Journal of Organometallic Chemistry, 465 (1994) 181–185

JOM 23947

A route to η^2-alkyne complexes of vanadium(I): crystal structure of *trans*-[IV(CO)$_2$(PMe$_2$Ph)$_2$(2-butyne)]

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(Received May 26, 1993)

Abstract

The reaction between [V(CO)$_6$]$^-$, halogens, phosphines and alkynes yields the complexes *trans*-[HalV(CO)$_2$(PR$_3$)$_2$(alkyne)], which have been characterized by IR and multinuclear NMR spectroscopy. The structure of the title compound has been determined by a single crystal X-diffraction study.

Key words: Vanadium; Alkyne; Crystal structure

1. Introduction

Alkyne complexes of the elements of the vanadium triade are of interest as being, *inter alia*, reactive intermediates in the *in vitro* and *in vivo* hydrogenations (reductive protonation) of alkynes. Stereo-selective *in vitro* hydrogenation of alkynes to Z-alkenes has been reported to occur in the presence of MCl$_5$/Zn (M = Nb, Ta) catalysts [1]. Acetylene is reductively protonated to give ethylene and ethane *in vivo* by vanadium nitrogenase [2]. In both reactions, coordination of the substrate alkyne to the metal is probably the initiating step. To obtain further insight into the role of the metal centre in these reactions we are carrying out isolation of well-defined alkyne complexes.

While several alkyne niobium and tantalum complexes mostly of the general compositions HalM(CO)$_2$L$_2$(alkyne) [3–5] and [Hal$_4$ML(alkyne)]$^-$ [6,7] have been reported recently, information on alkyne vanadium complexes is scarce. To date, the only known vanadium complexes carrying alkyne ligands in the side-on coordination mode are cyclopentadienyl complexes such as CpVL$_2$(alkyne) [8,9], the thermally unstable [V(CO)$_5$(alkyne)]$^-$ [10], and [V(dmpe)$_2$(RC≡CR)]$^+$, and the complexes BrV(dmpe)$_2$(RC≡CR) (R = Me$_3$SiO). The last items have been synthesized from [V(CO)$_2$(dmpe)$_2$]$^-$ by reductive CO coupling in the presence of Me$_3$SiX [11]. We showed previously that in HalNb(CO)$_4$(PR$_3$)$_2$ two of the CO ligands are substitution-labile and can be replaced by an alkyne acting as a four-electron donor [5]. Application of modified versions of this route to vanadium complexes has now enabled preparation of a variety of alkyne vanadium compounds HalV(CO)$_2$(PR$_3$)$_2$(alkyne) that are stable in an inert atmosphere.

2. Experimental details

2.1. General

All operations were carried out under inert gas by Schlenk techniques. Solvents were thoroughly dried and distilled under nitrogen. IR spectra were recorded on a Perkin-Elmer 1720 FT spectrometer as THF solutions in 0.1 mm CaF$_2$ cells. NMR spectra, obtained on a Bruker WH 360 spectrometer, were scanned in THF-d$_8$ (^{1}H) or toluene-d_8 (^{13}C, ^{51}V). δ(^{51}V) values are referenced against VOCl$_3$.

2.2. X-ray diffraction study of 3

Data were collected at room temperature in the $\theta/2\theta$ scan mode (θ range 2.48–25.06°) on a Syntex $P2_1$ diffractometer (Mo K$_\alpha$, graphite monochromator). The structure was solved with the program SHELXS-86. A full matrix block least squares (F^2) refinement was

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0022-328X/94/$7.00
SSDI 0022-328X(93)23947-V

carried out with the gamma version of the program SHELXL-92 [12]. The positions of the non-hydrogen atoms were obtained from a Patterson synthesis. The V, I and P atoms were refined anisotropically. Because of the small number of significant reflections (*cf*. Table 1), the two oxygens and all carbons were treated isotropically. The phenyl carbons were placed in fixed positions. Hydrogens were included in the later states of refinement with fixed positions and thermal parameters.

2.3. *Preparation of IV(CO)$_2$(PMe$_2$Ph)$_2$(2-butyne) (3)*

A solution of 350 mg (1.0 mmol) of [Et$_4$N][V(CO)$_6$] in 20 ml of THF was cooled to *ca*. 195 K in a dry-ice bath and treated with 250 mg (1.0 mmol) of iodine. A white powder, [Et$_4$N]I, separated out and the solution turned red {ν(CO) in THF at *ca*. 220 K: 2104w, *2027s*, *1931s*, 1973br, *1891m*; bands in italics correspond to [V$_2$(CO)$_8$(μ-I)$_3$]$^-$ (**1**) by analogy with the pattern reported for the Nb complex [13]}. The ^{51}V NMR at 253 K shows a main signal at $\delta = -983$ (-1011 at 223 K) assigned to **1**, and a minor signal at $\delta = -1251$ ppm (possibly IV(CO)$_6$)]. On addition of 0.28 ml (2.0 mmol) of PMe$_2$Ph, CO is evolved and the red colour intensi-

TABLE 1. Structural data for **3**

Crystal data	
Empirical formula	$C_{22}H_{28}IO_2P_2V$
Molecular mass, g mol^{-1}	564.26
Crystal dimensions, mm	0.2×0.2×0.3
Space group	*P*3(2)
Unit cell dimensions	
a, Å	14.305(2)
c, Å	32.852(7)
Volume, Å^3	5822(2)
Z	9
Density (calcd.), g cm^3	1.448
Absorption coefficient, cm^{-1}	17
F(000)	2538
Data collection, solution and refinement	
Index ranges	$-13 < h < 14$, $-13 < k < 14$, $-39 < l < 39$
Reflexions collected	13,760
Independent reflctns ($R_{int} = 0.2032$)	12,107
No. of refined parameters	325
Goodness of fit	0.672
$wR2 = \sqrt{\ }[\Sigma w(F_o^2 - F_c^2)_2 / \Sigma w F_o^4]$	0.162
Conventional *R* (based on 2506 reflctns with $I > 2\sigma(I)$	0.062
Largest diff. peak and hole, e Å^{-3}	0.370 and -0.322

TABLE 2. Selected spectroscopic data for some alkyne-vanadium complexes

Complex	ν(CO)/cm^{-1}		δ(^{1}H) [a]/ppm	δ(^{13}C)/ppm		δ(^{51}V)/ppm [c]
	Pentane	THF [b]		C≡C	CO	
BrV(CO)$_2$(PMe$_2$Ph)$_2$(1-hexyne)	1912	1981, 1903	10.73	216.8, 199.5	231.9	−370
IV(CO)$_2$(PMe$_2$Ph)$_2$(1-hexyne)	1911	1976, 1903	10.85	216,8, 200.0	232.7	−380
IV(CO)$_2$(PEt$_3$)$_2$(1-hexyne)	1908	1970, 1898	10.81	211.8, 195.1	233.8	−419
IV(CO)$_2$(PMe$_2$Ph)$_2$(2-butyne) (**3**) [d]	1906	1971, 1898		211	231.5	−455
IV(CO)$_2$(PMe$_2$Ph)$_2$(3-hexyne)	1904	1970, 1898		212.5	231.5	−410
IV(CO)$_2$(PEt$_3$)$_2$(3-hexyne)	1901	1964, 1891		209.9	233.6	−438
IV(CO)$_2$(PMe$_2$Ph)$_2$(PhC≡CH)	1928	1987, 1920	11.10	211.6, 206.8	[e]	−321
IV(CO)$_2$(PMe$_2$Ph)$_2$(HC≡CH)	1924	1986, 1913	10.87 [f]	200.7 [f]	[e]	−355

[a] For the protons attached to the trebly bonded carbons. [b] The relative intensities of the two CO stretching modes in THF are *w* and vs. [c] $W_{1/2}$ are around 2.5 kHz. [d] Additional ^{13}C NMR data for **3**: 18.2 (*Me*C≡C*Me*), 21.3 (P*Me*$_2$Ph), 141.5 ppm ["two triplets" (^{31}P-decoupled: one singlet), $J(^{31}P-^{13}C) = 14$ Hz; tentatively assigned C_{ipso} of PMe$_2$*Ph*]. [e] Not observed. [f] In C_6D_6.

$$\begin{tikzcd}
{[Et_4N][V(CO)_6] + Hal_2} \arrow[r, "-78^\circ C"] \arrow[d, "+PR_3,\ h\nu"] & {[\{V(CO)_4\}_2(\mu\text{-}Hal)_3]^- + [Et_4N]Hal} \arrow[d, "+PR_3\ (-78^\circ C)"] \\
{[Et_4N][V(CO)_4(PR_3)_2]} \arrow[r, "+I_2\ (-78^\circ C)"] & HalV(CO)_4(PR_3)_2 \arrow[d, "+RCCR' \\ -78^\circ C \rightarrow \text{room temp.}"] \\
& HalV(CO)_2(PR_3)_2(RCCR')
\end{tikzcd}$$

Scheme 1.

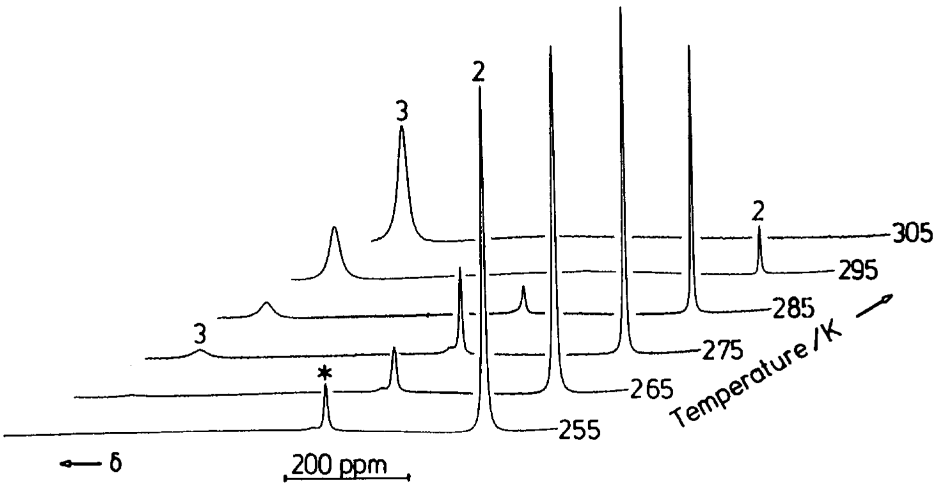

Fig. 1. Variable temperature 94.7 MHz ^{51}V NMR spectra, showing the formation of IV(CO)$_2$(PMe$_2$Ph)$_2$(2-butyne) (3) from IV(CO)$_4$(PMe$_2$Ph)$_2$ (2) on addition of 2-butyne and warming of the reaction mixture. The signal indicated * is possibly IV(CO)$_3$(PMe$_2$Ph)$_3$ or IV(CO)$_2$(PMe$_2$Ph)$_4$.

fies [the ^{51}V NMR at 253 K shows two new signals at $\delta = -1084$ ppm (main component, assigned IV(CO)$_4$(PMe$_2$Ph)$_2$, **2**) and -832 ppm, probably IV(CO)$_{6-n}$(PMe$_2$Ph)$_n$, $n = 3$ or 4]. After treatment with a ten-fold excess of 2-butyne, the suspension was warmed to room temperature during *ca.* 10 h, during which additional CO was evolved and the green complex **3** formed. [Et$_4$N]I was filtered off, and the filtrate evaporated *in vacuo*. The oily green residue was dissolved in 50 ml of boiling pentane and the solution filtered, then cooled initially to room temperature and then to 195 K. Green crystals of **3** separated from the solution. These were isolated, washed three times with cold pentane, and dried *in vacuo*. Yield: 250 mg (44%). Analysis: Calcd. for C$_{22}$H$_{28}$IO$_2$P$_2$V (564.26): C, 46.83; H, 5.00. Found: C, 45.83; H, 5.00%.

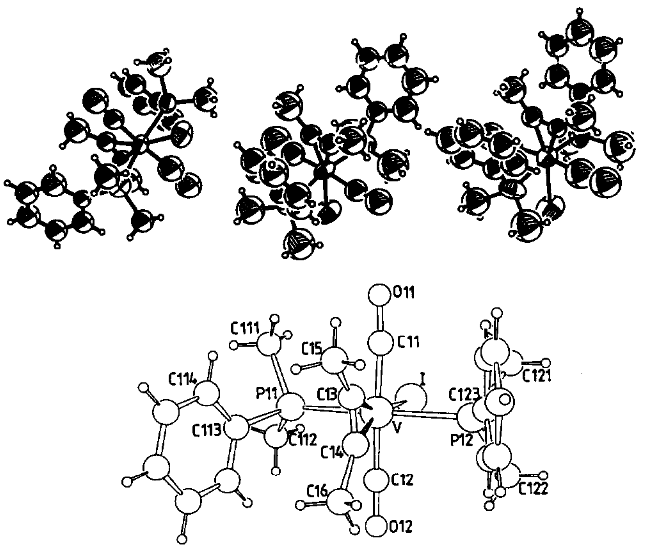

Fig. 2. ORTEP plot (50% probability ellipsoids for V, I and P) of the three independent molecules of the title compound **3**, and Schakal plot and numbering scheme for molecule number 1. Selected distances (Å) and angles (°): V1-I1 2.816(3), V1-P11 2.468(9), V1-P12 2.470(8), V1-C11 1.80(2), V1-C12 1.84(3), V1-C13 1.92(2), V1-C14 1.90(2), C13-C14 1.20(2); I1-V1-C11 87.4(7), I1-V1-C12 84.2(9), I1-V1-C13 162.3(7), I1-V1-C14 161.0(7), P11-V1-P12 169.2(2), C11-V1-C12 171.7(9), C13-V1-C14 36.6(6), V1-C13-C14 71(2), V1-C13-C15 144(2), V1-C14-C16 155(2).

The other complexes (Table 2) were prepared by analogous methods in about the same yields (except for IV(CO)$_2$(PMe$_2$Ph)$_2$(PhC≡CH), for which the yield was 11%). All the complexes slowly (within weeks) gave off CO even when stored as solids at 0°C. No complex formation was observed with tolane.

3. Results and discussion

3.1. Preparation and spectroscopic characteristics

The preparative routes are summarized in Scheme 1. Reaction of yellow hexacarbonylvanadate($-$I) with iodine or bromine in THF at dry-ice temperature leads to a red solution, apparently (IR evidence, see Experimental section) containing [{V(CO)$_4$}$_2$(μ-Hal)$_3$]$^-$ (**1**) as the main component. On addition of phosphine (PEt$_3$ or PMe$_2$Ph) the red HalV(CO)$_4$(PR$_3$)$_2$ (**2**) is formed. Addition of alkyne followed by warming to room temperature yields the green HalV(CO)$_2$(PR$_3$)$_2$(alkyne). This last step is confirmed by variable temperature ^{51}V NMR spectra shown in Fig. 1. The intermediate **2** can also be generated by the reaction between tetracarbonyl-bis(phosphine)vanadate and halogen. Compounds **1** and **2** are stable at low temperatures and in solution only, in contrast to their niobium analogues [13,14]; their formulae were assigned on the basis of IR and ^{51}V NMR data (see Experimental section).

Typical spectroscopic data of isolated complexes are collated in Table 1. The ν(C≡C) stretching frequency,

TABLE 3. Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement parameters $(A^2 \times 10^3)$ for IV(CO)$_2$(PMe$_2$Ph)$_2$(2-butyne). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
I(1)	10007(2)	2523(1)	7333(1)	106(1)
V(1)	10014(3)	588(3)	7330(2)	64(1)
I(2)	599(1)	4217(1)	9664(1)	142(1)
V(2)	2661(3)	6068(3)	9723(1)	77(2)
I(3)	4215(1)	600(1)	8337(1)	140(1)
V(3)	6065(3)	2666(3)	8274(1)	70(1)
P(11)	10467(5)	949(5)	8058(2)	76(2)
P(12)	9521(5)	471(5)	6605(2)	77(2)
P(21)	2753(6)	5692(5)	8999(2)	104(3)
P(22)	2215(5)	6028(5)	10451(2)	102(3)
P(31)	5688(5)	2770(6)	8999(2)	109(3)
P(32)	6019(5)	2200(5)	7550(2)	100(3)
C(11)	11410(18)	1317(17)	7183(7)	78(8)
O(11)	12369(14)	1812(13)	7112(5)	121(7)
C(12)	8591(23)	−29(22)	7479(10)	133(11)
O(12)	7624(15)	−518(14)	7564(6)	134(7)
C(13)	9550(19)	−953(19)	7341(7)	80(8)
C(14)	10507(19)	−448(17)	7292(7)	74(7)
C(15)	8561(18)	−2105(16)	7444(9)	136(11)
C(16)	11322(18)	−786(18)	7233(8)	127(10)
C(111)	9836(18)	1383(19)	8388(7)	124(10)
C(112)	11874(16)	1994(17)	8186(7)	121(10)
C(113)	10332(12)	−241(9)	8332(4)	67(6)
C(114)	9300(10)	−1017(12)	8454(4)	108(9)
C(115)	9125(8)	−1980(10)	8625(4)	96(8)
C(116)	9982(12)	−2168(9)	8675(4)	93(7)
C(117)	11014(10)	−1392(12)	8553(4)	95(8)
C(118)	11189(9)	−429(10)	8382(4)	83(7)
C(121)	8163(15)	147(16)	6475(6)	91(8)
C(122)	10423(16)	1661(15)	6307(7)	111(9)
C(123)	9731(12)	−541(10)	6338(4)	58(6)
C(124)	8851(9)	−1580(12)	6307(4)	90(8)
C(125)	8981(10)	−2400(8)	6139(5)	90(8)
C(126)	9990(13)	−2180(10)	6001(4)	106(8)
C(127)	10869(9)	−1141(12)	6032(4)	100(8)
C(128)	10739(9)	−322(8)	6201(4)	114(9)
C(21)	3247(19)	5153(20)	9818(8)	107(9)
O(21)	3650(15)	4658(14)	9914(6)	154(8)
C(22)	1989(25)	6800(25)	9567(10)	165(14)
O(22)	1559(17)	7332(18)	9507(7)	177(9)
C(23)	4273(17)	7032(16)	9782(7)	82(7)
C(24)	3764(15)	7555(16)	9696(6)	64(7)
C(25)	5342(17)	7240(18)	9885(8)	131(10)
C(26)	4064(19)	8717(17)	9666(9)	152(12)
C(211)	2732(20)	4451(18)	8860(8)	146(11)
C(212)	1809(20)	5724(22)	8627(10)	186(14)
C(213)	4071(9)	6634(12)	8768(5)	86(7)
C(214)	4856(13)	6353(9)	8696(5)	99(8)
C(215)	5850(11)	7110(14)	8536(5)	129(10)
C(216)	6060(10)	8148(12)	8448(5)	132(10)
C(217)	5275(14)	8429(9)	8521(5)	113(9)
C(218)	4280(11)	7672(13)	8681(5)	118(9)
C(221)	1215(21)	6443(21)	10560(9)	193(16)
C(222)	1730(23)	4856(23)	10718(11)	222(16)
C(223)	3408(9)	6916(12)	10738(4)	92(8)
C(224)	4121(13)	6596(9)	10881(4)	117(9)
C(225)	5098(11)	7351(14)	11054(4)	101(8)
C(226)	5363(10)	8425(12)	11084(5)	140(10)
C(228)	3673(12)	7990(14)	10768(5)	109(9)
C(31)	6828(20)	1933(19)	8389(9)	109(10)
O(31)	7303(17)	1481(16)	8525(6)	191(8)
C(32)	5178(18)	3227(18)	8146(8)	95(8)
O(32)	4660(13)	3676(13)	8087(5)	131(7)
C(33)	7122(17)	4190(18)	8205(7)	79(8)
C(34)	7571(18)	3764(17)	8274(7)	81(8)
C(35)	7203(19)	5304(17)	8127(8)	144(11)
C(36)	8778(18)	4012(20)	8353(9)	157(12)
C(311)	4446(21)	2530(23)	9123(9)	201(15)
C(312)	5765(23)	1842(21)	93344(10)	204(15)
C(313)	6624(11)	4071(9)	9210(4)	81(7)
C(314)	7649(13)	4252(11)	9305(5)	106(8)
C(315)	8413(9)	5234(13)	9472(5)	106(9)
C(316)	8152(12)	6034(9)	9544(5)	111(9)
C(317)	7127(14)	5852(11)	9449(5)	138(11)
C(318)	6364(10)	4871(14)	9282(5)	124(10)
C(321)	6365(19)	1202(19)	7397(9)	155(12)
C(322)	4817(20)	1771(22)	7287(10)	184(14)
C(323)	6957(11)	3390(9)	7270(4)	61(6)
C(324)	6563(9)	4041(12)	7127(4)	124(9)
C(325)	7260(13)	5031(11)	6949(4)	117(9)
C(326)	8353(12)	5371(9)	6914(4)	137(10)
C(327)	8747(8)	4720(12)	7057(5)	108(9)
C(328)	8050(12)	3730(11)	7235(4)	86(7)

reportedly between 1500 and 1630 cm^{-1} in other V(d^4) systems [8,11] was not detected in our complexes. There is only a single CO stretch in pentane, in accordance with the *trans* position of the two CO ligands revealed by X-ray structure analysis (*vide infra*). A second weak signal is observed in THF, indicative of some degree of distortion in this polar solvent. In IV(CO)$_2$(PMe$_2$Ph)$_2$-(PhC≡CH) and IV(CO)$_2$(PMe$_2$Ph)(HC≡CH), the C≡O bonds are clearly stronger than in the complexes containing alkylacetylenes, suggesting that there is a lower electron density in the C≡C bond of the complexes containing PhC≡CH and HC≡CH, where there are no inductive $(+I)$ effects from the substituents on the carbons. Reduced electron density in the alkyne will lead to lower electron density at the vanadium centre, and this in turn leads to diminished back-donation into π^* orbitals of CO.

The special situation of the complexes containing acetylene and phenylacetylene is also reflected in the significantly lower shielding of the ^{51}V nucleus. Generally, ^{51}V shielding is low in these V(d^4) alkyne complexes (see also Fig. 1), with the alkyne acting as a four-electron donor. A corresponding feature has been noted for $\delta(^{93}$Nb) in the related niobium complexes [14]. The 4e donation also induces marked low-field

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* Reference number with asterisk indicates a note in the list of references.

shifts of the ^{1}H and ^{13}C NMR resonances. As an example, coordination shifts for IV(CO)$_2$(PMe$_2$Ph)$_2$(1-hexyne) amount to $\Delta\delta(^1H) = 9.12$ ppm, and $\Delta\delta(^{13}C) = 131.9$ ppm for C1 and 132.3 ppm for C2.

The ^{13}C signals are sharp as a consequence of practically complete relaxation decoupling of the nuclei ^{13}C and ^{51}V ($I = 7/2$). For the CO ligands, some residual coupling is observed; the CO resonances therefore are relatively broad ($W_{1/2}$ *ca.* 170 Hz). The ^{31}P NMR spectrum of **3** exhibits a broad signal of $W_{1/2} = 1050$ Hz at 0.6 ppm. This plateau-like signal is typical of complete but unresolved ^{31}P–^{51}V coupling; $^1J(^{31}P-^{51}V)$ *ca.* 140 Hz.

3.2. *The crystal and molecular structures of 3*

The structure of the title compound, **3**, was solved and refined in the chiral space group $P3(2)$ (*cf.* Table 1 for structure data and Table 3 for fractional coordinates and isotropic temperature factors). A full list of bond lengths and angles, and tables of hydrogen atom coordinates and anisotropic thermal parameters have been departed at the Cambridge Crystallographic Data Centre. There are three independent molecules in the asymmetric unit (*cf.* Fig. 2) with insignificant differences in their bonding parameters (caption to Fig. 2). The molecule is best described as an octahedron, with iodine and butyne, the two CO ligands, and the two phosphines mutually *trans*. There are, however, distortions from ideal octahedral bond angles. The two phenyls of the phosphine ligands are in the *syn* position, in contrast to the situation in IV(CO)$_2$(PMe$_2$Ph)$_2$-(HC≡CH), in which the phenyls are *anti* to each other [15*]. This rules out the possibility that the size of iodine is responsible for the *syn* arrangement in **3**, and favours a stacking interaction between the phenyls and 2-butyne in **3**. The average distance between the phenyl carbons and the carbons forming the triple bond is 3.93 Å. The V–C(butyne) and C≡C bond lengths, and the bond angles within the V(η^2-C≡C) fragment, compare with those in η^5-IndV(CO)$_2$(η^2-PhC≡CH) [8a] and BrV(dmpe)$_2$(η^2-Me$_3$SiOC≡COSiMe$_3$) [11].

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