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Structure and Reactivity of Mono(cyclopentadienyl)vanadium Alkynyl and Aryne Complexes

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Starting from CpVCl$_2$(PMe$_3$)$_2$ (**1**) the paramagnetic mono- and bis(phenylethynyl) complexes CpVCl$_{2-n}$(C≡CPh)$_n$(PMe$_3$)$_2$ [n = 1 (**2**), 2 (**3**)] have been synthesized. Both compounds were characterized by X-ray diffraction and were found to be thermally more stable than other CpV^{III} hydrocarbyl complexes. The CpV^{III} bis(phenyl) complex CpVPh$_2$(PMe$_3$)$_2$ (**5**) decomposes at ambient temperature through β-hydrogen abstraction to give the first isolated vanadium benzyne complex, CpV(η^2-C$_6$H$_4$)(PMe$_3$)$_2$ (**6**). The molecular structure of **6** indicates that this compound can best be described as a high-spin d^2 vanadium(III) benzometallacyclopropene. The cyclopropene character is expressed in the reactivity of **6**, showing insertion of unsaturated substrates. Insertion of diphenylacetylene gives CpV(η^2-PhC=CPhC$_6$H$_4$)(PMe$_3$)$_2$ (**7**), with a planar vanadaindene structure, whereas terminal alkenes CH$_2$=CRR′ (R = H, Me; R′ = H, Me) insert regioselectively to give β-substituted metallaindanes CpV(η^2-CH$_2$-CRR′C$_6$H$_4$)PMe$_3$ (R and R′ = H, **8a**; R = H, R′ = Me, **8b**; R and R′ = Me, **8c**), which show a low thermal stability in case one of the β-substituents is a hydrogen. With *t*-BuCN double insertion followed by rearrangement of the intermediate diazametallacycle gives the isoindolenine-substituted vanadium(III) imido complex CpV[NC(*t*-Bu)N=C(*t*-Bu)C$_6$H$_4$](PMe$_3$)$_2$ (**9**). The benzyne complex **6** reacts with dihydrogen to form the known triple-decker CpV(C$_6$H$_6$)VCp through partial hydrogenation of the benzyne ligand.

Introduction

Recent years brought increased interest in hydrocarbyl complexes of trivalent vanadium.[1] Traditionally, studies in this area have dealt with (substituted) bis(cyclopentadienyl) systems Cp′$_2$VR (Cp′ = Cp or peralkylated Cp; R = alkyl, aryl, allyl, alkynyl),[2] although a number of homoleptic complexes, such as V[CH(SiMe$_3$)$_2$]$_3$[3] and VMes$_3$·THF (Mes = 2,4,6-trimethylphenyl),[4] have been reported. The last compound has recently been subject of an extensive reactivity study by Floriani *et al.*[1g−l]

A major contribution in this area has originated from the study of the mono(cyclopentadienyl)vanadium(III) dichloride complex CpVCl$_2$(PMe$_3$)$_2$,[5] which led to a range of organovanadium derivatives, not only of V(III) but also of V(II) and V(I). Important examples of the last two categories include hydride complexes of V(II)[1e] and the V(I) ethylene complex CpV(η^2-C$_2$H$_4$)(PMe$_3$)$_2$.[6]

Depending upon the steric demands of the alkyl group, V(III) dialkyl complexes[1b−d] with a varying

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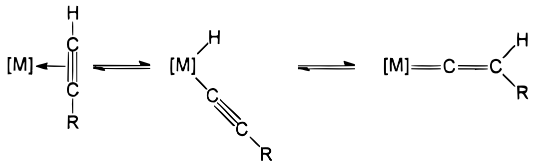
Scheme 1. 1-Alkyne to Vinylidene Tautomerization



degree of electron deficiency have been synthesized, ranging from 16-electron $CpVMe_2(PMe_3)_2$[1b,c] to 12-electron $CpV[CH(SiMe_3)_2]_2$.[1d] $CpVR_2$ complexes with alkyl groups containing β-hydrogens could however not be isolated, due to facile β-hydrogen transfer.[6] Hydrogen abstraction is important in the thermolysis of V(III) alkyl complexes, leading to interesting new species like metallacycles and alkylidenes.[1d,7] The 14-electron complex $CpV(CH_2\text{-}t\text{-}Bu)_2PMe_3$, for example, decomposes in the presence of dmpe through α-hydrogen transfer to give the first vanadium alkylidene $CpV({=}CH\text{-}t\text{-}Bu)(dmpe)$.[1d] Thermolysis of mono(cyclopentadienyl)vanadium(III) aryl complexes has however not been studied in detail yet.

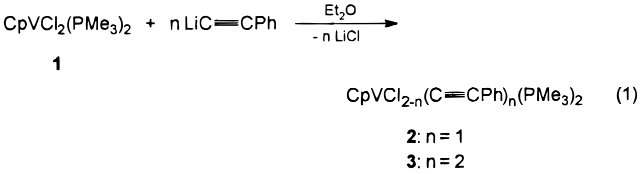
Transition metal alkynyl complexes have received much attention in recent years, largely due to the various bonding possibilities of acetylide anions and the ability of the ligands to react with both nucleophilic and electrophilic agents.[8] For vanadium, however, only the synthesis and characterization of several bis(cyclopentadienyl)vanadium(III) alkynyls have been reported.[2h,i,k] In this system, the stability of the V−C bond seems to depend largely on the steric and electronic nature of both the cyclopentadienyl and the alkynyl substituent: the simple cyclopentadienyl complexes $Cp_2VC{\equiv}CPh$[2h] and $Cp_2VC{\equiv}CC_6H_4C{\equiv}CVCp_2$[2i] were found to be thermally too unstable to be isolated chemically pure, whereas both the corresponding peralkylated cyclopentadienyl (C_5Me_4Et) derivatives[2h,i] as well as $Cp_2VC{\equiv}CCMe_3$[2k] were found to be stable.

The synthesis of mono- and bis(alkynyl) complexes of mono(cyclopentadienyl)vanadium(III) might lead to interesting starting materials for further reactivity studies, whereas their characterization could provide more structural information about the V−C single bond in low-valent vanadium complexes. For mono(alkynyl) complexes possible equilibria among metal−alkyne, metal−hydride alkynyl, and metal−vinylidene (Scheme 1), which have been shown to exist for several late transition-metal complexes,[9] could provide synthetic pathways to vanadium(III) vinylidene complexes. Bis(alkynyl)titanocene(IV) derivatives have been used as organometallic bidentate chelate ligands[10] in the preparation of homo- and heterobinuclear complexes containing bridging σ-π-alkynyl groups between the metal centers. Dependent on the arrangement of the alkynyl ligands, bis(alkynyl) complexes of vanadium(III) might display similar behavior.

In this paper we describe the syntheses and molecular structures of 16-electron CpV^{III} mono- and bis(alkynyl) complexes, as well as thermal decomposition studies of the diphenyl complex $CpVPh_2(PMe_3)_2$, which resulted in the formation of the first vanadium−benzyne complex. The molecular structure and some aspects of the reactivity of this CpV−benzyne complex will be discussed.

Results and Discussion

Syntheses and Molecular Structures of Mono(cyclopentadienyl)vanadium Alkynyl Complexes. Reaction of $CpVCl_2(PMe_3)_2$ (**1**)[5] with 1 or 2 equiv of (phenylethynyl)lithium in diethyl ether affords the mono- and bis(phenylethynyl) complexes $CpVCl_{2-n}(C{\equiv}CPh)_n(PMe_3)_2$ (**2**, $n = 1$; **3**, $n = 2$), respectively (eq 1).



$$\underset{\mathbf{1}}{CpVCl_2(PMe_3)_2} + n\,LiC{\equiv}CPh \xrightarrow[-\,n\,LiCl]{Et_2O} \underset{\mathbf{2}:\,n=1;\ \mathbf{3}:\,n=2}{CpVCl_{2-n}(C{\equiv}CPh)_n(PMe_3)_2} \quad (1)$$

Both are crystalline paramagnetic 16-electron compounds, which are thermally quite stable in hydrocarbon solvents. Solutions of **3** (benzene-d_6) can be kept at 100 °C for 16 h without significant decomposition. The ^1H NMR spectra of **2** and **3** show 2 broad resonances in each case. The resonances of the PMe_3 protons (δ −11.9 ppm for **2** and δ −8.8 ppm for **3)** follow the characteristic downfield trend upon progressive displacement of chlorine in **1** by hydrocarbyl ligands.[1c] Low-field resonances at δ 28.3 ppm for **2** and δ 23.9 ppm for **3** probably originate from some of the phenyl protons. No resonances for the cyclopentadienyl protons were observed, but this is normal for this type of CpV^{III} complex.[1c] The IR spectra of **2** and **3** show characteristic $\nu_{C{\equiv}C}$ vibrations at 2043 and 2041 cm^{-1}, respectively.[2g−k] Mixing of equimolar amounts of **1** and **3** in benzene-d_6 (1 week at 25 °C) does not result in the formation of **2** but leaves unreacted starting material, which is in marked contrast with the observed easy comproportionation of **1** and $CpVMe_2(PMe_3)_2$ to give the mono(methyl) complex $CpV(Me)Cl(PMe_3)_2$ (4−5 h at 25 °C).[1b,c] Alternatively, **2** could not be synthesized by σ-bond metathesis of $CpV(Me)Cl(PMe_3)_2$[1b,c] and phenylacetylene. In this experiment the acetylene is slowly polymerized to an insoluble polymer in a reaction reminiscent of the catalytic polymerization of ethyne by $CpVMe_2(PMe_3)_2$.[1c]

To elucidate the molecular structures of the two new vanadium alkynyl compounds, X-ray structure determinations were carried out. The crystal structure of the mono(phenylethynyl) compound **2** shows 4 molecules in the triclinic unit cell. The asymmetric unit contains two crystallographically independent, nearly identical molecules. The molecular structure of **2** is depicted in Figure 1 (one residue shown). Selected bond lengths and angles are given in Table 1.

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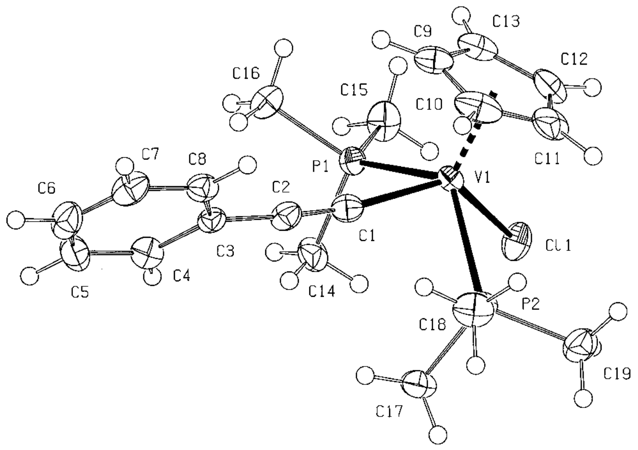

Figure 1. Molecular structure of CpVCl($C\equiv CPh$)(PMe_3)$_2$ (**2**). Only one of the two very similar but crystallographically independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Geometrical Data for CpVCl($C\equiv CPh$)(PMe_3)$_2$ (2)

residue 1		residue 2	
Bond Lengths (Å)			
V(1)−Cl(1)	2.4164(12)	V(2)−Cl(2)	2.4037(12)
V(1)−P(1)	2.4720(11)	V(2)−P(3)	2.4683(11)
V(1)−P(2)	2.4777(12)	V(2)−P(4)	2.4724(11)
V(1)−C(1)	2.060(4)	V(2)−C(20)	2.080(4)
V(1)−C(9)	2.276(3)	V(2)−C(28)	2.286(3)
V(1)−C(10)	2.266(5)	V(2)−C(29)	2.265(3)
V(1)−C(11)	2.295(5)	V(2)−C(30)	2.294(3)
V(1)−C(12)	2.325(4)	V(2)−C(31)	2.317(4)
V(1)−C(13)	2.307(4)	V(2)−C(32)	2.310(4)
C(1)−C(2)	1.214(5)	C(20)−C(21)	1.202(5)
C(2)−C(3)	1.437(5)	C(21)−C(22)	1.443(5)
Bond Angles (deg)			
Cl(1)−V(1)−C(1)	129.62(10)	Cl(2)−V(2)−C(20)	124.76(10)
Cl(1)−V(1)−P(1)	79.28(4)	Cl(2)−V(2)−P(3)	80.26(4)
Cl(1)−V(1)−P(2)	80.91(4)	Cl(2)−V(2)−P(4)	80.74(4)
C(1)−V(1)−P(1)	77.36(10)	C(20)−V(2)−P(3)	76.75(10)
C(1)−V(1)−P(2)	76.87(10)	C(20)−V(2)−P(4)	77.53(10)
P(1)−V(1)−P(2)	124.59(4)	P(3)−V(2)−P(4)	130.40(4)
V(1)−C(1)−C(2)	171.8(3)	V(2)−C(20)−C(21)	175.1(3)
C(1)−C(2)−C(3)	175.6(4)	C(20)−C(21)−C(22)	173.7(4)

The molecular structure of **2** can best be described as distorted square-pyramidal with the cyclopentadienyl function at the apical position.[11] The phosphine ligands are *trans* in the base plane. The V−Cl bond distances (2.416(1) and 2.404(1) Å for residues 1 and 2, respectively) are comparable to those found in the parent dichloride **1** (mean value of 2.403 Å).[1b,c] The V−P distances are in the range of those reported for other mono(cyclopentadienyl)vanadium bis(phosphine) compounds in medium to low oxidation states.[1b−e] The bond angles between the ligands in the square plane are unexceptional and show no sign of steric strain in the molecule.

The V−$C_{alkynyl}$ distances (2.060(4) and 2.080(4) Å for residues 1 and 2, respectively) and the $C\equiv C_{alkynyl}$ distances (1.214(5), 1.202(5) Å) are comparable to those observed in bis(cyclopentadienyl)vanadium(III) alkynyl complexes,[2j,k] whereas the V−C−$C_{alkynyl}$ bond angles (171.8(3), 175.1(3)°) are only slightly smaller than the corresponding angles in those complexes. As can be expected there is a clear elongation of the vanadium−carbon bond in mono(cyclopentadienyl)vanadium complexes with σ-bonded hydrocarbyl ligands on going from an sp-hybridized carbon (as in **2**, 2.060(4) Å) through an sp^2-hybridized carbon (as in CpV(η^2-PhC=CPhC$_6$H$_4$)(PMe_3)$_2$ (**7**), 2.110(2) Å; *vide infra*) to an sp^3-hybridized carbon (as in CpV(η^2-CH$_2$CMe$_2$C$_6$H$_4$)(PMe_3)$_2$, 2.194(3) Å).[1d]

Table 2. Selected Geometrical Data for CpV($C\equiv CPh$)$_2$(PMe_3)$_2$ (3)[a]

Bond Lengths (Å)			
V(1)−P(1)	2.4447(15)	V(1)−C(15)	2.297(14)
V(1)−C(1)	2.081(6)	V(1)−C(16)	2.294(13)
V(1)−C(12)	2.281(13)	C(1)−C(2)	1.208(8)
V(1)−C(13)	2.279(13)	C(2)−C(3)	1.425(8)
V(1)−C(14)	2.306(12)		
Bond Angles (deg)			
P(1)−V(1)−P(1)′	122.57(7)	C(1)−V(1)−P(1)′	79.25(14)
P(1)−V(1)−C(1)	77.06(13)	V(1)−C(1)−C(2)	175.3(4)
C(1)−V(1)−C(1)′	129.4(2)	C(1)−C(2)−C(3)	177.1(5)

[a] A prime indicates symmetry operation $-x, y, \frac{1}{2} - z$.

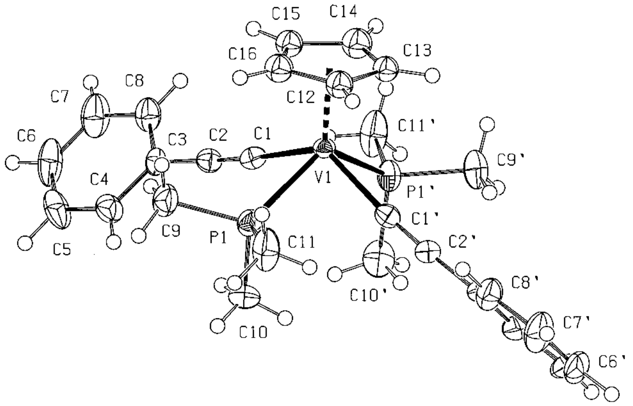

Figure 2. Molecular structure of CpV($C\equiv CPh$)$_2$(PMe_3)$_2$ (**3**). Thermal ellipsoids are drawn at the 50% probability level.

The bis(phenylethynyl) compound **3** crystallizes with 4 molecules in a monoclinic unit cell. Selected bond lengths and angles are given in Table 2.

The molecular structure of **3** (Figure 2) is very similar to that of **2** and can also best be described as distorted square-pyramidal,[12] with the cyclopentadienyl ligand in the apical position and the two phosphine ligands *trans* in the square plane. Due to crystallographic C_2 symmetry, with the 2-fold axis through the $Cp_{centroid}$ and the vanadium atom, only the bond distances and angles in half of the molecule are listed in Table 2. The cyclopentadienyl ring is disordered by the 2-fold axis in a 50:50 ratio. One of the two possible positions is shown in Figure 2. The V−P and V−$C_{alkynyl}$ bond distances of 2.4447(15) and 2.081(6) Å, respectively, are similar to those observed for **2**. The *trans* arrangement of the alkynyl ligands and the large C(1)−V(1)−C(1)′ bond angle of 129.4(2)° make the use of **3** as an organometallic bidentate chelate ligand unlikely.

Alkylation of **2** could provide alkyl−alkynyl complexes, which after hydrogenolysis of the V−alkyl bond might lead to vanadium hydride−alkynyl species. Unfortunately, salt metathesis of **2** and LiR [R = Me, Ph, CH$_2$-*t*-Bu, CH$_2$SiMe$_3$, CH(SiMe$_3$)$_2$] produces intractable

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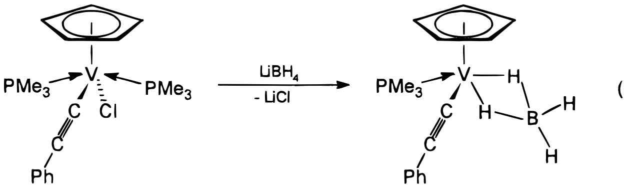
(11) Percentage along Berry pseudorotation coordinate (trigonal bipyramid to square pyramid): 80.1% for residue 1 and 78.6% for residue 2. See: Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119.

(12) Percentage along Berry pseudorotation coordinate (trigonal bipyramid to square pyramid): 76.5%. See ref 11.

materials. A more defined compound is observed in the reaction of **2** with 1 equiv of $LiBH_4$ (eq 2), where according to IR spectroscopy the vanadium(III) borohydride $CpV(\eta^2\text{-}BH_4)(C{\equiv}CPh)PMe_3$ (**4**) is produced.



(2)

2 **4**

The IR spectrum of **4** shows characteristic borohydride vibrations at 2363, 2342, and 2257 cm^{-1}, which correspond well with those observed for $CpV(\eta^2\text{-}BH_4)$dmpe[1c] and suggest η^2-coordination in **4** as well. Complex **4** is diamagnetic (by NMR spectroscopy) and represents one of the few examples of low-spin vanadium d^2 complexes.[1d] Formation of a low-spin $\eta^2\text{-}BH_4$ complex was also observed for the d^3 complex $CpV(BH_4)$dmpe.[1c] In the ^1H NMR spectrum four broadened doublets are observed for the BH_4 protons ($J_{BH} = 96$ Hz, $J_{PH} = 15$ Hz) and one doublet for the PMe_3 protons of **4**. However, multiple resonances in the cyclopentadienyl region indicate that this compound is not pure, as can also be seen from the elemental analysis. Repeated recrystallizations from pentane neither improved the elemental analysis nor gave less complicated ^1H NMR spectra.

Synthesis and Molecular Structure of $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$. Formation of monomeric η^2-benzyne species has been observed in a number of early[13] and late[14] transition metal systems. Given the instability of free aryne, benzyne complexes are generally synthesized by thermally induced elimination of alkanes or arenes from transition metal aryl complexes (eq 3).

$$L_xM(\text{aryl})R \xrightarrow[R\,=\,\text{alkyl, aryl}]{\Delta} L_xM(\eta^2\text{-aryne}) + RH \qquad (3)$$

Erker[15] has shown that the formation of aryne complexes during thermolysis of diarylzirconocenes follows a concerted elimination of arene. Zirconocene complexes with substituted benzynes have been used extensively by Buchwald *et al.* for selective transformations of use in organic synthesis.[13b]

Bis(aryl) $CpVPh_2(PMe_3)_2$ (**5**)[1b,c] was used as the starting material for the synthesis of an η^2-benzyne containing mono(cyclopentadienyl)vanadium complex. According to ^1H NMR spectroscopy, **5** is stable in benzene-d_6 at 25 °C for a period of over 2 weeks but decomposes at 50 °C ($t_{1/2} = 3{-}4$ h) through elimination of benzene to give $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$ (**6**), formally a vanadium(I) complex, which could be isolated as green crystals in moderate yield (50%) after recrystallization from pentane (eq 4).

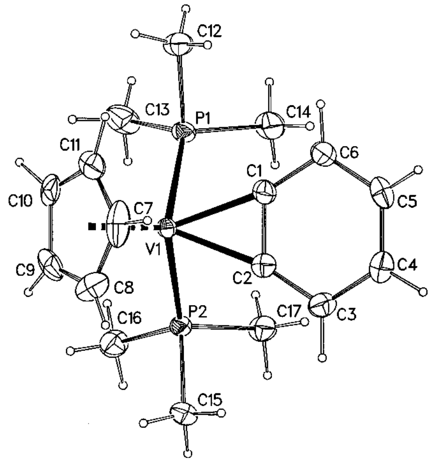
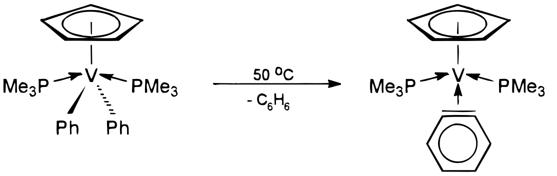


Figure 3. Molecular structure of $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$ (**6**). Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Geometrical Data for $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$ (6)

Bond Lengths (Å)			
V(1)–P(1)	2.4348(11)	V(1)–C(11)	2.297(4)
V(1)–P(2)	2.4272(11)	C(1)–C(2)	1.368(5)
V(1)–C(1)	2.055(3)	C(1)–C(6)	1.384(5)
V(1)–C(2)	2.049(3)	C(2)–C(3)	1.385(5)
V(1)–C(7)	2.291(4)	C(3)–C(4)	1.404(5)
V(1)–C(8)	2.292(4)	C(4)–C(5)	1.382(5)
V(1)–C(9)	2.303(3)	C(5)–C(6)	1.398(5)
V(1)–C(10)	2.302(3)		

Bond Angles (deg)			
C(1)–C(2)–C(3)	121.2(3)	P(1)–V(1)–C(1)	81.72(9)
C(2)–C(3)–C(4)	118.1(3)	P(1)–V(1)–C(2)	109.89(9)
C(3)–C(4)–C(5)	120.5(3)	P(2)–V(1)–C(1)	110.69(10)
C(4)–C(5)–C(6)	120.7(3)	P(2)–V(1)–C(2)	81.29(9)
C(1)–C(6)–C(5)	118.1(3)	C(1)–V(1)–C(2)	38.95(13)
P(1)–V(1)–P(2)	95.79(4)	V(1)–C(1)–C(2)	70.28(18)



(4)

5 **6**

The absorption at 1547 cm^{-1} in the IR spectrum of **6** is characteristic for a $\nu_{C{\equiv}C}$ vibration in η^2-benzyne complexes.[14] It is at lower energy than in the vanadium(I) η^2-alkyne complex $CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2$[6b] (1600 cm^{-1}), indicating more pronounced π-back-donation in case of the benzyne ligand, as can be expected for an alkyne system with substituents more bent away from the metal.

To further elucidate the bonding in **6** an X-ray structure determination was carried out. The molecular structure is depicted in Figure 3, and selected bond lengths and angles are given in Table 3.

Compound **6** exhibits a simple piano-stool geometry with a regular η^5-cyclopentadienyl and two phosphine ligands in an eclipsed geometry. The η^2-benzyne ligand is perpendicular to the plane through the Cp centroid and the metal center that bisects the P(1)–V(1)–P(2) angle. A similar orientation of the η^2-ligand has been observed in $CpV(\eta^2\text{-ethene})(PMe_3)_2$,[6] but in the diphenylacetylene complex $CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2$[6b] the

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(13) (a) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, 88, 1047 and references cited therein. (c) Cockscroft, J. K.; Gibson, V. C.; Howard, A. K.; Poole, A. D.; Siemeling, U.; Wilson, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1668. (d) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 262. (e) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697.

(14) (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3403. (b) Bennet, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(15) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

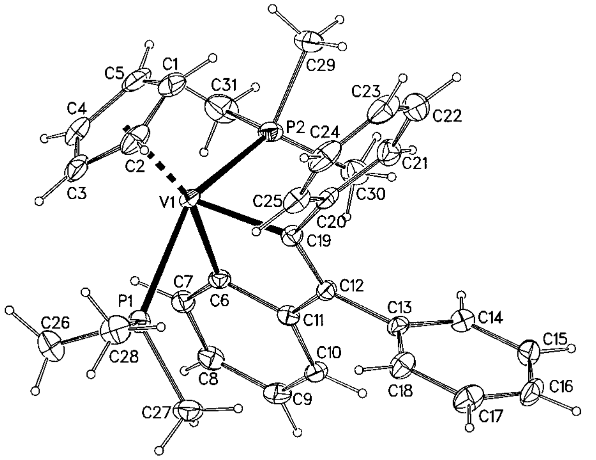


Figure 4. Molecular structure of CpV(η^2-PhC=CPhC$_6$H$_4$)(PMe$_3$)$_2$ (**7**). Thermal ellipsoids are drawn at the 50% probability level.

alkyne is oriented halfway between perpendicular and parallel, probably as a result of steric hindrance between the ligands in the complex. In Cp*TaMe$_2$(η^2-C$_6$H$_4$)[13d,e] a parallel orientation of the benzyne ligand and the plane through the Cp* centroid and the metal center that bisects the Me−Ta−Me angle has been found.

The V−C(benzyne) distances of 2.055(3) and 2.049(3) Å in **6** are in between the longer V−C(ethene) distances in CpV(η^2-ethene)(PMe$_3$)$_2$[6] (2.153(3) and 2.173(3) Å) and the shorter V−C(alkyne) distances in CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$[6b] (1.932(2) and 1.996(2) Å). The benzyne C(1)−C(2) distance of 1.368(5) Å is similar to the distances observed for other structurally characterized η^2-benzyne complexes[13,14] (ranging from 1.32(6) to 1.364(8) Å). Like in other η^2-benzyne complexes, except for Schrock's tantalum complex,[13d,e] no alternation of short and long C−C bonds corresponding to “frozen out” single and double bonds is found in the benzyne ligand of **6**. All C−C distances within the benzyne ring are identical within experimental error and vary little from the C−C bond in free benzene (1.392 Å),[16] while the angle between the benzyne plane and the plane containing V1, C1, and C2 is small (3.2(2)°). These data are consistent with a delocalized aromatic structure arising from electron pair donation from the in-plane π-orbital of the C$_6$ ring coupled with a high degree of back-donation from the metal to the benzyne π^* orbital. The benzyne in **6** may therefore be regarded as a 2-electron ligand resulting in an overall 16-electron count for the complex. This is in contrast with the alkyne ligand in CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$,[6b] which acts as a 4-electron donor, thereby allowing a formal 18-electron configuration. Complex **6** can best be regarded as a high-spin d^2 vanadium(III) benzometallacyclopropene.

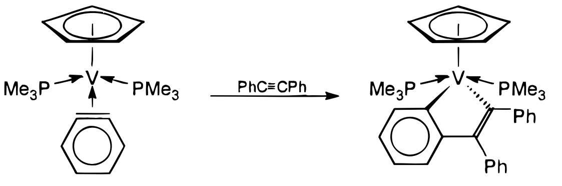
The high-spin character of **6** manifests itself in its paramagnetism (by NMR spectroscopy). The ^{1}H NMR spectrum shows several broad and shifted resonances. Resonances for the Cp and PMe$_3$ protons in a ratio of 5:18 are found at δ 158 and 7.13 ppm, respectively. The resonances due to the β- and γ-protons of the benzyne ligand were identified with the help of a ^{2}H NMR spectrum of CpV(η^2-C$_6$D$_4$)(PMe$_3$)$_2$ (**6-*d*$_4$**), prepared by thermolysis of CpV(C$_6$D$_5$)$_2$(PMe$_3$)$_2$ (**5-*d*$_{10}$**). This spectrum shows a broad resonance at δ −12.2 ppm for the β-deuterons, which corresponds to a resonance in the ^{1}H NMR spectrum of **6**, and a narrow resonance for the γ-deuterons at δ 7.46 ppm, which is overlapped by the PMe$_3$ signal in the ^{1}H NMR spectrum of **6**.

Table 4. Selected Geometrical Data for CpV(η^2-PhC=CPhC$_6$H$_4$)(PMe$_3$)$_2$ (7)

Bond Lengths (Å)			
V(1)−P(1)	2.5163(7)	C(6)−C(11)	1.432(3)
V(1)−P(2)	2.5077(8)	C(7)−C(8)	1.395(3)
V(1)−C(1)	2.317(3)	C(8)−C(9)	1.391(3)
V(1)−C(2)	2.317(3)	C(9)−C(10)	1.387(3)
V(1)−C(3)	2.342(2)	C(10)−C(11)	1.402(3)
V(1)−C(4)	2.366(2)	C(11)−C(12)	1.474(3)
V(1)−C(5)	2.334(2)	C(12)−C(19)	1.370(3)
V(1)−C(6)	2.143(2)	C(19)−C(20)	1.477(3)
V(1)−C(19)	2.110(2)	C(12)−C(13)	1.500(3)
Bond Angles (deg)			
P(1)−V(1)−P(2)	146.56(3)	V(1)−C(6)−C(11)	111.94(14)
P(1)−V(1)−C(6)	73.53(6)	C(6)−V(1)−C(19)	79.77(8)
P(2)−V(1)−C(6)	73.43(6)	C(6)−C(11)−C(12)	116.37(17)
P(1)−V(1)−C(19)	85.47(6)	C(11)−C(12)−C(19)	116.78(18)
P(2)−V(1)−C(19)	83.73(6)	Cp$_{\text{centroid}}$−V(1)−C(6)	150.22(18)
V(1)−C(19)−C(12)	115.12(15)	Cp$_{\text{centroid}}$−V(1)−C(19)	129.99(18)

Reactivity of CpV(η^2-C$_6$H$_4$)(PMe$_3$)$_2$. Reactions of CpV(η^2-C$_6$H$_4$)(PMe$_3$)$_2$ resemble those of CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$.[6b] With unsaturated substrates like alkynes, alkenes, and nitriles, C,C-coupled products are obtained.

Diphenylacetylene. In an NMR-tube experiment **6** reacts selectively with 1 equiv of diphenylacetylene. In this reaction a paramagnetic red-brown crystalline compound is formed, which was identified by X-ray diffraction as CpV(η^2-PhC=CPhC$_6$H$_4$)(PMe$_3$)$_2$ (**7**), a vanadaindene complex (eq 5).



6 **7** (5)

Complex **7** is thought to be formed by initial loss of a phosphine ligand, as indicated by the decrease of the rate of formation of **7** by the addition of extra PMe$_3$. The CpV(η^2-C$_6$H$_4$)PMe$_3$ fragment, formed under mild conditions (20 °C), then coordinates diphenylacetylene, whereupon the alkyne and benzyne ligand couple. Finally, trimethyl phosphine recoordinates to give **7**. During the reaction no intermediates could be detected by NMR spectroscopy.

The ^{1}H NMR spectrum of **7** shows several broad and shifted resonances. The aromatic indene ring protons give two broad resonances at δ −3.4 and −16.4 ppm. The assignment was made by comparing the ^{1}H NMR spectrum of **7** with that of the reaction product of CpV(η^2-C$_6$D$_4$)(PMe$_3$)$_2$ (**6-*d*$_4$**) and diphenylacetylene, in which these resonances were absent. The IR spectrum of **7** shows characteristic strong vibrations for the cyclopentadienyl and phosphine ligands at 793 and 945 cm^{-1}, respectively, as well as characteristic vibrations for the phenyl groups of the former diphenylacetylene moiety at 700, 721, and 1589 cm^{-1}.

The X-ray structure of **7** (Figure 4, selected geometrical data in Table 4) shows a distorted trigonal

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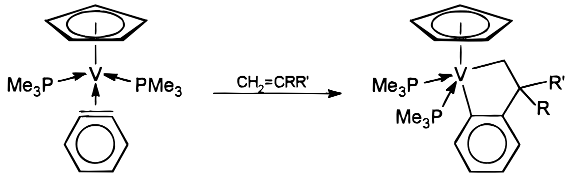
(16) Jeffrey, G. A.; Ruble, J. R.; Mc Mullan, R. K.; Pople, J. A. *Proc. R. Soc. London, A* **1987**, *414*, 47.

bipyramidal geometry around vanadium. The $Cp_{centroid}$ and the vanadaindene ring lie in the equatorial plane, the sum of the angles $Cp_{centroid}$−V(1)−C(6) (150.23(6)°), $Cp_{centroid}$-V(1)−C(19) (129.99(6)°), and C(6)−V(1)−C(19) (79.77(8)°) being 360°. The axial PMe_3 ligands exhibit angles smaller than 90° with the vanadaindene ring (72.77(3) and 73.76(4)°), probably due to steric reasons. The coordination geometry around vanadium contrasts markedly with the square-pyramidal geometry observed for the vanadaindane $CpV(\eta^2\text{-}CH_2CMe_2C_6H_4)(PMe_3)_2$, in which the phosphine ligands are in a *cis*-position.[1d] The bond angles in the vanadaindene fragment, all close to 120°, indicate sp^2-hybridization of the vanadium-bound C(6) and C(19). The more pronounced sp^2-character of the former acetylene carbon C(19) (V(1)−C(19)−C(12) = 115.12(15)°) compared to the former benzyne carbon C(6) (V(1)−C(6)−C(11) = 111.94(14)°) is expressed in the shorter V−C distance of the first (2.110(2) and 2.143(2) Å, respectively). Both V−C bonds are shorter than the $V-C_{sp^3}$ bond (2.194(3) Å) in the vanadaindane $CpV(\eta^2\text{-}CH_2CMe_2C_6H_4)(PMe_3)_2$[1d] but considerably longer than those in the metallacycle $CpV(\eta^2\text{-}C_4Me_2Ph_2)PMe_3$ (1.883(3) and 1.891(3) Å).[6b] This complex is the product of C,C-coupling of 2-butyne and diphenylacetylene on a CpV^IPMe_3 center, a coupling similar to the one which generates **7**. On the basis of the molecular structure and the ^{13}C NMR data of the metallacycle, it is however clear that this complex is not a metallacyclopentadiene but rather a bent metallacyclopentatriene. The V−C bonds are formally V=C bonds, and therefore their bond distances are much shorter than those of the V−C single bonds in **7**. In **7**, retaining aromaticity of the former benzyne fragment apparently prevails over formation of a more extended, but bent, π-system in a metallacyclopentatriene structure.

Insertion of alkynes in metal−benzyne bonds to form metallaindenes has been observed for a number of η^2-benzyne complexes, both of early[13b] and late[14a] transition metals. The nickel−benzyne complex $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$[14b] (Cy = cyclohexyl) reacts with diphenylacetylene through displacement of the benzyne ligand to give the corresponding η^2-alkyne complex, but with other unsaturated substrates like alkenes even this complex displays the common insertion chemistry, reflecting the high σ-bond character of the metal−benzyne bond in η^2-benzyne complexes in general.

Terminal Alkenes. With terminal alkenes $CH_2{=}CRR'$ (R = H, Me; R′ = H, Me) **6** reacts through regioselective insertion in one of the $V-C_{benzyne}$ bonds to give the corresponding β-substituted metallaindanes **8** (eq 6).



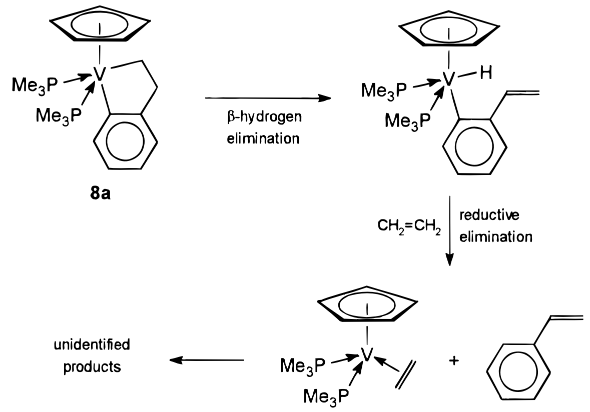
(6)

6

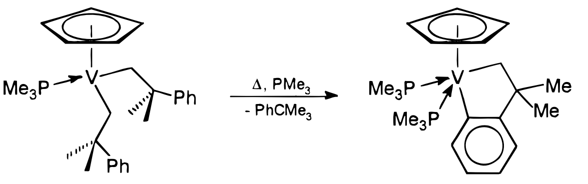
8 a: R, R′ = H
b: R = H, R′ = Me
c: R, R′ = Me

These paramagnetic complexes show in the ^1H NMR spectra high-field chemical shifts for the PMe_3 protons, characteristic for CpV^{III} bis(hydrocarbyl) complexes.[1b,c]

Scheme 2. Proposed Mechanism for Thermal Decomposition of 8a



Only the bis(β-methyl substituted) complex **8c** is thermally stable enough to allow isolation. It shows broad, shifted resonances in the ^1H NMR spectrum for the PMe_3 and vanadaindane methyl substituents (δ −2.1 and −4.7 ppm, respectively). The IR spectrum of **8c** shows the characteristic Cp C−H out of plane vibration at 795 cm^{-1} and a typical, strong PMe_3 absorption at 947 cm^{-1}. The ^1H NMR and the IR data of **8c** match exactly those of the thermolysis product of the bis(neophyl) complex $CpV(CH_2CMe_2Ph)_2PMe_3$[1d] in the presence of excess phosphine (eq 7).



(7)

8c

This thermolysis proceeds through δ-hydrogen abstraction to give the vanadaindane complex $CpV(\eta^2\text{-}CH_2CMe_2C_6H_4)PMe_3$, which can be trapped by excess PMe_3 to give **8c**. We recently reported the synthesis and full characterization of this complex.[1d] The molecular structure shows an essentially square pyramidally coordinated metal atom, with the PMe_3 ligands in a *cis*-position and a puckered vanadaindane ring structure.

The low thermal stability of the vanadaindanes **8a**,**b** can be ascribed to the presence of β-hydrogens in the alkyl and aryl fragments. Attempts to prepare $CpVR_2$ species with alkyl groups containing β-CH bonds have been unsuccessful so far. β-Hydrogen elimination was found to be facile in these systems.[1d] For instance, reaction of the mixed methyl chloride complex $CpV(Me)Cl(PMe_3)_2$[1b,c] with *n*-BuLi produces the V(I) 1-butene complex $CpV(\eta^2\text{-}CH_2{=}CHEt)(PMe_3)_2$, even at low temperatures, with no traces of intermediate mixed dialkyl $CpV(Me)(n\text{-}Bu)(PMe_3)_2$. For **8a** β-hydrogen transfer and reductive elimination would yield styrene (Scheme 2).

The styrene is probably at first complexed by the CpV^I fragment but then replaced by ethene (present in excess) to give the known V(I) ethene compound $CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2$.[6] Indeed, after 1 h at room temperature this compound is observed in the thermolyzing mixture (characteristic broad PMe_3 proton resonance in the ^1H NMR spectrum at δ 14.4 ppm). Simultaneously, resonances of free styrene are present (although partially hidden by excess ethene and solvent). However, the thermal decomposition is not clean, and at least two other CpV^I-containing species are formed, as can be seen by the characteristic low-field chemical shifts of the PMe_3 protons. The anticipated styrene complex CpV(η^2-$CH_2{=}CHPh$)(PMe_3)$_2$ is not present, as was established by a separate experiment in which it was made *in situ* from the ethene compound CpV(η^2-C_2H_4)(PMe_3)$_2$ with 1 mol of styrene. A new resonance at δ 11.4 ppm, assigned to the protons of complexed PMe_3 in CpV(η^2-styrene)(PMe_3)$_2$, appeared in the ^{1}H NMR spectrum within minutes after mixing, but it has not been observed during the thermal decomposition of **8a**. Furthermore, the products formed initially (CpV(η^2-C_2H_4)(PMe_3)$_2$ and styrene) disappear slowly (days), to give as yet unidentified products. The total ethene uptake during formation and thermal decomposition of **8a** was found to be 1.5 mol/mol of **6** (Töpler experiment, 24 h at room temperature). A similar thermal decomposition was observed for the β-methyl substituted vanadaindane **8b**, albeit this decomposition occurs at a slower rate compared to that of **8a**. Attempts to elucidate the nature of these thermal decompositions are severely hampered by the fact that paramagnetic intermediates are involved.

Metallaindanes are formed from η^2-benzyne complexes and terminal olefins.[13abd,17-19] Their formation and thermal stability vary however with the metal. Erker *et al.*[18a] established that zirconaindanes Cp_2Zr(η^2-$CH_2CHRC_6H_4$) are in equilibrium with the corresponding Cp_2Zr(η^2-benzyne)(η^2-$CH_2{=}CHR$) compounds, whereas even the unsubstituted zirconaindane (R = H) only shows appreciable thermal decomposition at temperatures above 100 °C. The ultimate products of these thermal decompositions are phenylalkanes, reflecting both β-hydrogen elimination and C−H activation of solvent and cyclopentadienyl rings to occur. The ruthenium η^2-benzyne complex (PMe_3)$_4$Ru(η^2-C_6H_4)[14a] gives with ethene an irreversible insertion to yield the ruthenaindane complex, which decomposes at 85 °C within several hours through β-hydrogen transfer and reductive elimination to give styrene and (PMe_3)$_3$Ru(η^2-C_2H_4)$_2$.

Judging from the initial products, thermal decomposition of vanadaindanes resembles that of late transition metal indanes (i.e. Ru). The vanadaindanes with β-hydrogens are much less stable than comparable zircona- or ruthenaindanes and even less stable than the vanadacyclopent-2-ene formed in the reaction of CpV(η^2-PhC≡CPh)(PMe_3)$_2$ and excess ethene.[6b] This vanadacyclopent-2-ene inserts ethene before β-hydrogen elimination takes place, yielding a vanadacyclohept-4-ene, which in turn undergoes a β-hydrogen elimination/reductive elimination sequence to give a substituted CpV^I η^4-hexadiene complex. Multiple insertion of ethene in **6** might play an important role in the reaction of **6** with ethene.

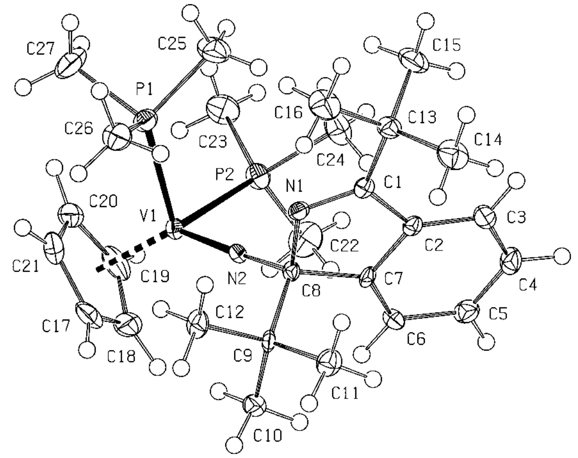
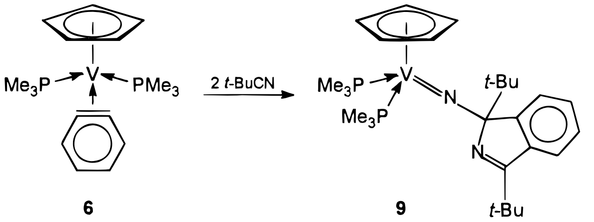


Figure 5. Molecular structure pf CpV[NC(*t*-Bu)N=C(*t*-Bu)C_6H_4](PMe_3)$_2$ (**9**). Thermal ellipsoids are drawn at the 50% probability level.

Table 5. Selected Geometrical Data for CpV[NC(*t*-Bu)N=C(*t*-Bu)C_6H_4](PMe_3)$_2$ (9)

Bond Lengths (Å)			
V(1)−P(1)	2.3559(12)	N(2)−C(8)	1.433(5)
V(1)−P(2)	2.3630(13)	N(1)−C(8)	1.483(4)
V(1)−C(17)	2.234(5)	N(1)−C(1)	1.269(5)
V(1)−C(18)	2.304(5)	C(1)−C(2)	1.507(6)
V(1)−C(19)	2.338(4)	C(2)−C(7)	1.392(4)
V(1)−C(20)	2.306(4)	C(7)−C(8)	1.537(6)
V(1)−C(21)	2.246(5)	C(8)−C(9)	1.576(5)
V(1)−N(2)	1.696(3)	C(1)−C(13)	1.511(5)
Bond Angles (deg)			
P(1)−V(1)−P(2)	96.58(5)	C(1)−N(1)−C(8)	110.4(3)
P(1)−V(1)−N(2)	93.22(10)	N(1)−C(8)−C(7)	103.6(2)
P(2)−V(1)−N(2)	96.40(10)	N(1)−C(1)−C(2)	112.6(3)
V(1)−N(2)−C(8)	177.3(2)	C(1)−C(2)−C(7)	105.5(3)
N(2)−C(8)−C(7)	110.3(3)	C(2)−C(7)−C(8)	107.7(3)
N(2)−C(8)−N(1)	110.5(3)	N(1)−C(1)−C(13)	122.7(4)
N(2)−C(8)−C(9)	111.3(3)		

Nitriles. When **6** is reacted with *t*-BuCN, 2 equiv of nitrile is consumed, and the green crystalline vanadium(III) imido complex **9** is produced in good yield (eq 8).



(8)

The compound was characterized by X-ray diffraction. The crystal structure of **9** involves the packing of 4 molecules in the orthorombic unit cell. The molecular structure of **9** is depicted in Figure 5. Selected bond lengths and angles are given in Table 5.

The molecular structure of **9** shows a simple piano-stool geometry, with the two phosphine ligands in an eclipsed position. The cyclopentadienyl ligand is not regularly pentahapto bonded, presumably as a result of competition for the metal-centered π-orbitals by the strongly π-donating imido and cyclopentadienyl ligands.[20] A distinct ring-slippage, leading to allyl−ene type cyclopentadienyl bonding, as observed for several half-

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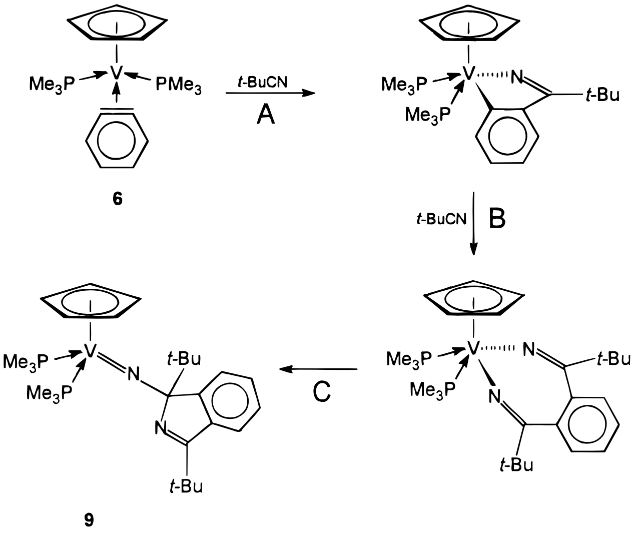
sandwich niobium,[21] molybdenum,[22] rhenium,[23] and vanadium[24] imido complexes, is clearly present in **9** (ene, V(1)−C(17) = 2.234(5) Å, V(1)−C(21) = 2.246(5) Å; allyl, V(1)−C(18) = 2.304(5) Å, V(1)−C(19) = 2.338(4) Å, V(1)−C(20) = 2.306(4) Å). The V(1)−N(2) distance of 1.696(3) Å is characteristic of V−N multiple bonding, as is the nearly linear V(1)−N(2)−C(8) angle of 177.3(2)°. The V−N distance is relatively long compared to most known V═N bonds in V(IV) or V(V) systems (usually 1.60−1.68 Å)[25] and similar to those found in the relatively electron-rich V(IV) bis(pentamethylcyclopentadienyl) systems $Cp^*_2V{=}NR$ (R = Ph, 1.730(5) Å;[26] R = $C_6Me_2H_3$, 1.707(6) Å[27]). The imido substituent is a flat, heterocyclic 1,3-disubstituted isoindolenine fragment, bonded at the 1-position, C(8), to the imido nitrogen. The isoindolenine character is clearly visible in the short N(1)−C(1) bond length of 1.269(5) Å.

Except for CpV[═N-C(*t*-Bu)═CH(*t*-Bu)][$Me_2PCH_2CH_2PMe_2$],[1d] no other vanadium(III) imido complexes are known. Compound **9** represents the first example of a transition metal imido complex bearing a 1-isoindolenine substituent. Due to this unsymmetrical ligand, the methyl protons of the two phosphine ligands exhibit different chemical shifts in the ^1H NMR spectrum of diamagnetic **9**. In the ^{51}V NMR spectrum a broad resonance is observed at δ 34 ppm ($\Delta\nu_{1/2}$ = 1790 Hz), lacking the V−P coupling observed for CpV(CH-*t*-Bu)dmpe,[1d] probably as a result of the low symmetry[28] in **9**, induced by the imido substituent. In addition to the characteristic Cp and PMe_3 absorptions at 791 and 941 cm^{-1}, the IR spectrum of **9** shows a V−N stretching vibration at 951 cm^{-1}, which compares well to other vanadium imido complexes.[26,27]

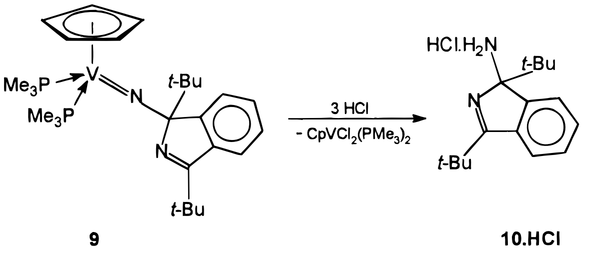
Regioselective monoinsertion of nitriles in metal−benzyne bonds to give azametallacycles has been observed for both zirconocene[13a,b,19] and ruthenium[14a] benzyne complexes. Presumably, this is also the first step (A) in the reaction that produces **9** (Scheme 3).

The formed azavanadacycle is subject to further insertion of a nitrile in the V−C bond (B) to give a diazavanadacycle, which then rearranges (C) to the thermodynamically more stable 1-isoindolenine imido group. Double insertion of nitriles is not observed in the zirconocene and ruthenium cases. The high reactivity of the azavanadacycle toward nitriles compared to the azazircona and -ruthena cycles could be explained by the increased strain in the azametallacycle due to the smaller size of V(III) compared to the 4d metals Zr and Ru. During the reaction, which is complete in 1 h at 25 °C, no intermediates could be observed by ^1H NMR spectroscopy. Attempted synthesis of the azavanadacycle by reaction of **6** with 1 mol of *t*-BuCN led to equimolar amounts of **9** and **6**, indicating that the first nitrile insertion is rate-limiting.

Scheme 3. Proposed Mechanism for Formation of 9

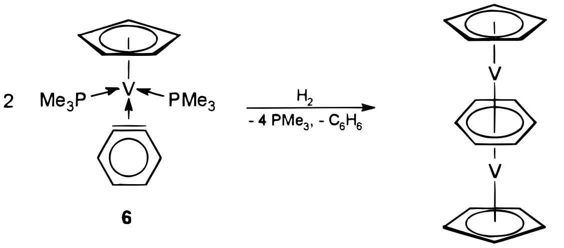


Hydrolysis of **9** with HCl gas in benzene requires 3 equiv of HCl (Töpler pump) and produces the hydrochloride salt of the 1-amine-substituted isoindolenine **10** in an instantaneous reaction (eq 9).



(9)

Dihydrogen. Cyclohexane-d_{12} solutions of **6** react slowly (7 days at 25 °C for completion) with dihydrogen to form an insoluble, green crystalline material (eq 10).



(10)

The ^1H NMR spectrum of the colorless, clear solution shows only resonances for PMe_3 and C_6H_6 (4:1 ratio). The green, crystalline material was identified as the V(I) triple-decker $CpV(C_6H_6)VCp$, which has previously been reported by Duff, Jonas, *et al.*[29] and is also formed in the reaction of $CpVMe_2(PMe_3)_2$ with H_2 in benzene.[1c]

Formation of the triple-decker indicates generation of CpV^I fragments during the reaction. They are probably formed through initial σ-bond metathesis of the benzyne complex **6** with H_2, followed by reductive elimination of benzene from the unstable phenyl−

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hydride intermediate. Other types of σ-bond metathesis reactions, like activation of benzene to give a bis(phenyl) complex, have so far not been found for **6**. Benzene-d_6 solutions of **6** can be kept at 100 °C for days without any sign of formation of **6-*d*$_4$** and C_6H_6. Likewise, no C−H activation was observed for **6-*d*$_4$** in benzene at 100 °C. In this respect **6** contrasts strongly with ruthenium and zirconocene η^2-benzyne complexes, which both show activation of aromatic C−H bonds.[14a,15]

Conclusions

Starting from $CpVCl_2(PMe_3)_2$, paramagnetic phenylethynyl complexes $CpVCl_{2-n}(C{\equiv}CPh)_n(PMe_3)_2$ (n = 1, 2) have been synthesized. Both compounds were characterized by X-ray diffraction and were found to be thermally more stable than other CpV^{III} hydrocarbyl complexes. The bis(phenyl) complex $CpVPh_2(PMe_3)_2$ decomposes thermally through β-hydrogen abstraction to give the first isolated vanadium benzyne complex $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$. The molecular structure of this complex indicates that it is best described as a high-spin d^2 vanadium(III) benzometallacyclopropene. The cyclopropene character is expressed in its reactivity, showing insertion of unsaturated substrates. With diphenylacetylene a vanadaindene complex with a planar metallacyclic structure is obtained, and terminal alkenes insert regioselectively to give β-substituted metallaindanes, which show a low thermal stability in case the β-substituent is hydrogen. With t-BuCN double insertion followed by rearrangement of the diazametallacycle to give an isoindolenine-substituted vanadium(III) imido complex is observed. The benzyne complex also reacts with dihydrogen to form a known triple-decker complex $CpV(C_6H_6)VCp$ through partial hydrogenation of the benzyne ligand.

Experimental Section

General Considerations. All manipulations were performed under nitrogen (using Schlenk techniques or a glovebox) or using vacuum line techniques. Gas uptakes were determined with a Töpler pump connected to a vacuum line. NMR spectra were recorded on a Varian VXR-300 (^{1}H, 300 MHz; ^{2}D, 46.044 MHz; ^{13}C, 75.4 MHz; ^{51}V, 78.9 MHz) spectrometer in benzene-d_6 at 25 °C (unless stated otherwise), and chemical shifts are in ppm, downfield from TMS (δ 0.00, ^{1}H, ^{2}D, ^{13}C) or $VOCl_3$ (δ 0.00, ^{51}V) positive. Coupling constants and half-width values, $\Delta\nu_{1/2}$, are reported in Hz. IR spectra were recorded on a Pye-Unicam SP3-300 or a Mattson-4020 Galaxy FT-IR spectrophotometer, from Nujol mulls between KBr disks (unless stated otherwise). Wavenumbers are reported in cm^{-1}. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Values given are the average of at least two independent determinations.

Compounds **1**,[5] **5**,[1b,c] and LiC≡CPh[30] were prepared according to published procedures. Solvents (diethyl ether, pentane (mixed isomers), n-hexane, benzene, and deuterated solvents except $CDCl_3$) were distilled from Na/K alloy before use. n-BuLi, diphenylacetylene, $LiBH_4$ (Janssen), ethene, propene (Matheson), isobutene (Aldrich), and HCl (Ucar) were used as received. Grignard reagents were prepared from the corresponding alkyl halides. t-BuCN was vacuum transferred and stored over molecular sieves (4 Å). PMe_3 was prepared according to an adapted literature procedure,[31] using MeMgI instead of MeMgBr.

$CpVCl(C{\equiv}CPh)(PMe_3)_2$ (2). A suspension of **1** (1.77 g, 5.22 mmol) and LiC≡CPh (0.59 g, 5.46 mmol) in 35 mL of diethyl ether was stirred for 1.5 h at 0 °C. After removal of the solvent *in vacuo* the residue was extracted twice with 30 mL of pentane. Concentrating and cooling of the extract to −25 °C yielded 0.77 g (1.19 mmol, 36%) of dark-green crystals in two crops: ^{1}H NMR δ 28.0 (2H, aryl, $\Delta\nu_{1/2}$ = 1400), −11.8 (18H, PMe_3, $\Delta\nu_{1/2}$ = 3600); IR 3069 (w), 3057 (w), 2043 (m), 1591 (m), 1564 (m), 1481 (s), 1439 (s), 1418 (m), 1308 (m), 1294 (m), 1277 (m), 1202 (m), 1171 (m), 1121 (w), 1067 (m), 1015 (s), 945 (vs, PMe_3), 909 (m), 841 (w), 824 (m), 799 (s), 758 (s), 727 (s), 694 (s), 669 (m), 529 (m), 519 (w). Anal. Calcd for $C_{19}H_{28}ClP_2V$: C, 56.38; H, 6.97; Cl, 8.76; V, 12.59. Found: C, 56.54; H, 7.07; Cl, 8.54; V, 12.48.

$CpV(C{\equiv}CPh)_2(PMe_3)_2$ (3). A suspension of **1** (1.13 g, 3.33 mmol) and LiC≡CPh (0.80 g, 7.40 mmol) in 30 mL of diethyl ether was stirred for 1.5 h at 0 °C. After removal of the solvent *in vacuo* the residue was extracted twice with 30 mL of pentane. Concentrating and cooling of the extract to −25 °C yielded 0.36 g (0.77 mmol, 23%) of brown crystals in three crops: ^{1}H NMR δ 23.9 (4H, aryl, $\Delta\nu_{1/2}$ = 4300), −8.8 (18H, PMe_3, $\Delta\nu_{1/2}$ = 5500); IR 3069 (w), 3041 (w), 2041 (s), 1589 (m), 1571 (w), 1479 (s), 1420 (m), 1292 (w), 1277 (m), 1200 (m), 1171 (w), 1121 (vw), 1067 (m), 1024 (m), 945 (vs, PMe_3), 907 (w), 843 (w), 799 (s), 777 (w), 756 (s), 727 (m), 694 (s), 671 (w), 529 (m), 519 (w). Anal. Calcd for $C_{27}H_{33}P_2V$: C, 68.93; H, 7.07; V, 10.83. Found: C, 68.90; H, 7.11; V, 10.65.

$CpV(\eta^2\text{-}BH_4)(C{\equiv}CPh)PMe_3$ (4). A mixture of **3** (0.45 g, 1.13 mmol) and $LiBH_4$ (0.08 g, 1.43 mmol) in 20 mL of diethyl ether was stirred for 2.5 h at 25 °C. After removal of the organic volatiles *in vacuo* the residue was extracted with 40 mL of pentane. Concentrating and cooling of the extract to −80 °C gave 0.19 g (0.62 mmol, 55%) of brown microcrystals: ^{1}H NMR δ 1.97, 1.50, 1.16, 0.84 (4 d, each 1H, J_{BH} = 96, J_{PH} = 15), 0.66 (d, 9H, J_{PH} = 10.7); IR 2363 (s), 2344 (s), 2257 (w), 2047 (w), 2029 (w), 1588 (m), 1481 (m), 1429 (m), 1294 (m), 1136 (w), 1117 (w), 1071 (m), 1011 (m), 974 (s), 949 (s), 889 (w), 793 (m), 758 (m), 708 (m), 669 (w), 569 (w). Anal. Calcd for $C_{16}H_{23}BPV$: C, 62.38; H, 7.52;V, 16.53. Found: C, 62.68; H, 7.69; V, 14.28.

$CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$ (6). A solution of **5** (0.55 g, 1.30 mmol) in 20 mL of benzene was stirred for 17 h at 50 °C. After removal of the solvent *in vacuo* the residue was extracted with 60 mL of pentane. Concentrating and cooling of the extract to −25 °C yielded 0.22 g (0.65 mmol, 50%) of dark-green crystals: ^{1}H NMR δ 157.0 (5H, Cp, $\Delta\nu_{1/2}$ = 4500), 7.13 (20H, PMe_3 and β-C_6H_4, $\Delta\nu_{1/2}$ = 460), −12.22 (2H, γ-C_6H_4, $\Delta\nu_{1/2}$ = 240); ^{1}H NMR (THF-d_8) δ 157 (5H, Cp, $\Delta\nu_{1/2}$ = 4500), 7.30 (20H, PMe_3 and β-C_6H_4, $\Delta\nu_{1/2}$ = 340), −15.3 (2H, γ-C_6H_4, $\Delta\nu_{1/2}$ = 460); IR 3092 (w), 3013 (w), 1547 (w), 1420 (m), 1406 (m), 1325 (m), 1296 (m), 1279 (s), 1235 (w), 1142 (m), 1117 (w), 1092 (w), 1057 (w), 1009 (m), 990 (m), 941 (s), 835 (w), 799 (m), 781 (s), 727 (s), 718 (s), 665 (m), 654 (m). Anal. Calcd for $C_{17}H_{27}P_2V$: C, 59.31; H, 7.90; V, 14.80. Found: C, 59.09; H, 7.79; V, 14.91.

$CpV(C_6D_5)_2(PMe_3)_2$ (5-*d*$_{10}$). To a suspension of **1** (0.66 g, 1.95 mmol) in 20 mL of diethyl ether cooled to −55 °C, 7.1 mL of a 0.55 M C_6D_5MgBr solution in diethyl ether was added dropwise. The mixture was allowed to warm to 0 °C and stirred for 1.5 h at this temperature. After removal of the solvent *in vacuo* the residue was extracted with 60 mL of pentane. Concentrating and cooling of the extract to −25 °C yielded 0.57 g (1.32 mmol, 68%) of red-brown crystals: ^{1}H NMR δ −11.10 (18H, PMe_3, $\Delta\nu_{1/2}$ = 1680).

$CpV(\eta^2\text{-}C_6D_4)(PMe_3)_2$ (6-*d*$_4$). A solution of **5-*d*$_{10}$** (0.515 g, 1.214 mmol) in 20 mL of benzene was stirred for 25 h at 50 °C. After removal of the solvent *in vacuo* the residue was

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extracted with 35 mL of pentane. Concentrating and cooling of the extract to −25 °C yielded 0.019 g (0.055 mmol, 5%) of dark-green crystals: ^{1}H NMR δ 158 (5H, Cp, $\Delta\nu_{1/2} = 2500$), 7.13 (18H, $\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 175$); ^{2}H NMR ($\mathrm{C_6H_6}$) δ 7.46 (2H, β-$\mathrm{C_6H_4}$, $\Delta\nu_{1/2} = 2.2$), −12.38 (2H, γ-$\mathrm{C_6H_4}$, $\Delta\nu_{1/2} = 11$).

CpV(η^2-$\mathrm{PhC{=}CPhC_6H_4}$)($\mathrm{PMe_3}$)$_2$ (7). A suspension of **6** (0.31 g, 0.90 mmol) and $\mathrm{PhC{\equiv}CPh}$ (0.18 g, 1.01 mmol) in 20 mL of pentane was stirred for 19 h at 25 °C. After removal of the solvent *in vacuo* the residue was extracted with 30 mL of diethyl ether. Concentrating and cooling of the extract to −80 °C yielded 0.27 g (0.52 mmol, 57%) of red-brown crystals: ^{1}H NMR δ 154 (5H, Cp, $\Delta\nu_{1/2} = 3750$), 18.30 (Ph, $\Delta\nu_{1/2} = 75$), 16.44 (Ph, $\Delta\nu_{1/2} = 75$), −3.43 (β-$\mathrm{C_6H_4}$, $\Delta\nu_{1/2} = 600$), −5.72 (Ph, $\Delta\nu_{1/2} = 100$), −9.53 (18H, $\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 500$), −16.43 (γ-$\mathrm{C_6H_4}$, $\Delta\nu_{1/2} = 600$); IR 3067 (w), 3032 (w), 1589 (s), 1564 (w), 1547 (w), 1505 (w), 1487 (m), 1424 (s), 1325 (w), 1298 (m), 1279 (s), 1242 (w), 1200 (w), 1171 (vw), 1136 (w), 1119 (vw), 1092 (vw), 1067 (w), 1022 (m), 1007 (m), 945 (vs), 903 (m), 837 (w), 793 (vs), 758 (m), 721 (vs), 700 (s), 664 (m), 600 (m). Anal. Calcd for $\mathrm{C_{31}H_{37}P_2V}$: C, 71.26; H, 7.14; V, 9.75. Found: C, 71.62; H, 7.12; V, 9.89.

CpV(η^2-$\mathrm{CPh{=}CPhC_6D_4}$)($\mathrm{PMe_3}$)$_2$ (7-*d*$_4$). A green solution of **6-*d*$_4$** (26 mg, 74 μmol) and $\mathrm{PhC{\equiv}CPh}$ (13 mg, 74 μmol) in 0.4 mL of $\mathrm{C_6D_6}$ in a sealed NMR tube was kept at 25 °C for 20 h: ^{1}H NMR δ 157 (5H, Cp, $\Delta\nu_{1/2} = 3750$), 18.27 (Ph, $\Delta\nu_{1/2} = 79$), 16.38 (Ph, $\Delta\nu_{1/2} = 68$), −5.84 (Ph, $\Delta\nu_{1/2} = 90$), −8.8 ($\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 675$).

CpV(η^2-$\mathrm{CH_2CH_2C_6H_4}$)($\mathrm{PMe_3}$)$_2$ (8a). A 5 mm NMR tube equipped with a Teflon needle valve was charged with a solution of **6** (15 mg, 0.048 mmol) in 0.5 mL of benzene-*d*$_6$. On a vacuum line ethene (0.094 mmol) was condensed into the NMR tube at −196 °C. After warming of the sample to 25 °C a ^{1}H NMR spectrum was taken immediately: δ 0.26 ($\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 460$). The decomposition of **8a** was then monitored by taking ^{1}H NMR spectra periodically: CpV($\mathrm{C_2H_4}$)($\mathrm{PMe_3}$)$_2$, δ 14.4 ($\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 260$); styrene (resonances partially overlapped by reaction byproducts), δ 7.1 (m, Ph), 6.6 (dd, PhC*H*=), 5.6 (d, =C*H*H), 5.1 (d, =CH*H*).

The corresponding propene derivative **8b** was prepared similarly: δ −0.11 ($\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 225$), −7.24 (Me, $\Delta\nu_{1/2} = 450$).

Determination of Ethene Uptake by 6. On a vacuum line equipped with a Töpler pump a solution of **6** (137 mg, 397 μmol) in 4 mL of benzene was degassed by repeated freeze−thaw cycles. Ethene (1.05 mmol) was condensed onto the solution, which was then stirred for 24 h at 25 °C. After cooling of the solution to −80 °C, the excess ethene was pumped off (0.46 mmol) with the Töpler pump, resulting in a total ethene uptake of 0.58 mmol (1.5 equiv).

CpV(η^2-$\mathrm{CH_2CMe_2C_6H_4}$)($\mathrm{PMe_3}$)$_2$ (8c). A solution of **6** (0.038 g, 0.11 mmol) in 0.6 mL of benzene-*d*$_6$ was stirred under 1 atm of isobutene in a 15 mL vessel at 25 °C for 3 h. Part of the resulting brown solution (0.4 mL) was transferred to a 5 mm NMR tube: ^{1}H NMR δ 4.72 (s, 2H, =C*H*$_2$, isobutene), 1.60 (s, 6H, =C*Me*$_2$, isobutene), −2.1 (18H, $\mathrm{PMe_3}$, $\Delta\nu_{1/2} = 420$), −4.7 (6H, C*Me*$_2$, $\Delta\nu_{1/2} = 110$). Removal of the organic volatiles *in vacuo* from the rest of the brown solution gave a brown residue: IR 3090 (vw), 3025 (m), 2775 (vw), 1560 (vw), 1418 (m), 1358 (w), 1340 (w), 1300 (mw), 1282 (m), 1009 (mw), 945 (vs), 817 (mw), 795 (s), 728 (s), 715 (m), 662 (w). The obtained spectra are identical to those reported for the complex obtained by thermolysis of CpV($\mathrm{CH_2CMe_2Ph}$)$_2$$\mathrm{PMe_3}$ in the presence of extra $\mathrm{PMe_3}$.[1d] The material obtained this way was also characterized by elemental analysis and X-ray diffraction.

CpV(NC(*t*-Bu)N=C(*t*-Bu)$\mathrm{C_6H_4}$)($\mathrm{PMe_3}$)$_2$ (9). To a suspension of **6** (0.24 g, 0.69 mmol) in 20 mL of pentane cooled to −55 °C, *t*-BuCN (152 μL, 1.38 mmol) was added dropwise. The mixture was allowed to warm to 25 °C and stirred for 18 h. After filtration the residue was extracted with 20 mL of pentane. Concentrating and cooling of the combined filtrate and extract to −80 °C yielded 0.21 g (0.40 mmol, 59%) of green crystals: ^{1}H NMR δ 7.49 (q, 1H, $^{3}J_{\mathrm{HH}} = 2.8$, $\mathrm{C_6H_4}$ α-H), 7.37 (q, 1H, $^{3}J_{\mathrm{HH}} = 3.0$, $\mathrm{C_6H_4}$ α-H), 7.05 (q, 2H, $^{3}J_{\mathrm{HH}} = 1.5$, $\mathrm{C_6H_4}$ β-H's), 4.87 (br s, 5H, Cp), 1.50 (s, 9H, C*Me*$_3$), 1.19 (d, 9H, $^{2}J_{\mathrm{PH}} = 4.7$, P*Me*$_3$), 1.15 (s, 9H, C*Me*$_3$), 0.57 (d, 9H, $^{2}J_{\mathrm{PH}} = 3.9$, P*Me*$_3$); ^{13}C NMR δ 174.2 (N=*C*-(*t*-Bu)), 138.0 (N−*C*−N), 129.6 ($\mathrm{C_6H_4}$, α-*C*), 126.9 ($\mathrm{C_6H_4}$, β-*C*), 126.6 ($\mathrm{C_6H_4}$, α-*C*), 126.3 ($\mathrm{C_6H_4}$, β-*C*), 125.2 ($\mathrm{C_6H_4}$, γ-*C*), 122.4 ($\mathrm{C_6H_4}$, γ-*C*), 93.7 (Cp), 36.2 (*C*Me$_3$), 28.6 (C*Me*$_3$), 26.8 (C*Me*$_3$), 24.2 (P*Me*$_3$); ^{51}V NMR δ 34.0 ($\Delta\nu_{1/2} = 1790$); ^{31}P NMR δ 45.2 ($\Delta\nu_{1/2} = 8730$); IR 3082 (w), 3065 (w), 3032 (w), 1595 (m), 1566 (m), 1424 (m), 1364 (m), 1333 (w), 1306 (w), 1294 (m), 1269 (m), 1248 (s), 1215 (s), 1200 (m), 1171 (w), 1155 (w), 1107 (m), 1051 (m), 1011 (m), 995 (w), 972 (w), 951 (vs), 941 (vs), 891 (w), 872 (w), 843 (w), 791 (s), 750 (s), 718 (m), 704 (m), 656 (s). Anal. Calcd for $\mathrm{C_{27}H_{45}N_2P_2V}$: C, 63.52; H, 8.88; N, 5.49; V, 9.98. Found: C, 63.65; H, 8.97; N, 5.52; V, 9.88.

$\mathrm{H_2NC}$(*t*-Bu)N=C(*t*-Bu)$\mathrm{C_6H_4}$ (10). On a vacuum line equipped with a Töpler pump a solution of **11** (45.7 mg, 90 μmol) in 4 mL of benzene was degassed by repeated freeze−thaw cycles and then allowed to react with 0.47 mmol of HCl gas. The solution turned dark-red, and a solid precipitated immediately. After 10 min the mixture was cooled to −80 °C and the excess HCl was pumped off with the Töpler pump. The total HCl uptake was 270 μmol (3.0 equiv). After removal of the solvent *in vacuo* the residue was dissolved in 0.1 N NaOH/$\mathrm{H_2O}$. Extraction with diethyl ether and removal of the solvent *in vacuo* yielded a yellow oil, which was dissolved in chloroform-*d*$_1$: ^{1}H NMR δ 7.63 (2H, m, $\mathrm{C_6H_4}$ α-H's), 7.32 (2H, m, $\mathrm{C_6H_4}$ β-H's), 1.45 (9H, s, $\mathrm{CMe_3}$), 1.00 (9H, s, $\mathrm{CMe_3}$).

Reaction of 6 with $\mathrm{H_2}$. A 5 mm NMR tube equipped with a Teflon needle valve was charged with a solution of **6** (14 mg, 0.04 mmol) in 0.5 mL of cyclohexane-*d*$_{12}$. On a vacuum line the inert atmosphere was replaced by 1 atm of $\mathrm{H_2}$. After 7 days a green crystalline material had separated and a ^{1}H NMR spectrum was taken: δ 7.13 (6H, $\mathrm{C_6}$*H*$_6$), 0.84 (36H, P*Me*$_3$). The volatile compounds were removed *in vacuo* after which an IR spectrum of the green material was taken: IR 1422 (w), 1364 (m), 1103 (s), 1069 (w), 1053 (w), 1001 (s), 968 (w), 937 (s), 841 (w), 789 (s), 762 (vs), 675 (w). An identical spectrum was reported for the product of the reaction of $\mathrm{CpVMe_2(PMe_3)_2}$ with $\mathrm{H_2}$ in benzene.[1c]

X-ray Structure Determinations of 2, 3, 6, 7, and 9. Pertinent crystal data and data collection parameters can be found in Table 6. Crystals suitable for X-ray diffraction were grown by cooling a saturated solution from +20 to −30 °C at 3 °C/h (**2**, pentane, greenish block-shaped crystals; **3**, pentane, brown-yellow rod-shaped crystals; **6**, diethyl ether, greenish plate-shaped crystals; **7**, diethyl ether, red-brown parallelepiped-shaped crystals; **9**, pentane, dark-green block-shaped crystals).

Crystals were mounted on top of a glass fiber (except for **9**, which was introduced in a Lindemann glass capillary) and transferred to the cold nitrogen stream of either an Enraf-Nonius CAD4T diffractometer (**2**, **3**, and **9**) or an Enraf-Nonius CAD-4F diffractometer on a rotating anode, interfaced to a VAX-11/730 (**6** and **7**) for data collection.

Unit cell parameters were determined from a least-squares treatment of the SET4[32] setting angles of 25 reflections with high θ (around 15°). The unit-cell parameters were checked for the presence of higher lattice symmetry;[33] examination of the final atomic coordinates of the structure of **6** and **7** did not yield extrametric symmetry elements.[34]

Intensity data were corrected for Lorentz and polarization effects, for a linear decay (8.4% over 24.5 h for **2**, 1.2% over 8.6 h for **3**, 1.9% over 21 h for **9**) of the three intensity control reflections during the X-ray exposure time, and for absorption in the case of **2** and **9** (using the DIFABS method;[35] correction

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Table 6. Crystallographic Data for 2, 3, 6, 7, and 9

	2	**3**	**6**	**7**	**9**
formula	$C_{19}H_{28}ClP_2V$	$C_{27}H_{33}P_2V$	$C_{17}H_{27}P_2V$	$C_{31}H_{37}P_2V$	$C_{27}H_{45}N_2P_2V$
fw	404.77	470.45	344.29	522.52	510.56
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$	$Pna2_1$
a, Å	11.0992(10)	17.8100(12)	8.805(1)	9.191(1)	14.7216(7)
b, Å	11.7098(10)	16.5034(11)	14.049(2)	19.909(1)	19.1511(14)
c, Å	16.990(2)	9.8384(5)	14.610(1)	15.072(1)	9.9347(4)
α, deg	105.977(10)				
β, deg	96.562(10)	117.515(10)	90.143(8)	98.687(7)	
γ, deg	93.918(10)				
V, Å^3	2097.4(4)	2564.7(3)	1807.3(4)	2726.3(4)	2800.9(3)
Z	4	4	4	4	4
d_{calcd}, g cm^{-3}	1.2819(2)	1.2184(2)	1.265	1.273	1.2107(1)
$F(000)$, e	848.0	992.0	728	1104	1096.0
μ(Mo Kα), cm^{-1}	7.3	5.2	7.0	4.8	4.7
cryst size, mm	0.20 × 0.20 × 0.23	0.08 × 0.10 × 0.25	0.07 × 0.30 × 0.37	0.12 × 0.28 × 0.35	0.13 × 0.25 × 0.50
T, K	150	100	130	130	150
no. of data collcd	12 524	3225	4435	7247	4939
no. unique data	9632	2950	3536	5912	3381
no. reflns obsd	6161 [$I > 2.5\sigma(I)$]	1717 [$I > 2.5\sigma(I)$]	2964 [$I > 2.5\sigma(I)$]	4733 [$I > 2.5\sigma(I)$]	2630 [$I > 2.5\sigma(I)$]
no. of params refined	453	144	290	456	326
$R(F)$	0.043	0.058	0.038	0.033	0.039
$R_w(F)$	0.046	0.064	0.047	0.037	0.026
w	$\{\sigma^2(F) + 0.000285F^2\}^{-1}$	$\{\sigma^2(F) + 0.000297F^2\}^{-1}$	1	1	$1/\sigma^2(F_o)$

range 0.862−1.133 for **2**, 0.91−1.08 for **9**). The intensities of the three standard reflections of **6** showed no statistically significant change over the 96.3 h of data collection; those of **7** showed some decay (5%) over the 107.0 h of data collection.

For **2**, **3**, and **9**, the structures were solved by direct methods (**2**, **3**, SHELXS86;[36] **9**, SIR92[37]) and subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced on calculated positions (C−H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-hydrogen atoms (except the atoms of the disordered Cp rings of **3** and **9**) were refined with anisotropic thermal parameters; hydrogen atoms of **2** and **3** were refined with one common isotropic thermal parameter [$U = 0.053(2)$ Å^2 for **2**, 0.057(5) Å^2 for **3**], and hydrogen atoms of **9** were refined with two common isotropic thermal parameters [$U = 0.023(4)$ and $U = 0.044(2)$ Å^2 for CH and CH_3 groups, respectively]. Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.0425$ for **2**, 0.0582 for **3**, and 0.0392 for **9**. The absolute structure of **9** was checked by refinement with opposite anomalous dispersion factors ($-if''$) resulting in $R = 0.0405$. A final difference Fourier map showed no features outside the range −0.36 to 0.42 e/Å^3 for **2**, −0.55 to 0.58 e/Å^3 for **3**, and −0.55 to 0.58 e/Å^3 for **9**.

For **6** and **7**, the structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to the difference structure factors using the program DIRDIF.[38] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ)[39] minimizing the function $Q = \sum_{\mathbf{h}}[w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis gave all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined. The crystals exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter.[40] One reflection for **6** with $(w(||F_o| - |F_c||) > 20)$ was excluded from the final refinement cycle. Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms converged at $R = 0.038$ for **6** and $R = 0.033$ for **7**. One peak in the final difference Fourier map of **6**, showing a residual electron density of 1.01 e/Å^3, was located in the vicinity of the V position but was of no chemical significance: the rest of the difference Fourier map did not show residual peaks outside the range ±0.57 e/Å^3 (±0.42 e/Å^3 for **7**).

Neutral atom scattering factors were taken from ref 41 and corrected for anomalous dispersion.[42] For **2**, **3**, and **9**, all calculations were performed with SHELX76[43] and the PLATON package[44] (geometrical calculations and illustrations) on a DEC-5000 cluster at the University of Utrecht. For **6** and **7**, all calculations were performed with XTAL,[45] the PLATON package (calculation of geometric data), and ORTEP[46] on the CDC-Cyber 962-31 computer at the University of Groningen.

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Supporting Information Available: Details of the structure determinations, including tables of atomic coordinates, bond lengths and angles, and thermal parameters for **2**, **3**, **6**, **7**, and **9** (38 pages). Ordering information is given on any current masthead page.

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