in III. The effect of the high oxidation state and lack of d electrons of the vanadium on the Cp* ligand in I is shown by the ^{1}H and ^{13}C NMR spectra: δ(CH$_3$) is 1.81 ppm, comparable to that of Cp*Re(O)$_3$ (1.63 ppm) and Cp*ReBr$_2$(O) (2.28 ppm);[14] δ(C$_5$) (133.64 ppm) and δ(CH$_3$) (13.31 ppm) are also similar to Cp*Re(O)$_3$ (120.35 and 10.24 ppm, respectively).

The structure of II (see Figure 2 and Table VI) is similar to those of [(η-C$_5$H$_4$CH$_3$)TiCl(μ-O)]$_4$[44] and [(η-C$_5$H$_5$)TiCl(μ-O)]$_4$,[45] the main difference being that the [V(μ-O)]$_4$ ring of II is essentially planar. The four oxygen atoms lie in a crystallographically fixed plane, and the V atoms alternate 0.047 Å above and below this plane. The dihedral angle of the butterfly as defined by Petersen[44] is 175.7° compared to 154.0° in [(η-C$_5$H$_4$CH$_3$)TiCl(μ-O)]$_4$[44] and 146.2° in [(η-C$_5$H$_5$)TiCl(μ-O)]$_4$.[45] As with the titanium compounds the Cp* and Cl ligands in II alternate above and below the [V(μ-O)]$_4$ plane to reduce steric hindrance. The V–Cl distance in II is 2.294 (5) Å; this is longer than in I as expected because of the lower oxidation state of the vanadium. In (η-C$_5$H$_4$CH$_3$)$_2$VCl$_2$ V–Cl is 2.398 (2) Å;[46] the lengthening compared to II is caused by the higher coordination number.[47]
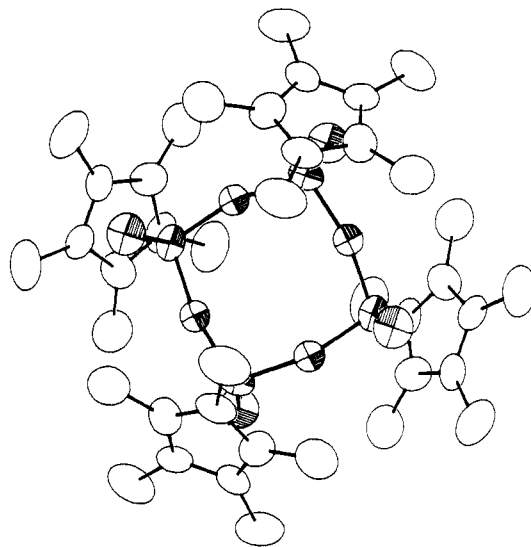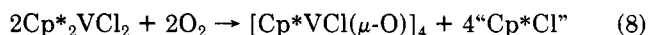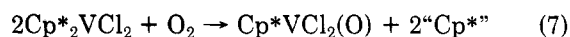
The V–O distance in II (1.800 (2) Å) is shorter than

Figure 2. Geometry of [Cp*VCl(μ-O)]$_4$.

observed in compounds with nonplanar V^{IV}–O–V^{IV} bridges.[3,5,48] In addition II is antiferromagnetic, the magnetic moment at 20° being 2.27 μ_B (corrected for ligand diamagnetism according to the values in ref 49). The antiferromagnetism is deduced from the field dependence of the magnetic moment. The planarity of the [V(μ-O)]$_4$ ring, the short V–O distance, and the magnetism of II are related. Each vanadium is formally V(IV) (d^1) and has piano-stool geometry of its ligands. An extended Hückel molecular orbital calculation shows that two d orbitals from each vanadium are involved in σ-bonding to the Cp*, Cl, and O ligands and one is involved in π-bonding, perpendicular to the [V(μ-O)]$_4$ plane, with the O atom. This π-bonding is maximised by a planar [V(μ-O)]$_4$ ring and accounts for the short V–O distance. Two d orbitals per vanadium remain essentially nonbonding, and these are forbidden by symmetry from interacting with those on a neighboring vanadium via the bridging oxygen. The lowest energy state is one in which each vanadium retains a single electron. The observed magnetic moment is much lower than expected for four unpaired electrons. One reason for this is that pairing of electrons by direct overlap of V–V orbitals in the plane of the [V(μ-O)]$_4$ ring is symmetry-allowed, and with a V–V distance of 3.569 (4) Å an interaction is possible. Such a direct interaction would also account for the deviation of the V–O–V angle (165.1 (5)°) from 180°. Note that although II exists as an antiferromagnetic tetramer in the solid state, it can be expected that other oligomers of formula [Cp*VCl(μ-O)]$_n$ will exist in solution. The magnetic properties of these will depend on the value of n.

There was no reaction between Cp*$_2$VCl$_2$ and N$_2$O. With O$_2$ a very slow reaction took place which was similar to that between NO and Cp*$_2$VCl$_2$. The major product was I, with II as a minor byproduct. The reactions may be written formally as eq 7 and 8. The remarks made above

$$2Cp*_2VCl_2 + O_2 \rightarrow Cp*VCl_2(O) + 2\text{“Cp*”} \quad (7)$$

$$2Cp*_2VCl_2 + 2O_2 \rightarrow [Cp*VCl(\mu\text{-}O)]_4 + 4\text{“Cp*Cl”} \quad (8)$$

about the formation of II from Cp*$_2$VCl$_2$ and NO apply also to reaction 8. The much slower rate of the reaction between O$_2$ and Cp*$_2$VCl$_2$ compared to NO and Cp*$_2$VCl$_2$

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is probably due to the necessity of forming a species containing the V-O-O-V unit in which at least one V still carries two Cp* ligands.

Reaction of Cp*$_2$VI$_2$ with NO: Formation of [Cp*$_2$V(NO)]$_2$I$_8$. The reaction between a toluene suspension of Cp*$_2$VI$_2$ and NO (1:1 mole ratio) gave a brick-red precipitate of [Cp*$_2$V(NO)]$_2$I$_8$ in 47% yield. There were no gaseous products of the reaction; when the volume was reduced and the filtrate set aside after removal of [Cp*$_2$V(NO)]$_2$I$_8$, a brown material precipitated. This showed no ν(NO) absorptions in the infrared spectrum but was intractable. The reaction may be considered to take place in two stages, eq 9 and 10. The intractable, brown product "Cp*$_2$VNO" obtained from Cp*$_2$V and NO, which shows no ν(NO) vibrations, has been mentioned previously.[22]

$$4Cp*_2VI_2 + 2NO \rightarrow [Cp*_2V(NO)]_2I_8 + 2Cp*_2V \quad (9)$$

$$2Cp*_2V + 2NO \rightarrow 2\text{"}Cp*_2VNO\text{"} \quad (10)$$
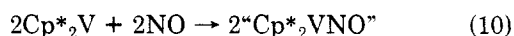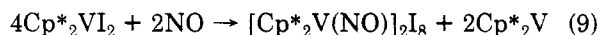
The complex [Cp*$_2$V(NO)]$_2$I$_8$ was soluble and nonconducting in tetrahydrofuran or CH$_2$Cl$_2$ but decomposed slowly above -30 °C in either solvent to give a green material which did not have a nitrosyl ligand. [Cp*$_2$V(NO)]$_2$I$_8$ was thermally stable in the solid state but extremely air- and water-sensitive. The structure is proposed as

Cp*$_2$V(-NO)(-I)(-I)(-I)(-I)(-I)(-I)(-I)(-I)(-I)VCp*$_2$(-ON)
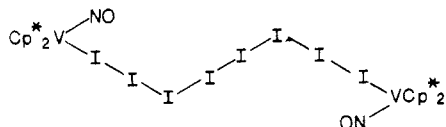
The unusual formulation as a complex containing [Cp*$_2$V(NO)]$^+$ units linked by the I$_8$$^{2-}$ anion is supported by the following evidence, in addition to its very reproducible formation and microanalysis. The ESR spectrum (24 lines, g_{iso} = 1.9943, A_{iso}(^{15}V) = 12.37 G, A_{iso}(^{14}N) = 4.12 G) was identical with that of Cp*$_2$VI(NO) (g_{iso} = 1.9942, A_{iso}(^{51}V) = 12.26 G, A_{iso}(^{14}N) = 4.02 G[22]). The ^{1}H NMR spectrum showed a single broad and weak resonance at 5.37 ppm due to the CH$_3$ protons. There is only a small shift due to the paramagnetism of the molecule because the unpaired electron is localized in a {VNO} orbital.[50] The infrared spectrum of [Cp*$_2$V(NO)]$_2$I$_8$ (ν(NO) 1760 cm^{-1} (Nujol mull) or 1743 cm^{-1} (THF solution)) was also similar to that of Cp*$_2$VI(NO) (1704, 1695 cm^{-1} (Nujol mull) or 1710 cm^{-1} (CH$_2$Cl$_2$ solution)[22]). Attempts to obtain a Raman spectrum were unsuccesful due to the decomposition of the sample in the laser beam. The mass spectrum showed I$_2$$^+$ as by far the largest peak; fragments with up to three iodine atoms attached to Cp*V but no parent ion were observed.

The I$_8$$^{2-}$ ion is known to have a planar zig-zag structure;[51] it can be regarded as two I$_3$$^-$ ions linked by I$_2$. Why it should be so readily formed in the reaction between Cp*$_2$VI$_2$ and NO is not clear.

Reaction of Cp*$_2$VI$_2$ with O$_2$: Formation of [Cp*VI$_2$]$_2$(μ-O) and [Cp*VI(O)]$_2$(μ-O). There was no reaction between Cp*$_2$VI$_2$ and N$_2$O, but with O$_2$ a rapid reaction took place. Two products were obtained depending on the ratio of the reactants. With a Cp*$_2$VI$_2$:O$_2$ ratio of 4:1 the product was the yellow paramagnetic vanadium(IV) complex [Cp*VI$_2$]$_2$(μ-O) (III). With a
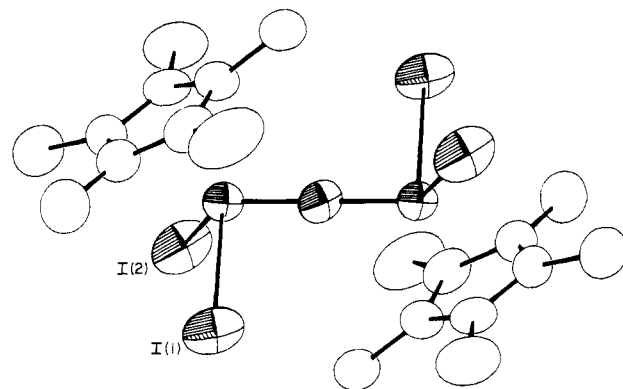
Figure 3. Geometry of [Cp*VI$_2$](μ-O).

Cp*$_2$VI$_2$:O$_2$ ratio of 2:1 the product was the green vanadium(V) complex [Cp*VI(O)]$_2$(μ-O). Since the oxidation state of the product increases but the number of iodide ligands decreases as the amount of O$_2$ increases, it is believed that [Cp*VI(O)]$_2$(μ-O) is produced by further oxidation of III (eq 11 and 12). The production of I$_2$ in reaction 12 is reasonable, unlike the production of Cp*Cl or Cl$_2$ in reactions 4, 5, and 8 since I$^-$ can be oxidized to I$_2$ by O$_2$.[52]

$$2Cp*_2VI_2 + O_2 \rightarrow 2[Cp*VI_2]_2(\mu\text{-O}) + 2\text{"}Cp*\text{"} \quad (11)$$

$$[Cp*VI_2]_2(\mu\text{-O}) + O_2 \rightarrow [Cp*VI(O)]_2(\mu\text{-O}) + I_2 \quad (12)$$
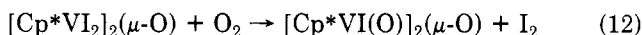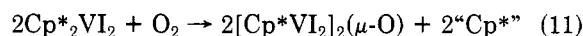
Yellow, air-sensitive III contains two Cp*VI$_2$ units bridged by an oxygen atom (see Figure 3 and Table VII). It has a very similar structure to [CpTiCl$_2$]$_2$(μ-O).[1] In each case the geometry around the metal is a piano-stool, the M-O-M bridge is symmetrical and linear, and the dihedral angle between the two Cp'MX$_2$ units is 180°. III is paramagnetic, each vanadium being formally V(IV), d^1; because of the problem of impurities noted in the Experimental Section a quantitative determination of the magnetic moment was not possible. The V-O distance (1.765 (1) Å) is much shorter than in II (1.800 (2) Å). This is to be expected because as discussed above, in II there are eight π-electrons from the oxo bridges which are shared over eight V-O bonds; in III there are two π-electrons from the vanadiums and four from the oxo bridge which can be shared over two V-O bonds. Hence a much higher bond order is possible in III compared to II. The V-I distances in III, 2.614 (1) and 2.618 (2) Å, are shorter than that in [CpVI]$_2$[CpV(NO)]$_2$(μ-O)$_4$ (2.653 (2) Å[23]). However the oxidation state of the vanadium in the latter compound is uncertain.

The green, air-stable complex [Cp*VI(O)]$_2$(μ-O) has ν(V=O) at 955 cm^{-1} in the infrared spectrum, similar to I, since it too contains vanadium(V) and is diamagnetic as expected. It is exactly analogous to [CpMoI(O)]$_2$(μ-O) which has two CpMoI(O) units linked by a symmetrical, linear Mo-O-Mo bridge.[53] We therefore propose the same structure for [Cp*VI(O)]$_2$(μ-O).

(50) Small paramagnetic shifts appear to be general for Cp*V derivatives. For instance the ^{1}H NMR of Cp*$_2$VCl$_2$ has the CH$_3$ resonance at 9.5 ppm, Cp*$_2$VCl at 7.6 ppm, and II at 10.4 ppm. In all cases the resonances are very weak and broad. Of complexes investigated by us only Cp*VCl$_3$ shows an intense resonance, at -28.7 ppm.

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some of the experiments on Cp*$_2$VCl$_2$, and the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

[Cp*$_2$V(NO)]$_2$I$_8$, 104090-40-6; [Cp*VI(O)]$_2$(μ-o), 104090-41-7.

Alkyne Adducts of Mixed Chloro–Dimethylamido Ditungsten Compounds

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Alkyne adducts of formula W$_2$Cl$_2$(NMe$_2$)$_4$(μ-C$_2$RR$'$)(py)$_2$ (R = R$'$ = H; R = R$'$ = Me; R = Me, R$'$ = H; R = Ph, R$'$ = H) have been isolated from the reactions of alkynes with W$_2$Cl$_2$(NMe$_2$)$_4$ in the presence of pyridine. These compounds, with the exception of W$_2$Cl$_2$(NMe$_2$)$_4$(μ-C$_2$H$_2$)(py)$_2$ (III), undergo thermal ligand redistribution reactions in hydrocarbon solvents to produce compounds having the general formula W$_2$Cl$_x$(NMe$_2$)$_{6-x}$(μ-alkyne)(py)$_2$, where x = 3 and 4, and W$_2$(NMe$_2$)$_6$. Thus, W$_2$Cl$_2$(NMe$_2$)$_4$(μ-PhC$_2$H)(py)$_2$ reacts in toluene at ca. 50 °C to produce W$_2$Cl$_3$(NMe$_2$)$_3$(μ-PhC$_2$H)(py)$_2$·^{1}/$_2$C$_7$H$_8$ (V) in good yields. Compound V is very sparingly soluble in hydrocarbon solvents, and no further decomposition has been observed. By contrast, W$_2$Cl$_2$(NMe$_2$)$_4$(μ-C$_2$Me$_2$)(py)$_2$ undergoes ligand redistribution in toluene and, at ca. 55 °C, yields W$_2$Cl$_4$(NMe$_2$)$_2$(μ-C$_2$Me$_2$)(py)$_2$ (VI) presumably via the initial formation of W$_2$Cl$_3$(NMe$_2$)$_3$(μ-C$_2$Me$_2$)(py)$_2$. No further decomposition of compound VI has been observed. Single-crystal X-ray studies reveal pseudotetrahedral W$_2$(μ-C$_2$) cores in both III and V, arising from the "perpendicular" addition of the alkynes to the (W≡W)$^{6+}$ centers. The C–C (1.38 (1) Å in III, 1.40 (1) Å in V) and the W–W (2.597 (1) Å in III, 2.657 (1) Å in V) distances approach C–C and W–W single bond distances and conform closely to the description of dimetallatetrahedranes. The overall geometry around each of the tungsten atoms, in III and V, can be considered pseudooctahedral, and these octahedra are joined together through the agency of the μ-C$_2$H$_2$ and two μ-NMe$_2$ ligands in III and by the ligands μ-PhC$_2$H and μ-Cl and one μ-NMe$_2$ in V. Compound VI, on the other hand, contains a μ-C$_2$Me$_2$ moiety which shows a large deviation, θ = 35°, from being in an ideal perpendicular orientation, θ = 0. There are two significantly different W–C distances, 2.02 (1) and 2.44 (1) Å, approaching W–C double and nonbonding distances, respectively. These data, coupled with the observed short W–W distance of 2.436 (1) Å, indicate incipient 1,2-dimetallacyclobutadiene characteristics within the W$_2$(μ-C$_2$) core in VI. These studies are compared with the related alkyne adducts of W$_2$(OR)$_6$ compounds. Crystal data for (i) W$_2$Cl$_2$(NMe$_2$)$_4$(μ-C$_2$H$_2$)(py)$_2$·CH$_2$Cl$_2$ at −160 °C: a = 17.123 (5) Å, b = 12.012 (3) Å, c = 7.410 (1) Å, α = 105.80 (1)°, β = 94.71 (1)°, γ = 101.93 (1)°, Z = 2, d_{calcd} = 2.069 g cm^{-3}, and space group P$\bar{1}$. (ii) W$_2$Cl$_3$(NMe$_2$)$_3$(μ-PhC$_2$H)(py)$_2$·^{1}/$_2$C$_7$H$_8$ at −161 °C: a = 14.701 (7) Å, b = 12.137 (6) Å, c = 17.632 (9) Å, β = 103.15 (3)°, Z = 4, d_{calcd} = 1.979 g cm^{-3}, and space group P2$_1$/n. (iii) W$_2$Cl$_4$(NMe$_2$)$_2$(μ-C$_2$Me$_2$)(py)$_2$ at −160 °C: a = 10.918 (4) Å, b = 13.440 (5) Å, c = 16.558 (7) Å, β = 104.45 (2)°, Z = 4, d_{calcd} = 2.287 g cm^{-3}, and space group P2$_1$/n.

Introduction

Recent interest in the study of the reactivity between alkynes and ditungsten hexaalkoxides has resulted in a fascinating array of novel organometallic compounds.[1] The products depend on the specific substituents on the alkoxide and the alkyne ligands and also on the reaction conditions. In all, three general reaction types are observed which are summarized in eq 1–3.

$$W_2(OR)_6 + py + R'C\equiv CR \qquad (1)$$

$$W_2(O\text{-}t\text{-}Bu)_6 + RC\equiv CR \rightarrow 2(Bu\text{-}t\text{-}O)_3W\equiv CR \quad (2)$$

R = Me, Et, Pr, etc (see *Organometallics* **1985**, *4*, 69)

$$W_2(O\text{-}t\text{-}Bu)_6 + 2C_2H_2 \rightarrow W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4) \qquad (3a)$$

$$W_2(OR)_6 + 3R'C\equiv CR' \rightarrow W_2(OR)_6(\mu\text{-}C_4R_4')(C_2R_2') \qquad (3b)$$

R = *i*-Pr, CH$_2$-*t*-Bu; R$'$ = H, Me

It is clearly evident that the steric bulk of the alkoxide ligands as well as the substituents on the alkynes play a major role in determining the nature of the products.

With this background, attention was turned to reactions of alkynes with (W≡W)$^{6+}$ centers containing other ligands. It has been observed that W$_2$(NMe$_2$)$_6$ does not react with alkynes.[2] However, substitution of two NMe$_2$ ligands by

(1) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69.

(2) Ahmed, K. J.; Chisholm, M. H., unpublished work.