parameters, except for H(1), whose position was taken from a difference synthesis and refined. All non-hydrogen atoms were refined anisotropically. Positional parameters are given in Table V and important distances and angles in Table II; full details have been deposited as supplementary material.

Crystal and Refinement Data for $[CpNb(H_2O)Cl_3]_2(\mu\text{-}O)\cdot 2THF\cdot 0.5Et_2O$ (1). Crystals were obtained as described and were mounted as described for **2** above. Crystal data: dimensions 0.36 × 0.28 × 0.07 mm, $C_{20}H_{35}Cl_6Nb_2O_{5.5}$, $M_r = 762.05$, monoclinic, $C2/c$, $a = 22.105$ (4) Å, $b = 11.366$ (1) Å, $c = 15.563$ (2) Å, $\beta = 124.707$ (9)°, $V = 3214.5$ (7) Å^3, $Z = 4$, $F(000) = 1532$, $D_{calc} = 1.57$ Mg m^{-3}, μ(Mo Kα) = 12.1 cm^{-1}; cell dimensions from 25 reflections with $30 < 2\theta < 40°$; intensities of 4201 reflections measured to $2\theta = 45°$, of which 1444 had $I > 2.5\sigma(I)$; no absorption correction; refinement as for **2**; final $R = 0.056$, $R_w = 0.076$, goodness of fit 2.22, for 165 parameters; maximum Δ/σ 0.21; highest peak 0.83 e Å^{-3}, deepest hole −0.55 e Å^{-3}. Positional parameters are given in Table VI and important distances and angles in Table I; full details have been deposited as supplementary material.

Acknowledgments. We thank the Natural Sciences and Engineering Research Council of Canada, the Imperial Oil Research Fund, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. Rod McGregor is thanked for assistance with the ESR spectra, Ljubica Bottomley for the atomic absorption analyses, Andrew Sharpe for the preparation of starting materials, and Friedrich Grein for assistance with the extended Hückel calculations.

Registry No. 1, 112942-46-8; 1·2THF·0.5Et$_2$O, 126752-69-0; 2, 126752-72-5; 2·THF, 126821-22-5; 3, 126752-70-3; 5, 126752-71-4; CpNbCl$_4$, 33114-15-7.

Supplementary Material Available: Figures showing the positions of the adduct molecules, tables giving the hydrogen atom positions, thermal parameters, bond lengths and angles, and contributions of the Nb d orbitals to the frontier orbitals of 1 and 2, and a table giving the distances from the least-squares planes of 2 (19 pages); tables of the observed and calculated structure factors for 1 and 2 (45 pages). Ordering information is given on any current masthead page.

Chemistry of Carbon Monoxide Free Cyclopentadienylvanadium(I) Alkene and Alkyne Complexes

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The compounds $CpV(L)(PMe_3)_2$ (L = η^2-ethene (**2**), η^2-alkyne) form a new class of highly reactive CO-free CpV^I complexes. Paramagnetic **2** was prepared from $CpVCl(PMe_3)_2$ and 0.5 mol of $BrMg(CH_2)_4MgBr$. An X-ray structure determination shows a relatively short ethene C═C distance of 1.365 (5) Å. The η^2-alkyne complexes are readily available by Mg reduction of $CpVCl_2(PMe_3)_2$ in the presence of the alkyne. The X-ray structure of $CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2$ (**4**) shows the alkyne ligand to be asymmetrically oriented relative to the other ligands in the complex. The ethene ligand in **2** is readily replaced by CO or PhC≡CPh. 2,2′-Bipyridine displaces a phosphine as well to produce the paramagnetic $CpV(\eta^2\text{-}bpy)PMe_3$ (**5**). C,C coupling is observed in the reaction of **2** with CO_2 to form the vanadalactone $CpV[CH_2CH_2C(O)O]PMe_3$ (**6**). PhSSPh oxidatively adds to **2** to form $[CpV(\mu\text{-}SPh)_2]_2$. 1-Hexene is slowly catalytically dimerized by **2**. The alkyne complex **4** reacts with various hydrocarbon substrates through initial phosphine loss and subsequent C,C coupling. With 1,3-butadiene the hexadienediyl complex $CpV(\eta^1,\eta^3\text{-}C_2Ph_2C_4H_6)PMe_3$ (**9**) is formed. With ethene 2:1 cotrimerization with the alkyne ligand occurs to produce an η^4-diphenylhexadiene complex, $CpV[\eta^4\text{-}CH_2{=}CHC(Ph){=}C(Ph)Et]PMe_3$ (**10**), which was characterized by X-ray diffraction. With 2-butyne, **4** reacts to give $CpV(\eta^2\text{-}MeC{\equiv}CMe)(\eta^2\text{-}PhC{\equiv}CPh)PMe_3$ (**13**), which subsequently forms the metallacycle $CpV(C_4Me_2Ph_2)PMe_3$ (**14**). An X-ray structure determination shows **14** to have a bent metallacyclopenta-1,3,5-triene structure (formally an V(V) dicarbene) with V═C bond distances of 1.891 (3) and 1.893 (3) Å. Analogous bicyclic products are formed through reduction of $CpVCl_2(PMe_3)_2$ in the presence of diynes. A summary of the crystal data is as follows: for **2**, $Pbca$, $a = 12.351$ (3) Å, $b = 15.526$ (4) Å, $c = 16.948$ (3) Å (130 K), $Z = 8$; for **4**, $P2_1/n$, $a = 8.249$ (2) Å, $b = 17.619$ (2) Å, $c = 16.278$ (2) Å, $\beta = 100.61$ (2)° (130 K), $Z = 4$; for **10**, $P\bar{1}$, $a = 8.875$ (3) Å, $b = 9.589$ (2) Å, $c = 15.081$ (6) Å, $\alpha = 90.95$ (3)°, $\beta = 91.54$ (3)°, $\gamma = 117.44$ (2)° (130 K), $Z = 2$; for **14**, $P2_12_12_1$, $a = 12.957$ (3) Å, $b = 19.205$ (5) Å, $c = 9.155$ (2) Å (170 K), $Z = 4$.

Introduction

The organometallic chemistry of vanadium(I) has hitherto been based mainly on $CpV(CO)_4$.[1] CO ligands in this compound can be photochemically or thermally replaced by one or more Lewis-base type ligands. In this way, a range of $CpV(L)_n(CO)_{4-n}$ (L = PR_3,[2] CS,[3] RC≡CR′ (=2L),[4]

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[1] Fischer, E. O.; Haffner, W. *Z. Naturforsch.* **1954**, *9B*, 503.

[2] (a) Strohmeier, W.; Müller, F.-J. *Chem. Ber.* **1967**, *100*, 2812. (b) Rehder, D. *J. Magn. Reson.* **1977**, *25*, 177. (c) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 779.

[3] Rajan, S. *Indian J. Chem., Sect. A* **1977**, *15*, 920.

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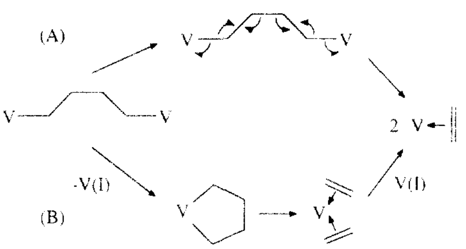
Scheme I



tetrahydrothiophene,[5] etc.) derivatives has been prepared, also with bidentate ligands such as $R_2X(CH_2)_nXR_2$ (X = P, As; R = alkyl, aryl; n = 0–4)[6] or 1,3-dienes.[7] However, the main drawback of these complexes is that (apart from $CpV[F_2PN(Me)PF_2]_2$[8]) they still contain a number of CO ligands that are less labile than the other coordinated ligands,[2c] which keep the compounds electronically saturated. Furthermore, the CO ligands are often not inert under conditions required for reaction,[4c] thus severely limiting the scope of reactivity. Disproportionation to form the thermodynamically stable $CpV(CO)_4$ has also posed problems in reactivity studies.[5] It thus seems desirable to have CO-free CpV^I complexes available, from which the reactivity of univalent vanadium can be more readily appreciated. In recent years Jonas et al. have produced two relevant types of compounds, $CpV(\eta^6\text{-arene})$[9] and $CpV(\eta^4\text{-butadiene})PMe_3$,[10] but their chemistry has been described only sparingly.[11]

The usefulness of the 16e paramagnetic (S = 1) V(III) complex $CpVCl_2(PMe_3)_2$[12] as a precursor for CpV^{III} and CpV^{II} species has been discussed earlier.[13] It also provides a convenient route to CO-free CpV^I complexes, and in this paper the synthesis, structure, and reactivity of CpV^I olefin and alkyne complexes, prepared directly or indirectly from $CpVCl_2(PMe_3)_2$, are described. The compounds appear to be much more reactive than the CO-containing complexes, reacting readily under ambient conditions with alkenes, alkynes, CO_2, etc. without the need for photochemical activation. Parts of this investigation have been communicated earlier.[14]

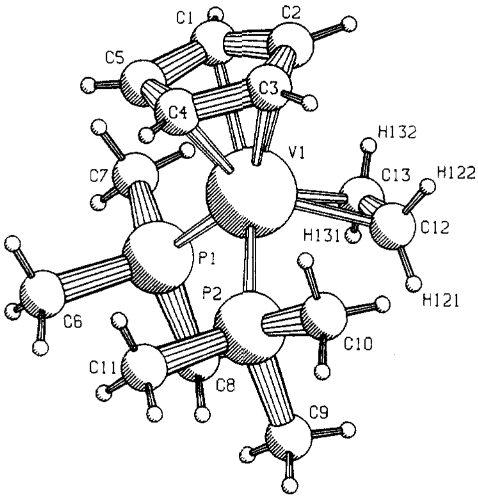


Figure 1. Molecular structure of $CpV(\eta^2\text{-ethene})(PMe_3)_2$ (**2**).

Synthesis and Structure of $CpV(\eta^2\text{-ethene})(PMe_3)_2$

The reaction of $CpVCl_2(PMe_3)_2$ (**1**) with the 1,4-di-Grignard species $BrMg(CH_2)_4MgBr$ (a common reagent to induce metallacycle formation[15]) does not produce the anticipated metallacyclopentane species but forms the green, paramagnetic (by NMR) ethene complex $CpV(\eta^2\text{-ethene})(PMe_3)_2$ (**2**) in 38% yield. The compound was characterized by X-ray diffraction (vide infra). The blue $CpVCl(PMe_3)_2$[13d] was observed as an intermediate in the reaction, indicating that one-electron reduction to V(II) is involved initially. Although V(III) dialkyls $CpVR_2(PMe_3)_n$ (R = Me, n = 2;[13a,b] R = CH_2CMe_3, n = 1[16]) can be directly prepared from **1** and the corresponding alkylating agent when the alkyl group does not contain β-hydrogens, reactions with β-H-containing Grignard reagents lead to reduction through β-H abstraction and subsequent reductive-elimination processes.[17] A better yield of **2** (49%) can be obtained when **1** is first reduced to $CpVCl(PMe_3)_2$, which is then allowed to react with 0.5 mol of the di-Grignard reagent (eq 1). It thus seems likely that

$$\underset{\mathbf{1}}{CpVCl_2(PMe_3)_2} + Na/Hg \xrightarrow[-NaCl]{THF}$$

$$CpVCl(PMe_3)_2 \xrightarrow{{}^1/_2BrMg(CH_2)_4MgBr} \underset{\mathbf{2}}{Cp(\eta^2\text{-ethene})(PMe_2)_2} \qquad (1)$$

the reaction proceeds through a V(II) 1,4-divanadabutane intermediate, $Cp(PMe_3)_2V(CH_2)_4V(PMe_3)_2Cp$. It may be noted here that, in contrast with CpV^{III} compounds, the V(II) alkyl complex CpV(nPr)dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) does not give β-H elimination under the applied reaction conditions (0 °C).[13a] From the presumed 1,4-divanadabutane intermediate two possible routes can be considered leading to the ethene complex, as shown in Scheme I. The first one (A) involves an internal electron-transfer reaction and can be thought of as a radical analogue of the anionic Grob fragmentation from organic chemistry.[18] This appears to be unprecedented for 1,4-dimetallabutanes but has been observed for a 1,2-dimetallacyclo-1-hexyne, $Mo_2(CH_2)_4(NMe_2)_4$[19] and

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(4) (a) Tsumura, R.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1901. (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. *Dokl. Chem.* (*Engl. Transl.*) **1968**, *182*, 789. (c) Foust, D. F.; Rausch, M. D. *J. Organomet. Chem.* **1982**, *239*, 321.

(5) Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1988**, *27*, 99.

(6) (a) Rehder, D.; Dahlenburg, L.; Müller, I. *J. Organomet. Chem.* **1976**, *122*, 53. (b) Roose, W. R. W.; Rehder, D.; Luders, H.; Theopold, K. *J. Organomet. Chem.* **1978**, *157*, 311. (c) King, R. B.; Kapoor, P. N.; Kapoor, R. N. *Inorg. Chem.* **1971**, *10*, 1841.

(7) Fischer, E. O.; Kögler, H. P.; Kuzel, P. *Chem. Ber.* **1960**, *93*, 3006.

(8) King, R. B.; Chen, K.-N. *Inorg. Chim. Acta* **1977**, *23*, L19.

(9) (a) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. (b) Jonas, K.; Rüsseler, W.; Angermund, K.; Krüger, C. *Angew. Chem.* **1986**, *98*, 904.

(10) (a) Jonas, K.; Wiskamp, V. *Z. Naturforsch.* **1983**, *38B*, 1113. (b) Jonas, K. *Pure Appl. Chem.* **1984**, *56*, 63.

(11) (a) Jonas, K.; Rüsseler, W.; Krüger, C.; Raabe, E. *Angew. Chem.* **1986**, *98*, 907. (b) Milczarek, R.; Rüsseler, W.; Binger, P.; Jonas, K.; Angermund, K.; Krüger, C.; Regitz, M. *Angew. Chem.* **1987**, *99*, 957.

(12) (a) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193. (b) Nieman, J.; Scholtens, H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *186*, C12.

(13) (a) Hessen, B.; Lemmen, T. H.; Luttikhedde, H. J. G.; Teuben, J. H.; Petersen, J. L.; Huffman, J. C.; Jagner, S.; Caulton, K. G. *Organometallics* **1987**, *6*, 2354. (b) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946. (c) Hessen, B.; van Bolhuis, F.; Teuben, J. H.; Petersen, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 295. (d) Nieman, J.; Teuben, J. H. *Organometallics* **1986**, *5*, 1149.

(14) (a) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4860. (b) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *367*, C18.

(15) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739 and references cited therein.

(16) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 5977.

(17) Nieman, J. Ph.D. Thesis, Groningen, The Netherlands, 1982.

(18) Becker, K. B.; Grob, C. A. In *The Chemistry of Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; pp Supplement A, Part 2, 653–723.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for $CpV(\eta^2\text{-ethene})(PMe_3)_2$ (2)

V(1)-P(1)	2.429 (1)	V(1)-C(1)	2.304 (3)
V(1)-P(2)	2.497 (1)	V(1)-C(2)	2.295 (3)
V(1)-C(12)	2.153 (3)	V(1)-C(3)	2.292 (4)
V(1)-C(13)	2.173 (3)	V(1)-C(4)	2.280 (5)
C(12)-C(13)	1.365 (5)	V(1)-C(5)	2.296 (3)
av $(C-C)_{Cp}$	1.389 (7)	av (P-C)	1.826 (3)
P(1)-V(1)-P(2)	95.97 (3)	C(12)-V(1)-C(13)	36.8 (2)
P(1)-V(1)-C(12)	112.62 (9)	V(1)-C(12)-C(13)	72.4 (2)
P(2)-V(1)-C(12)	83.40 (8)	V(1)-C(13)-C(12)	70.8 (2)

Table II. Structural Parameters of the Coordinated Ethene Ligand (X-ray Diffraction Data) in Selected Ethene Complexes

compd	C-C, Å	α, deg	ref
C_2H_4[a]	1.337 (2)	0	26
$CpRh(\eta^2\text{-}C_2F_4)(\eta^2\text{-}C_2H_4)$	1.358 (9)	42	27
$CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2$	1.365 (5)	47 (3)	this work
$Cp_2Nb(\eta^2\text{-}C_2H_4)Et$	1.406 (13)	52	28
$Cp^*_2Ti(\eta^2\text{-}C_2H_4)$	1.438 (5)	70 (4)	23
$Cp_2Zr(\eta^2\text{-}C_2H_4)PMe_3$	1.486 (8)		29

[a] Electron diffraction.

is one of the mechanisms suggested for the production of ethene in the reduction of 1,4-dibromobutane by a nickel tetraazaannulene complex.[20] The other pathway (B) involves a disproportionation into an unsaturated CpV^I fragment and a metallacyclopentane. For the latter the isomerization to a bis(olefin) complex and subsequent ethene loss could then be kinetically favored above β-H abstraction and reductive elimination to form 1-butene.[21] The ethene produced could then be absorbed again by the CpV^I species generated earlier. We observed a comparable disproportionation in the reaction of Cp^*_2TiCl[22] (Cp^* = $\eta^5\text{-}C_5Me_5$) with 0.5 mol of $ClMg(CH_2)_4MgCl$, which yields Cp^*_2Ti (as indicated by the intense purple color of its N_2 adduct[23]) and the metallacyclopentane complex $Cp^*_2Ti(CH_2)_4$ (**3**; eq 2). The latter could be obtained at 0 °C as

$$2Cp^*_2TiCl + ClMg(CH_2)_4MgCl \rightarrow \underset{\mathbf{3}}{Cp^*_2Ti(CH_2)_4} + Cp^*_2Ti + 2MgCl_2 \quad (2)$$

red crystals. It is interesting to note that **3** has been reported as being in equilibrium with $Cp^*_2Ti(\eta^2\text{-ethene})$ under ethene but was too thermodynamically disfavored to be isolated.[24] Apparently it can thus be isolated as a kinetically stable product from the 1,4-di-Grignard reaction. When pure **3** is dissolved in benzene-d_6 at room temperature, slow ethene loss occurs to reach the equilibrium mentioned above. So far we have been unable to determine which pathway is effective in the formation of **2**. In this case it seems unlikely that THF acts as a source of ethene:[25] reaction of **1** with 2 equiv of the *n*-propyl Grignard reagent in THF produced a poorly soluble brown mixture, and not a trace of **2** was observed.

An X-ray structure determination of **2** (Figure 1; bond lengths and angles in Table I) shows that the compound has a simple piano-stool geometry, with a regularly η^5-bound Cp group and the two phosphine ligands in an eclipsed geometry. The η^2-ethene ligand is oriented perpendicularly to the plane through the Cp centroid and the metal center that bisects the P(1)-V-P(3) angle. This contrasts with the parallel orientation of the alkyne ligand in $(Ind)V(\eta^2\text{-}HC{\equiv}CPh)(CO)_2$ (Ind = η^5-indenyl).[26] The V-C(ethene) distances of 2.153 (3) and 2.173 (3) Å in **2** are close to the Ti-C(ethene) distances in $Cp^*_2Ti(\eta^2\text{-ethene})$ (2.160 (4) Å).[24] The most striking feature of the structure of **2** is the ethene C(12)-C(13) distance of 1.365 (5), Å, considerably shorter than in most other transition-metal ethene complexes (Table II). Together with the small value (47 (3)°) for the acute dihedral angle α between the two planes through each of the two CH_2 groups, this indicates only a very small amount of π-back-donation into the ethene π* orbital.[31] The compound can therefore be described better as a d^4 V^I–η^2-ethene complex than as a d^2 V^{III} metallacyclopropane. The metallacyclopropane character is much more pronounced in $Cp_2V(\eta^2\text{-}EtO_2CCH{=}CHCO_2Et)$[32] (C-C = 1.468 (11) Å), the only other structurally characterized olefin complex of vanadium, containing a much more electrophilic olefin. Due to the lack of strong π-back-donation the V-ethene bond in **2** is probably quite weak, and easy loss of the ethene ligand can be expected.

Reactivity of $CpV(\eta^2\text{-ethene})(PMe_3)_2$

The most prominent feature of **2** in its reactivity toward various substrates is the ease with which the ethene ligand is displaced under mild conditions (≤0 °C). This makes **2** a good source of $CpV(PMe_3)_2$ fragments. NMR-tube reactions show that with CO and diphenylethyne the ethene ligand is rapidly displaced quantitatively to yield $CpV(CO)_2(PMe_3)_2$[2b] and $CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2$ (**4**) respectively (eqs 3 and 4). From the latter reaction the

$$\underset{\mathbf{2}}{CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2} + 2CO \rightarrow CpV(CO)_2(PMe_3)_2 + C_2H_4 \quad (3)$$

$$\underset{\mathbf{2}}{CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2} + PhC{\equiv}CPh \rightarrow \underset{\mathbf{4}}{CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2} + C_2H_4 \quad (4)$$

red diamagnetic **4** can be obtained in high yield. However, over a long period the ethene produced in the reaction is consumed again in a consecutive reaction (after 1 h at 0 °C only 0.72 mol of ethene/mol of V could be recovered in a Töpler pump experiment). The structure and chemistry of **4** (including the reaction with ethene) are described below.

With 2,2′-bipyridine, displacement of both the ethene ligand and one of the phosphines is observed to produce

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(19) (a) Chetcuti, M. J.; Chisholm, M. H.; Chiu, H. T.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1213. (b) Chisholm, M. H. *Polyhedron* **1986**, *5*, 25.

(20) Espenson, J. H.; Ram, M. S.; Bacac, A. *J. Am. Chem. Soc.* **1987**, *109*, 6892.

(21) (a) Grubbs, R. G.; Myashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300. (b) Grubbs, R. H.; Myashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (c) Brown, M. P.; Hollings, A.; Houston, K. J.; Puddephatt, R. J.; Rashidi, M. *J. Chem. Soc., Dalton Trans.* **1976**, 786. (d) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138.

(22) (a) Pattiasina, J. W.; Heeres, H. J.; van Bolhuis, F.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *Organometallics* **1987**, *6*, 1004. (b) de Boer, E. J. M.; ten Cate, L. C.; Staring, A. G. J.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *181*, 61.

(23) (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087. (b) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (c) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358.

(24) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(25) (a) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560. (b) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, *43*, 3791.

(26) Alt, H. G.; Engelhardt, H. E.; Razavi, A.; Rausch, M. D.; Rogers, R. D. *Z. Naturforsch.* **1988**, *43B*, 438.

(27) Bartell, L. S.; Roth, E. A.; Hollowell, C. D.; Kuchitzu, K.; Young, J. E. *J. Chem. Phys.* **1965**, *42*, 2683.

(28) Guggenberger, L. J.; Cramer, R. *J. Am. Chem. Soc.* **1972**, *94*, 3779.

(29) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

(30) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83.

(31) Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 5333.

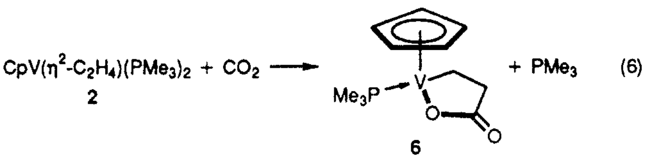
(32) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282.

the paramagnetic 16e complex $\mathrm{CpV(\eta^2\text{-}bpy)PMe_3}$ (5; eq 5).

$$\underset{2}{\mathrm{CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2}} + \mathrm{bpy} \rightarrow \underset{5}{\mathrm{CpV(\eta^2\text{-}bpy)PMe_3}} + \mathrm{C_2H_4} + \mathrm{PMe_3} \tag{5}$$

This shows the tendency of CO-free $\mathrm{CpV^I}$ complexes stabilized by phosphines to remain electronically unsaturated due to the steric bulk of the $\mathrm{PMe_3}$ ligands relative to that of CO; $\mathrm{CpV(\eta^2\text{-}bpy)(CO)_2}$[5,33] is a diamagnetic 18e complex. Despite the paramagnetism of 5, all the bpy protons could be observed in the ^{1}H NMR spectrum.

The ethene ligand is retained in the reaction of 2 with $\mathrm{CO_2}$. In a Töpler pump experiment 0.98 mol of $\mathrm{CO_2}$/mol of V was consumed, and no ethene was produced. The (very poorly soluble) vanadalactone $\mathrm{Cp\overline{V[CH_2CH_2C(O)O}]PMe_3}$ (6) was isolated in good yield (eq 6). The IR



spectrum of 6 shows the ν_{CO} vibration of the uncoordinated carbonyl functionality at 1655 cm^{-1}. The reaction is equivalent to that observed for $\mathrm{Cp^*{}_2Ti(\eta^2\text{-}ethene)}$.[34] It seems remarkable that here a $\mathrm{CpV^{III}}$-alkyl complex containing β-H atoms is apparently stable toward β-H abstraction, but recently an X-ray structure determination of the comparable nickel complex $\mathrm{(dbu)_2\overline{Ni[CH_2CH_2C(O)O}]}$[35] (dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene) revealed that in these complexes the lactone ring is nearly planar, considerably increasing the distance between the metal center and the β-H atoms. This will make β-H abstraction less favorable.

The low-valent metal center in 2, combined with the lability of the ethene ligand, should make it suitable for oxidative-addition reactions. With diphenyl disulfide, 2 reacts at −30 °C in pentane to form initially a yellow solution, possibly of $\mathrm{CpV(SPh)_2(PMe_3)}_n$, but above −20 °C phosphine loss occurs to produce the insoluble $\mathrm{[CpV(\mu\text{-}SPh)_2]_2}$[36] (eq 7). When it is dissolved in 1-hexene, 2 slowly

$$\underset{2}{\mathrm{CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2}} + \mathrm{PhSSPh} \xrightarrow{-\mathrm{C_2H_4}} [\mathrm{CpV(SPh)_2(PMe_3)}_n] \xrightarrow{-n\mathrm{PMe_3}} \tfrac{1}{2}[\mathrm{CpV(\mu\text{-}SPh)_2}]_2 \tag{7}$$

catalyzes the dimerization of this α-olefin. After 48 h at 20 °C 38 mol of 1-hexene/mol of V is transformed into $\mathrm{C_{12}H_{24}}$ dimers. Three isomers are formed in nearly equimolar amounts. On the basis of the GC-MS, IR, and ^{13}C NMR spectra the products are identified as 2-butyl-3-methyl-1-heptene (tt), 7-methyl-5-undecene (ht), and 2-butyl-1-octene (ht). Dimer formation very likely occurs via metallacyclopentane intermediates,[37] formed through reductive coupling of the α-olefins on the $\mathrm{CpV^I}$ fragment generated by ethene loss. More detailed selectivity studies would be necessary to establish if the ring contraction to metallacyclobutanes, as proposed by Schrock et al.[37a] for the $\mathrm{Cp^*TaCl_2}$ system, is also involved here. The catalytic species appears to be thermally quite labile, as increasing the reaction temperature to 50 °C does not, even at prolonged reaction time, increase dimer yield.

Magnesium Reduction of $\mathrm{CpVCl_2(PMe_3)_2}$: Structure of $\mathrm{CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2}$

Although 2 is a good starting material to prepare various CO-free $\mathrm{CpV^I}$ complexes, a more convenient synthetic route for, for example, $\mathrm{CpV(\eta^2\text{-}alkyne)(PMe_3)_2}$ is reduction of 1 in the presence of free alkyne. Earlier it was reported that Zn and Al will reduce 1 only to V(II).[13d,38] Mg proved to be a suitable reducing agent for clean reduction to V(I). Magnesium reduction of 1 in THF in the presence of free alkyne produces $\mathrm{CpV(\eta^2\text{-}RC{\equiv}CR')(PMe_3)_2}$ (R, R′ = Ph, Ph (4), Ph, Me (7), Et, Et (8)) in 60–85% yield (eq 8).

$$\underset{1}{\mathrm{CpVCl_2(PMe_3)_2}} + \mathrm{Mg} + \mathrm{RC{\equiv}CR'} \xrightarrow{\mathrm{THF}} \underset{4,7,8}{\mathrm{CpV(\eta^2\text{-}RC{\equiv}CR')(PMe_3)_2}} + \mathrm{MgCl_2} \tag{8}$$

R, R′ = Ph, Ph (4), Ph, Me (7), Et, Et (8)

Compound 4 was also prepared by starting from $\mathrm{VCl_3\cdot 3THF}$ in 70% overall yield without isolating intermediate 1. This thus appears to be a very convenient route to highly reactive CO-free $\mathrm{CpV^I}$ complexes. The method is not limited to alkynes: the η^4-diene complex $\mathrm{CpV(\eta^4\text{-}2,3\text{-}dimethyl\text{-}1,3\text{-}butadiene)PMe_3}$[13a] could also be obtained by reduction of 1 in the presence of free diene (eq 9). Reduction of 1 in the presence of the smaller alkyne 2-butyne leads to cyclotrimerization of the alkyne, forming $\mathrm{CpV(\eta^6\text{-}C_6Me_6)}$ in moderate yield (eq 10).

$$\underset{1}{\mathrm{CpVCl_2(PMe_3)_2}} + \mathrm{Mg} + 2,3\text{-dimethyl-1,3-butadiene} \xrightarrow{\mathrm{THF}} \mathrm{CpV(\eta^4\text{-}2,3\text{-}dimethyl\text{-}1,3\text{-}butadiene)PMe_3} + \mathrm{MgCl_2} + \mathrm{PMe_3} \tag{9}$$

$$\underset{1}{\mathrm{CpVCl_2(PMe_3)_2}} + \mathrm{Mg} \xrightarrow[\mathrm{Mg,\ THF}]{\mathrm{MeC{\equiv}CMe}} \mathrm{CpV(\eta^6\text{-}C_6Me_6)} + 2\mathrm{PMe_3} \tag{10}$$

The alkyne complexes 4, 7, and 8 are diamagnetic. The downfield shift of the ^{13}C NMR resonances of the carbon atoms in the alkyne C≡C moiety (δ 226.8 ppm in 4) and the low IR frequency of the ν_{CC} vibration (1595 cm^{-1} in 7) indicate that the alkyne acts as a four-electron donor,[39] as in $\mathrm{CpV(\eta^2\text{-}RC{\equiv}CR')(CO)L}$ (L = CO, $\mathrm{PR_3}$).[4,40] This allows the compounds to reach a formal 18e configuration. The ^{51}V NMR resonances of the alkyne complexes lie at very low field (4, +209 ppm; 7, +211 ppm; relative to $\mathrm{VOCl_3}$) compared to those of both the dicarbonyl and monocarbonyl monophosphine analogues ($\mathrm{CpV(\eta^2\text{-}PhC{\equiv}CPh)(CO)_2}$, δ −626 ppm; $\mathrm{CpV(\eta^2\text{-}PhC{\equiv}CPh)(CO)PMe_3}$, δ −498 ppm (−10 °C)[40]). The much larger downfield shift upon replacement of the second CO ligand by $\mathrm{PMe_3}$ is probably related to the strongly increased steric hindrance within complex 4. From earlier investigations this is known to lead to a significant deshielding of the metal center through an increased contribution of the paramagnetic deshielding component.[41]

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[33] Hoch, M.; Rehder, D. *J. Organomet. Chem.* **1985**, *288*, C25.

[34] Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

[35] Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem.* **1987**, *99*, 799.

[36] Muller, F. G.; Watkins, S. F.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 73.

[37] (a) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610. (b) Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416. (d) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353.

[38] Nieman, J.; Teuben, J. H.; Hulsbergen, F. B.; de Graaff, R. A. G.; Reedijk, J. *Inorg. Chem.* **1987**, *26*, 2376.

[39] Templeton, J.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288 and references cited therein.

[40] Alt, H. G.; Engelhardt, H. E. *Z. Naturforsch.* **1985**, *40B*, 1134.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$ (4)[a]

V(1)-P(1)	2.3952 (9)	V(1)-C(1)	2.337 (2)
V(1)-P(2)	2.4099 (9)	V(1)-C(2)	2.358 (2)
V(1)-C(6)	1.932 (2)	V(1)-C(3)	2.274 (2)
V(1)-C(7)	1.996 (2)	V(1)-C(4)	2.204 (2)
C(6)-C(7)	1.328 (3)	V(1)-C(5)	2.242 (2)
C(6)-C(8)	1.473 (3)	C(7)-C(14)	1.471 (3)
av (C-C)$_{Cp}$	1.411 (3)	av (P-C)	1.832 (2)
av (C-C)$_{Ph1}$	1.391 (3)	av (C-C)$_{Ph2}$	1.389 (3)
P(1)-V(1)-P(2)	92.27 (3)	C(6)-V(1)-C(7)	39.48 (8)
P(1)-V(1)-C(6)	121.48 (6)	P(1)-V(1)-C(7)	82.07 (6)
P(2)-V(1)-C(6)	94.35 (7)	P(2)-V(1)-C(7)	99.05 (7)
X-V(1)-P(1)	113.43	X-V(1)-C(6)	117.40
X-V(1)-P(2)	111.73	X-V(1)-C(7)	144.18
V(1)-C(6)-C(7)	72.9 (1)	C(7)-C(6)-C(8)	135.5 (2)
V(1)-C(7)-C(6)	67.7 (1)	C(6)-C(7)-C(14)	135.9 (2)

[a] X is the Cp ring centroid; Ph1 = C(8)-C(13), Ph2 = C(14)-C(19).

An X-ray structure determination was carried out on the diphenylethyne complex 4 (Figure 2; bond lengths and angles in Table III). The alkyne C(6)-C(7) distance of 1.328 (3) Å and the "bending-back" angles of the aryl substituents from the C_2 moiety of around 136° are consistent with the alkyne acting as a four-electron donor. These features are comparable to those in Cp*Ta(η^2-PhC≡CPh)Cl$_2$[42] (1.337 (8) Å and 139°) and clearly differ from those in Cp$_2$V(η^2-MeO$_2$CC≡CCO$_2$Me)[32] (1.287 (4) Å and 143.5°), where the alkyne acts only as a two-electron donor. Of interest is the orientation of the alkyne ligand relative to the plane through the Cp centroid and the metal atom bisecting the P-V-P angle, which is halfway between the perpendicular orientation of the C_2 ligand in 2 and the parallel orientation in (Ind)V(η^2-HC≡CPh)(CO)$_2$[26] (see Figure 2b). The dihedral angle between the V-X and C(6)-C(7) vectors (X = Cp-ring centroid) in 4 is 45.5°. This may indicate that in 4 the conformation of the alkyne ligand is distorted from the electronically most favorable orientation by steric hindrance between the ligands. Relatively short nonbonded contacts can be observed for C(3)···H(9) = 2.79 (2) Å and C(19)···H(221) = 2.66 (2) Å (the sum of C and H contact radii is 2.90 Å;[43] H(221) is a hydrogen of the C(22) methyl group). A comparable distortion was observed in the structure of the isoelectronic Re complex Cp*Re(η^2-EtC≡CEt)Cl$_2$.[44] In low-temperature ^{13}C NMR spectra of 4 in toluene-d_8 the alkyne carbon resonance shows, after initial narrowing of the signal due to relaxation decoupling of the quadrupolar ^{51}V nucleus (revealing a triplet with J_{PC} = 13 Hz at 230 ppm, -40 °C), coalescence broadening below -65 °C. Although the process could not be frozen out completely, it indicates an asymmetric ground-state structure in solution as well. In 4 the Cp ligand is also much more distorted from the regular η^5 bonding mode than in 2. The average V-C(Cp) distance in 4 is 2.283 (2) Å, with maximum deviations from the mean value of +0.075 Å (C(2)) and -0.079 Å (C(4)). For 2 these figures are 2.293 and +0.011/-0.013 Å, respectively. The V-C(alkyne) distances in 4 (V-C(6) = 1.932(2) Å, V-C(7) = 1.996 (2) Å) are considerably shorter than the V-C(alkene) distances in 2, indicating that the C_2 ligand in 4 is more strongly bound. This is reflected in the reactivity of the alkyne complex.

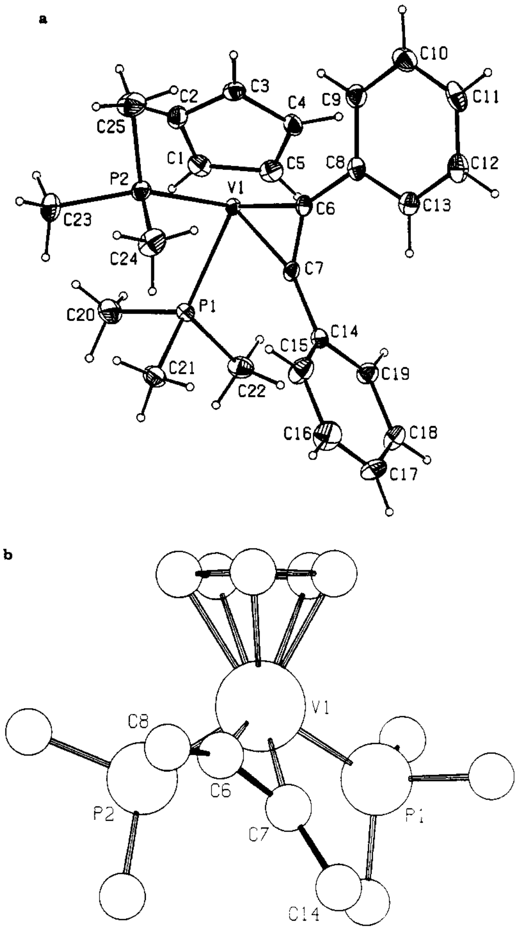

Figure 2. Molecular structure of CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$ (4): (a) ORTEP representation; (b) orientation of the coordinated diphenylethyne ligand (shaded bonds) in 4. Hydrogen and phenyl carbon atoms (except ipso carbons) are omitted for clarity.

Reactivity of CpV(η^2-PhC≡CPh)(PMe$_3$)$_2$

In contrast to the case for the ethene complex 2, the reactivity of 4 is initiated by loss of a phosphine ligand. Thus, 4 acts in its reactions as a source of CpV(η^2-PhC≡CPh)PMe$_3$ fragments. With alkenes and alkynes, 4 reacts under mild conditions (20 °C, atmospheric pressure), without need for photochemical activation, and as such appears to be much more reactive than the CpV(η^2-RC≡CR')(CO)$_2$ complexes.

With 1,3-butadiene 4 reacts to give a paramagnetic compound of stoichiometry CpV(C$_2$Ph$_2$C$_4$H$_6$)PMe$_3$ (9), which can be isolated as red-brown crystals in good yield. The IR spectrum of 9 shows a characteristic allylic vibration absorption at 1525 cm^{-1}, indicating the formation of an η^1,η^3-1,2-diphenylhexa-1,4-dien-1,6-diyl complex (eq 11). The compound resembles the η^1,η^3-2-hexene-1,6-diyl

(11)

complex CpV(η^1,η^3-CH$_2$CH$_2$C$_4$H$_6$)PMe$_3$, produced in the reaction between CpV(η^4-butadiene)PMe$_3$ and ethene,[10a] which shows an allylic absorption in the IR spectrum at the same wavenumber. After PMe$_3$ dissociation, η^2-coordination of the diene, followed by C,C coupling to the alkyne to form a 2-vinylmetallacyclopentene, can lead to the η^1,η^3-hexadienediyl ligand. Similar coupling reactions

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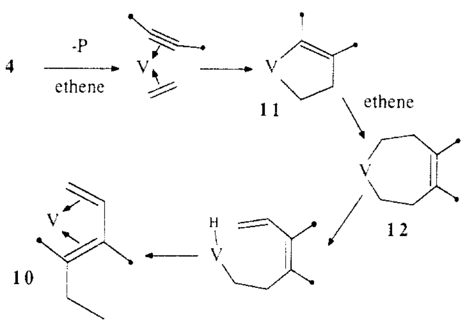
(41) (a) Rehder, D. *J. Magn. Reson.* **1980**, *28*, 419. (b) Hoch, M.; Rehder, D. *Chem. Ber.* **1988**, *121*, 1541.

(42) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. *Inorg. Chem.* **1981**, *20*, 387.

(43) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

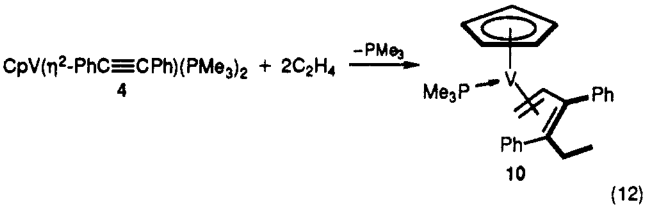
(44) Fischer, R. A. Ph.D. Thesis, Technische Universität München, 1989.

Scheme II



between a diene and an alkyne have been reported for the Cp_2Zr(1,3-diene) system.[45]

In a Töpler pump experiment 4 is observed to react selectively with 2 mol of ethene/mol of vanadium. In this reaction a paramagnetic brown crystalline compound is formed, which was identified by X-ray diffraction as $CpV[\eta^4\text{-}CH_2{=}CHC(Ph){=}C(Ph)Et]PMe_3$ (**10**), an *s-cis*-3,4-(*E*)-diphenyl-1,3-hexadiene complex (eq 12). This



(12)

ligand is produced in a linear 1:2 cotrimerization of diphenylacetylene with ethene. Although (catalytic) 2:1 cotrimerization of alkynes and alkenes is known to occur with several late-transition-metal complexes (e.g. $Fe(C_8H_8)_2$, $(C_2H_2)_2RhCl_2$, $Ni(CO)_4/PPh_3$),[46] 1:2 cotrimerizations are quite rare. For substrates bearing electron-withdrawing substituents ($MeO_2CCH{=}CHCO_2Me$, $NCCH{=}CHCN$, etc.), this reaction has been studied by Wakatsuki et al.[47] for $CpCo(\eta^2\text{-alkyne})PPh_3$ and was shown to proceed through a cobaltacyclopent-2-ene species. The reaction of 4 with ethene probably proceeds through the reaction sequence depicted in Scheme II. Apparently, β-H abstraction in the V^{III} vanadacyclopent-2-ene intermediate **11** is considerably slower than insertion of a second ethene molecule (otherwise the product would have been a 1,2-diphenyl-1,3-butadiene complex; cf. the reaction product of $Cp^*Re(\eta^2\text{-alkyne})Cl_2$ with ethene[48]). Together with earlier observations, this would indicate a sequence of decreasing β-H abstraction rate in monomeric V^{III}–alkyl complexes in the order $V(CH_2CH_2R)X$ > vanadacyclohept-4-ene **12** ≥ vanadacyclopentane > vanadacyclopent-2-ene **11** ≥ vanadalactone **6**.

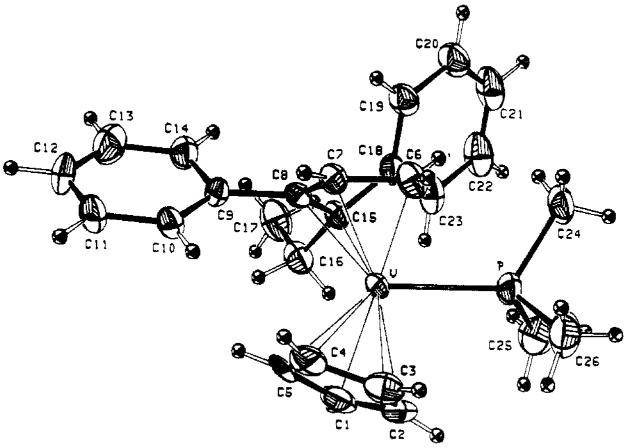


Figure 3. Molecular structure of $CpV[\eta^4\text{-}CH_2{=}CHC(Ph){=}C(Ph)Et]PMe_3$ (**10**).

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $CpV[\eta^4\text{-}CH_2{=}CHC(Ph){=}C(Ph)Et]PMe_3$ (10)

V–P	2.511 (1)	V–C(1)	2.313 (5)
V–C(6)	2.209 (4)	V–C(2)	2.317 (5)
V–C(7)	2.212 (4)	V–C(3)	2.322 (6)
V–C(8)	2.241 (4)	V–C(4)	2.294 (5)
V–C(15)	2.251 (5)	V–C(5)	2.285 (4)
av (P–C)	1.827 (6)	av $(C–C)_{Cp}$	1.411 (7)
C(6)–C(7)	1.421 (5)	C(8)–C(9)	1.510 (5)
C(7)–C(8)	1.410 (6)	C(15)–C(16)	1.547 (6)
C(8)–C(15)	1.454 (6)	C(15)–C(18)	1.495 (6)
C(16)–C(17)	1.530 (8)		
C(6)–C(7)–C(8)	125.3 (4)	C(7)–C(8)–C(15)	123.3 (3)
C(7)–C(8)–C(9)	115.0 (3)	C(9)–C(8)–C(15)	121.7 (4)
C(8)–C(15)–C(16)	118.3 (3)	C(8)–C(15)–C(18)	121.7 (3)
C(16)–C(15)–C(18)	113.3 (4)		

The X-ray structure of **10** (Figure 3; bond lengths and angles in Table IV) shows a purely η^4-bound planar diene ligand, without any of the metallacyclopent-3-ene character observed in the higher valent Nb and Ta diene complexes $Cp^*M(1,3\text{-diene})Cl_2$:[49] for both the substituted and unsubstituted halves of the *s-cis*-bound diene the V–C distances for the terminal and internal carbon atoms are approximately the same. Probably due to steric reasons, the V–C and C–C distances pertaining to the substituted (C(8), C(15)) side of the diene are all slightly longer than those for the unsubstituted side. The complex as a whole appears to be sterically quite crowded, as all the metal–ligand distances (especially the V–P distance of 2.511 (1) Å) are longer than in the ethene complex **2**, although both compounds are 16e $S = 1$ V(I) complexes. The Et and Ph substituents on C(15) are strongly twisted out of the plane of the diene (torsion angles C(7)–C(8)–C(15)–C(16) = 155.4° and C(7)–C(8)–C(15)–C(18) = −55.2°). It is remarkable that in **10** the phenyl substituents of the original diphenylethyne ligand are *E* relative to each other in the newly formed diene ligand, whereas *Z* isomers are produced in reactions of the CpCo system. Possibly *Z*,*E* isomerization takes place in the complex to attain a sterically more favorable orientation. Such an isomerization was observed in the formation of $Cp_2V(\eta^2\text{-}EtO_2CCH{=}CHCO_2Et)$, where an *E* configuration was found for products obtained from the reaction of Cp_2V with both diethyl maleate and diethyl fumarate.[32]

The diene ligand in **10** is displaced from the metal center upon reaction with CO, producing free 3,4-(*E*)-diphenyl-1,3-hexadiene and a mixture of four different CpV carbonyls, $CpV(CO)_{4-n}(PMe_3)_n$ (n = 0, 1, 2 (cis, trans)).

The reaction of 4 with 2-butyne proceeds in a stepwise fashion. Initially, displacement of a phosphine ligand occurs to give the bis(alkyne) complex $CpV(\eta^2\text{-}MeC{\equiv}$

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(45) (a) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1982**, 1979. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120 and references cited therein.

(46) (a) Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. *J. Am. Chem. Soc.* **1976**, *98*, 8494. (b) Brown, L. D.; Itoh, K.; Suzuki, H.; Hirai, K.; Ibers, J. *J. Am. Chem. Soc.* **1978**, *100*, 8232. (c) Chalk, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5928. (d) Singleton, D. M. *Tetrahedron Lett.* **1973**, 1245.

(47) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123.

(48) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem.* **1988**, *27*, 1509.

(49) (a) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410. (b) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

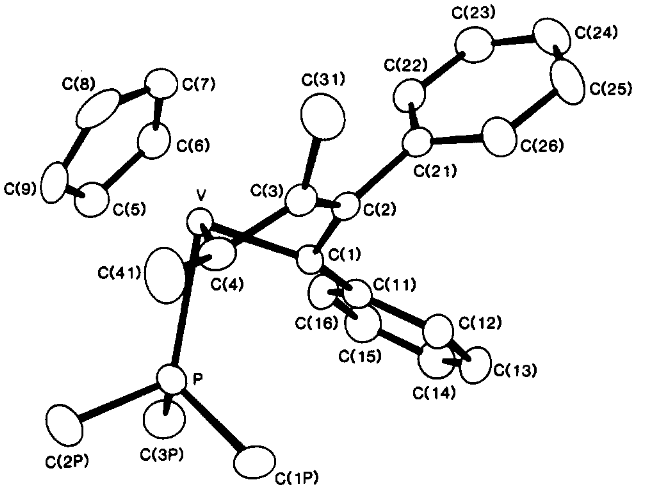
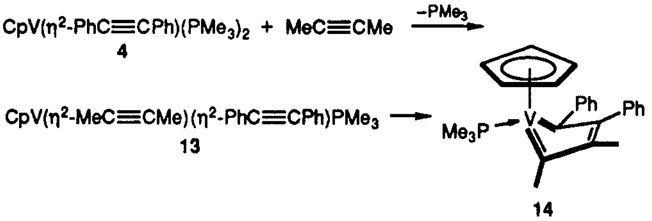


Figure 4. Molecular structure of $CpV(C_4Me_2Ph_2)PMe_3$ (**14**). Hydrogen atoms are omitted for clarity.

$CMe)(\eta^2\text{-}PhC{\equiv}CPh)PMe_3$ (**13**). Although thermally quite labile, it can be isolated as an orange-brown crystalline solid. At or above room temperature C,C coupling between the alkyne ligands takes place to form the green metallacycle $CpV(C_4Me_2Ph_2)PMe_3$ (**14**; eq 13). The bis(alkyne)



(13)

complex **13** shows fluxional behavior (rotation around the 2-butyne–metal bond) in solution, which can be studied by NMR spectroscopy. $\Delta G^{\ddagger}$ for the process at the coalescence temperature (245 K) of the butyne methyl protons is estimated[50] to be 47.3 kJ mol^{-1}, between the two values found for $CpV(\eta^2\text{-}MeC{\equiv}CMe)(CO)L$ ($L = PMe_3$, 54.5 kJ mol^{-1}; L = tBuNC, 42.0 kJ mol^{-1}). At −50 °C all four individual acetylenic carbon atoms in **13** can be observed in the ^{13}C NMR spectrum ($\delta({\equiv}CPh)$ 190.10 (J_{PC} = 10.1 Hz), 164.52 (40.3 Hz); $\delta({\equiv}CMe)$ 198.49 (J_{PC} = 12.8 Hz), 157.87 (43.7 Hz)), with the carbon atoms showing the largest J_{PH} values positioned trans relative to the PMe_3 ligand. The compound is probably isostructural with $CpNb(\eta^2\text{-}PhC{\equiv}CPh)_2CO$.[51] The ${\equiv}CMe$ resonances coalesce around 179 ppm at 20 °C. The average shift of the diphenylacetylenic carbons in **13** is approximately 50 ppm upfield from those in **4**, as in **13** the two alkynes have only to contribute six electrons between them for the complex to reach a formal 18e state. This is also reflected in the relatively high $\nu(C{\equiv}C)$ frequencies in the IR spectrum of **13** (1720, 1727 (sh) cm^{-1}).

The metallacyclic C,C-coupling product **14** is diamagnetic and shows the ^{13}C NMR resonances of the metallacycle strongly shifted downfield (δ 273 and 257 ppm) for the two vanadium-bound atoms, strongly broadened by unresolved quadrupolar coupling with the ^{51}V nucleus, and upfield (δ 80.80 and 88.72 ppm) for the other two. These shifts indicate that **14** is not a metallacyclopenta-2,4-diene but, rather, a (bent) metallacyclopenta-1,3,5-triene complex, as recently discovered in two 4d/5d group 6 transition-metal complexes, $CpMo(C_4Ph_4)Cl$[52] and (2,6-diphenylphenoxide)$_2W(C_4Et_4)$.[53] This was confirmed by an X-ray structure determination of **14** (Figure 4; bond lengths and angles in Table V). The distances V–C(1) = 1.891 (3) Å and V–C(4) = 1.883 (3) Å are significantly shorter than usually observed for V–C single bonds.[54] The metallacycle is clearly folded (toward the Cp ring, in contrast to the case for $CpMo(C_4Ph_4)Cl$), with a "fold angle" (between the V–C(1)–C(4) and C(1)–C(2)–C(3)–C(4) planes) of 117.6°. The V–C(2) and V–C(3) distances (both 2.247 (3) Å) are short enough to indicate interaction between V and the C(2)–C(3) bond. This is also supported by the large X–V–C(1/4) angles (X = Cp centroid) of 133.7 and 126.3°, respectively. The metallacycle C–C distances are all approximately equal within 3σ and do not show the characteristic alteration observed for metallacyclopentadiene complexes (a recent example is (2,6-diisopropylphenoxide)$_3Ta(C_4Et_4)$[55]). Thus, **14** is the first bent metallacyclopentatriene complex of a transition metal other than a group 6 metal and is one of the very rare vanadium complexes containing V–C multiple-bond character (the only alkylidene complex of vanadium, $CpV(CHCMe_3)(dmpe)$,[16] has a V=C bond distance of 1.809 (3) Å). Compound **4** also reacts with diphenylethyne to give the related 2,3,4,5-tetraphenylvanadacyclopentatriene complex $CpV(C_4Ph_4)PMe_3$, but this reaction only proceeds at higher temperatures (60 °C), and no intermediate bis(alkyne) adduct could be observed. In this product the ^{13}C NMR resonances of the V=C carbons are significantly less broadened than those in **14**, revealing a large PC coupling constant of 63 Hz. The observed product formation strongly contrasts with that found in the reaction of $CpV(\eta^2\text{-}PhC{\equiv}CPh)(CO)_2$ with diphenylethyne, which produces, after formation of an intermediate bis(alkyne) adduct, the η^4-cyclobutadiene complex $CpV(\eta^4\text{-}C_4Ph_4)(CO)_2$.[4b] The reluctance of **14** to bind a second

Table V. Selected Interatomic Distances (Å) and Angles (deg) for $CpV(C_4Me_2Ph_2)PMe_3$ (14)[a]

V–C(1)	1.891 (3)	V–C(5)	2.294 (3)
V–C(2)	2.247 (3)	V–C(6)	2.298 (3)
V–C(3)	2.247 (3)	V–C(7)	2.273 (4)
V–C(4)	1.883 (3)	V–C(8)	2.293 (4)
V–P	2.367 (1)	V–C(9)	2.312 (3)
C(1)–C(11)	1.450 (4)	C(2)–C(21)	1.504 (4)
C(3)–C(31)	1.516 (5)	C(4)–C(41)	1.490 (5)
V–X	1.960	av $(C–C)_{Cp}$	1.401 (5)
C(1)–C(2)	1.438 (4)	av $(C–C)_{Ph1}$	1.387 (5)
C(2)–C(3)	1.413 (4)	av $(C–C)_{Ph2}$	1.385 (5)
C(3)–C(4)	1.427 (4)	av (P–C)	1.820 (4)
C(1)–V–X	133.66	C(3)–V–X	130.00
C(2)–V–X	133.89	C(4)–V–X	126.26
V–C(4)–C(3)	84.3 (2)	V–C(4)–C(41)	144.1 (2)
V–C(1)–C(2)	83.7 (2)	V–C(1)–C(11)	148.6 (2)
P–V–C(1)	80.87 (9)	P–V–C(4)	82.84 (10)
P–V–X	116.34		

[a] X is the Cp ring centroid; Ph1 = C(11)–C(16), Ph2 = C(21)–C(26).

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(50) Günther, H. *NMR Spektroskopie*; G. Thieme Verlag: Stuttgart, FRG, 1973; p 248.

(51) Nesmeyanov, N.; Gusev, A. I.; Pasynskii, A. A.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *J. Chem. Soc. D* **1969**, 277.

(52) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218.

(53) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235.

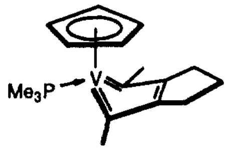
(54) V–C σ-bonds generally fall in the range 2.05–2.18 Å; see for example: (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1984**, 886. (b) Ciurli, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1401. (c) Wills, A. R.; Edwards, P. G.; Harman, M.; Hursthouse, M. B. *Polyhedron* **1989**, *8*, 1457. (d) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1986**, *304*, 41.

(55) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.

PMe_3 ligand is probably the cause for this difference in behavior.

Bicyclic vanadacyclopentatriene complexes $CpV[C_4Me_2(CH_2)_n]PMe_3$ (n = 3 (**15**), 4 (**16**)) can be obtained directly when **1** is reduced with Mg in the presence of 2,7-nonadiyne (eq 14) or 2,8-decadiyne, respectively. They show basically the same features in the NMR spectra as **14**, confirming the bent metallacyclopentene structure of the compounds. Thus, formally vanadium(V) dicarbene complexes are formed by alkyne C,C coupling under reducing circumstances. Because vanadium dicarbene complexes are otherwise unknown, it would be very interesting to see if this carbene character could be expressed in carbene reactivity. We are presently exploring this possibility. It is probably important for obtaining carbenic reactivity that an added substrate does not occupy an extra coordination site in the complex but rather displaces the phosphine ligand. In the first reported (planar) metallacyclopentatriene, $CpRu(C_4Ph_2H_2)Br$,[56] it was found that coordination of an extra Lewis-base ligand converts it into an "ordinary" metallacyclopentadiene. This is probably also the case for the vanadium complexes. In an NMR-tube experiment **16** was allowed to react with CO and rapid formation of the η^4-cyclopentadienone complex $CpV[\eta^4\text{-}O{=}CC_4Me_2(CH_2)_4](CO)PMe_3$ (**17**) was observed (eq 15), as expected for the reactivity of a metallacyclopentadiene. From the ^{31}P couplings on the Cp protons and the cyclopentadienone carbonyl carbon atom it can be seen that the PMe_3 ligand remains coordinated throughout the reaction: only in a slower subsequent reaction is it replaced by another CO molecule to produce the dicarbonyl derivative $CpV[\eta^4\text{-}O{=}CC_4Me_2(CH_2)_4](CO)_2$ (**18**).

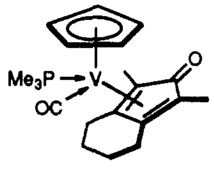
$CpVCl_2(PMe_3)_2$ + Mg + $MeC{\equiv}C(CH_2)_3C{\equiv}CMe$ →
1



+ $MgCl_2$ + PMe_3 (14)

15

$CpV[C_4Me_2(CH_2)_4]PMe_3$ + 2CO →
15



(15)

17

Concluding Remarks

Cyclopentadienylvanadium(I) complexes $CpV(L)(PMe_3)_2$ (L = η^2-ethene, η^2-alkyne) form a class of highly reactive compounds that are readily available from $CpVCl_2(PMe_3)_2$. The lability of the ethene and phosphine ligands makes them a good source for unsaturated intermediates through which complexes of vanadium in various formal oxidation states (+1, +3, +5) can be obtained. Essential to this reactivity is the use of PMe_3 as Lewis-base ligand instead of CO. This influences the reactivity of the complexes in two main ways. First, the PMe_3 ligands in $CpV(L)(PMe_3)_2$ are thermally much more labile than the CO ligands in corresponding $CpV(L)(CO)_2$ complexes. This allows smooth reactivity under ambient conditions, even with substrates that are not strongly Lewis basic. Second, the size of the PMe_3 ligand prevents it from occupying small vacant coordination sites in the products, allowing multistep reactions and formation of electronically unsaturated products, suitable for further reactivity. An added advantage is the inertness of the PMe_3 ligand itself, which considerably increases the scope of reactivity of CpV^I compounds.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere (by Schlenk techniques or in a glovebox), or with use of vacuum-line techniques. Gas uptakes were determined with a Töpler pump connected to a vacuum line.[57] Solvents (diethyl ether, THF, toluene, pentane, and deuterated solvents except $CDCl_3$) were distilled under nitrogen from Na/K alloy before use. NMR spectra were recorded on a Varian VXR-300 (^1H 300 MHz; ^{13}C, 75.4 MHz; ^{51}V, 78.9 MHz) or a Bruker WH-90DS (^1H, 90 MHz) spectrometer, with chemical shifts in ppm downfield from TMS (δ 0.00, ^1H, ^{13}C) or $VOCl_3$ (δ 0.00, ^{51}V) positive. IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer, from Nujol mulls between KBr disks (unless stated otherwise). $CpVCl_2(PMe_3)_2$[12a] and $Cp^*{}_2TiCl$[22a] were prepared according to published procedures. $VCl_3\cdot 3THF$ was prepared from VCl_3 (Merck) by continuous extraction with THF and subsequent cooling of the extract to -30 °C. $RC{\equiv}CR'$ (R, R' = Ph, Ph; Et, Et; Ph, Me; Me, Me) (Aldrich) and $MeC{\equiv}C(CH_2)_nC{\equiv}CMe$ (n = 3, 4) and 2,2'-bipyridine (Prolabo) were purchased and used without further purification, as were ethene and 1,3-butadiene (Matheson). 2,3-Dimethyl-1,3-butadiene (Aldrich) was degassed, dried over 4-Å molecular sieves, and vacuum-transferred before use. 1-Hexene was passed over alumina, degassed, and stored over molecular sieves (4 Å). Diphenyl disulfide (Aldrich) was recrystallized from ether. $XMg(CH_2)_4MgX$ (X = Cl, Br) was prepared in THF with use of purcahsed $X(CH_2)_4X$ (Aldrich) and Mg turnings. Solutions (<0.5 M) were calibrated and used within 1–2 h after preparation. GC-MS spectra were recorded by Dr. A. P. Bruins (Pharmaceutical Department, Rijksuniversiteit Groningen) on a Finnigan 3300 instrument. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Reported values are the average of at least two independent determinations.

$CpV(\eta^2$-ethene)$(PMe_3)_2$ (2). In 60 mL of THF, **1** (4.830 g, 14.24 mmol) was stirred over an amalgam made of 3.4 mL of Hg and 0.327 g (14.24 mmol) of Na sand for 16 h at room temperature. The deep blue solution was decanted into another vessel and cooled to 0 °C. After 30 min 18.5 mL of a 0.39 M $BrMg(CH_2)_4MgBr$ solution in THF was added dropwise; then the resultant green solution was stirred for another 45 min at 0 °C. THF was pumped off at 0 °C; the solid was stripped of residual THF by adding and then pumping off 15 mL of pentane and subsequently extracted twice with 60 mL of pentane at 0 °C. Concentrating and cooling the extract to -30 °C yielded 2.053 g (6.93 mmol, 49%) of green crystalline **2** in two crops. ^1H NMR (benzene-d_6, 30 °C, 90 MHz): δ 14.4 ($\Delta\nu_{1/2}$ = 253 Hz, PMe_3). IR: 3095 (w), 2800 (vw), 1422 (s), 1293 (mw), 1275 (m), 1103 (s, $\delta_{CH_2} + \nu_{CC}$), 1009 (m), 940 (br, vs), 823 (mw), 772 (vs), 717 (s), 666 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{27}P_2V$: C, 52.71; H, 9.19; V, 17.20; P, 20.9. Found: C, 52.62; H, 9.13; V, 17.17; P, 21.4.

Reaction of 1 with $BrMg(CH_2)_4MgBr$. To a purple solution of **1** (1.31 g, 3.88 mmol) in 50 mL of THF was added dropwise 13.8 mL of a 0.28 M $BrMg(CH_2)_4MgBr$ solution in THF, over 80 min at 0 °C. The solution changed from purple via deep blue (at this stage of the reaction $CpVCl(PMe_3)_2$ can be isolated) to olive green. After workup similar to the procedure described above, 0.433 g (1.46 mmol, 38%) of green **2** was isolated.

Reaction of $Cp^*{}_2TiCl$ with $ClMg(CH_2)_4MgCl$. At -30 °C, 2.3 mL of a 0.40 M solution of $ClMg(CH_2)_4MgCl$ in THF was added dropwise to a solution of $Cp^*{}_2TiCl$ (0.648 g, 1.832 mmol) in 15 mL of THF. The mixture was warmed to 0 °C and stirred for 1 h more. The solvent was pumped off at 0 °C and the solid stripped of residual THF by stirring with 5 mL of pentane, which was subsequently pumped off (0 °C). Extracting with 20 mL of

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[56] Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.

[57] Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; p 79.

pentane at 0 °C and concentrating and cooling the extract to −80 °C yielded 0.160 g (0.427 mmol, 47%) of red crystalline $Cp^*_2Ti(CH_2)_4$ (**3**). ^1H NMR (300 MHz, benzene-d_6, 25 °C): δ 1.85 (m, 4 H, CH_2), 1.81 (s, 30 H, Cp*), 0.63 (m, 4 H, Ti–CH_2); contains <3% Cp^*_2Ti(ethene). ^{13}C NMR (75.4 MHz, benzene-d_6, 25 °C): δ 12.32 (q, 125.5 Hz, Cp*–Me), 32.89 (t, 122.6 Hz, CH_2), 62.23 (t, 122.6 Hz, Ti–CH_2), 120.73 (s, C_5Me_5). IR: 2835 (vs), 2720 (w), 1487 (m), 1372 (s), 1325 (w), 1300 (w), 1229 (w), 1180 (mw), 1017 (m), 938 (vw), 810 (w), 720 (w), 513 (w), 477 (mw), 410 (m) cm^{-1}.

Reaction of 2 with Diphenylethyne. To a solution of **2** (0.116 g, 0.39 mmol) in 15 mL of pentane was quickly added a solution of 71 mg (0.39 mmol) of diphenylethyne in 5 mL of pentane, at −12 °C. The solution immediately turned deep cherry red. After 15 min the solution was concentrated and cooled to −80 °C, yielding 0.130 g (0.29 mmol, 75%) of deep red crystalline **4**. Physical characteristics of **4** are described below. In a Töpler pump experiment the mixture was stirred for 1 h at 0 °C. In several freeze–thaw cycles only 0.72 mol of ethene (GC)/mol of **2** could be pumped off. NMR-tube reactions showed that the reaction is fast and quantitative but that the ethene produced in the reaction is consumed again in a sequential reaction (forming **10**, vide infra).

$CpV(\eta^2\text{-bpy})PMe_3$ (5). To a solution of **2** (0.27 g, 0.91 mmol) in 25 mL of pentane was quickly added a solution of 2,2′-bipyridine (0.15 g, 0.95 mmol) in 5 mL of pentane, at 0 °C. The solution slowly turned red-brown. After 45 min the solution was concentrated and cooled to −80 °C. A total of 0.19 g (0.55 mmol, 60%) of brown crystals (with a greenish hue) of **5** was isolated. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 6.68 ($\Delta\nu_{1/2}$ = 282 Hz, 9 H, PMe_3), 39.05 ($\Delta\nu_{1/2}$ = 197 Hz) + 39.81 ($\Delta\nu_{1/2}$ = 257 Hz, total 4 H, bpy), −30.2 ($\Delta\nu_{1/2}$ = 1790 Hz, 2 H, bpy), 99.6 ($\Delta\nu_{1/2}$ = 1610 Hz, 2 H, bpy); Cp resonance not observed. Anal. Calcd for $C_{18}H_{22}N_2PV$: C, 62.07; H, 6.37; V, 14.63. Found: C, 62.81; H, 6.54; V, 14.52.

Reaction of 2 with PhSSPh. To a solution of **2** (0.16 g, 0.55 mmol) in 15 mL of pentane was added over 5 min a solution of 0.55 mmol PhSSPh in 7.5 mL of pentane, at −30 °C. Initially a clear yellow solution was formed, but when it was warmed to −20 °C, a brown solid precipitated. The solvent was decanted and the brown powder dried after a washing with 10 mL of pentane. A total of 0.093 g (0.14 mmol, 51%) of $[CpV(\mu\text{-SPh})_2]_2$ was isolated. The IR spectrum was identical with that reported in ref 35.

$CpV[\overline{CH_2CH_2C(O)O}]PMe_3$ (6). On a vacuum line 1.58 mmol of CO_2 (produced by oxidation of CO over CuO at 250 °C) was condensed into a frozen solution of **2** (0.25 g, 0.84 mmol) in 10 mL of toluene. The mixture was thawed out and warmed to room temperature overnight. Red crystals had formed from a brown solution. The liquid was decanted, and the crystals were washed several times with pentane and dried in vacuo; yield 0.17 g (0.64 mmol, 76%) of **6**. Anal. Calcd for $C_{11}H_{18}O_2P$: C, 50.01; H, 6.87; V, 19.24. Found: C, 50.56; H, 6.90; V, 19.21. IR: 3085 (w), 3065 (w), 2800 (w), 1655 (br vs, ν_{CO}), 1420 (mw), 1295 (vs), 1279 (m), 1256 (vs), 1209 (vs), 1033 (mw), 1215 (m), 1179 (mw), 950 (vs), 892 (w), 862 (w), 840 (mw), 827 (s), 792 (vs), 730 (s), 608 (w), 467 (mw), 422 (w) cm^{-1}. In a Töpler pump experiment a consumption of 0.98 mol of CO_2/mol of **2** was observed. No ethene was produced in the reaction.

Catalytic Dimerization of 1-Hexene by 2. At room temperature **2** (31 mg, 0.105 mmol) was dissolved in 1-hexene (5 mL). The green solution turned brown in 30 min. After 48 h the volatile components were vacuum-transferred. The nonvolatile fraction was extracted with pentane (atmospheric conditions). The extract was passed over a short alumina column to remove inorganic residues, after which the pentane was evaporated: yield 0.34 g (2.02 mmol) of $C_{12}H_{24}$; conversion of 38.5 mol of 1-hexene/mol of **2**. The product was shown by GC-MS to consist mainly of three isomers (all M^+ = 168) in a 4:3:3 ratio. From ^1H and ^{13}C NMR (APT) and IR spectroscopy the products were characterized as 2-butyl-1-methyl-1-heptene (tt), 7-methyl-5-undecene (ht), and 2-butyl-1-octene (ht). ^{13}C NMR (APT, 75.4 MHz, chloroform-d_1, 20 °C): δ 154.90, 150.22 ($RR'C{=}CH_2$), 108.35, 107.04 ($RR'C{=}CH_2$), 131.33, 129.02 ($RCH{=}$), 40.09, 33.35 ($RR'CH(Me)$); for the mixture.

$CpV(\eta^2\text{-PhC}{\equiv}\text{CPh})(PMe_3)_2$ (4). **1** (1.78 g, 5.26 mmol) and diphenylethyne (0.94 g, 5.26 mmol) were stirred together with magnesium turnings (1.0 g, excess) in 30 mL of THF at room temperature. The solution changed from purple-blue to deep cherry red. The solvent was removed in vacuo and the solid stripped of residual THF by stirring with 10 mL of toluene, which was then pumped off. After it was dried in vacuo, the mixture was extracted with 50 mL of toluene. The extract was concentrated, 15 mL of pentane was added in portions, and after gradual cooling to −80 °C red crystalline **4** (2.00 g, 4.49 mmol, 85%) was isolated in two crops. Anal. Calcd for $C_{25}H_{33}P_2V$: C, 67.26; H, 7.45; V, 11.41. Found: C, 67.20; H, 7.46; V, 11.43. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 7.3–7.0 (m, 10 H, Ph), 4.93 (s, 5 H, Cp), 0.87 (s, 18 H, PMe_3). ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 24.57 (q, 126 Hz, PMe_3), 93.84 (d, 172.5 Hz, Cp), 124.56 (d, 160.6 Hz, Ph *C*H), 126.57 (d, 156.2 Hz, Ph *C*H), 128.05 (d, 158.0 Hz, Ph *C*H), 148.96 (s, Ph *C*), 226.8 (br, $\Delta\nu_{1/2}$ = 48 Hz, $\equiv C-$). ^{51}V NMR (78.9 MHz, benzene-d_6, 21 °C): δ +209 ($\Delta\nu_{1/2}$ = 2870 Hz). IR: 3050 (w), 3025 (vw), 1600 (s), 1482 (mw), 1430 (mw), 1288 (mw), 1273 (m), 1112 (wm), 1070 (w), 1025 (w), 1006 (mw), 948 (vs), 936 (vs), 870 (vw), 838 (w), 810 (mw), 771 (s), 729 (w), 702 (s), 633 (m), 590 (w), 564 (w) cm^{-1}.

Synthesis of 4 from $VCl_3\cdot 3THF$. To a suspension of $VCl_3\cdot 3THF$ (4.06 g, 10.8 mmol) in 80 mL of THF was added 2.5 mL of PMe_3 at room temperature. The resultant brown solution was cooled to −70 °C, after which a solution of Cp_2Mg (0.94 g, 6.11 mmol) in 16 mL of THF was added over 30 min. The mixture was warmed slowly to room temperature, after which the purple-blue solution was poured onto a mixture of 1.0 g of magnesium turnings (excess) and 1.99 g (11.16 mmol) of diphenylethyne. The mixture was stirred for 6 h at room temperature, and the solvent was subsequently removed in vacuo. Following workup as described above, 3.38 g (7.56 mmol, 70%) of **4** was isolated in two crops. The product was spectroscopically pure (NMR).

$CpV(\eta^2\text{-EtC}{\equiv}\text{CEt})(PMe_3)_2$ (8) and $CpV(\eta^2\text{-PhC}{\equiv}\text{CMe})(PMe_3)_2$ (7). **1** (0.87 g, 2.58 mmol) was stirred with magnesium turnings (0.5 g, excess) in 15 mL of THF after addition of 0.30 mL (2.64 mmol) of 3-hexyne at room temperature for 3 h. The solution turned orange-brown. The solvent was pumped off, and the solid was stripped of residual THF by stirring with 5 mL of pentane, which was subsequently pumped off. After it was dried in vacuo, the mixture was extracted with 35 mL of pentane. After the extract was concentrated and cooled to −80 °C, orange-brown crystalline **8** was isolated (0.54 g, 1.52 mmol, 59%). Anal. Calcd for $C_{17}H_{33}P_2V$: C, 58.28; H, 9.49. Found: C, 58.07; H, 9.34. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 4.74 (s, 5 H, Cp), 3.45 (q, 7.3 Hz, 4 H, CH_2), 1.35 (t, 7.3 Hz, 6 H, CH_3), 0.89 (d, J_{PH} = 4.4 Hz, 18 H, PMe_3). ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 15.67 (q, 125.7 Hz, t, $^2J_{CH}$ = 4.8 Hz, Me), 24.35 (q, 126 Hz, d, J_{PC} = 8.0 Hz, PMe_3), 31.55 (t, 125.7 Hz, q, $^2J_{CH}$ = 4.8 Hz, CH_2), 92.65 (d, 170.8 Hz, Cp), 225.5 (br, $\Delta\nu_{1/2}$ = 166 Hz, $\equiv C-$). IR: 3100 (w), 2945 (s), 2890 (s), 1620 (br, w), 1421 (m), 1286 (mw), 1276 (s), 1008 (w), 1010 (w), 1000 (mw), 945 (sh), 932 (vs), 827 (mw), 785 (mw), 768 (sh), 715 (w), 696 (m), 655 (m), 449 (w) cm^{-1}.

7 was prepared similarly, but it is an oil and could not be crystallized. Evaporation of the pentane from the extract yielded 75% of **7** as a red oil (spectroscopically pure by NMR). ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 7.33 (t, 7.3 Hz, 2 H, *m*-Ph), 7.18 (2 H, *o*-Ph, partly overlapped by solvent resonance), 7.08 (t, 7.3 Hz, 1 H, *p*-Ph), 4.80 (s, 5 H, Cp), 3.21 (s, 3 H, Me), 0.87 (d, J_{PH} = 5.1 Hz, 18 H, PMe_3). ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 22.55 (d, 125.8 Hz, Me), 23.65 (q, 130 Hz, d, J_{PC} = 8.9 Hz, PMe_3), 93.69 (d, 170.8 Hz, Cp), 124.05 (d, 161.3 Hz, Ph *C*H), 125.50 (d, 157.9 Hz, Ph *C*H), 125.5 (d, 151.5 Hz, Ph *C*H), 150.35 (s, Ph *C*); $\equiv C-$ not observed. ^{51}V NMR (78.9 MHz, benzene-d_6, 21 °C): δ +211 ($\Delta\nu_{1/2}$ = 1010 Hz). IR: $\nu(C{\equiv}C)$ at 1595 cm^{-1}.

$CpV(\eta^6\text{-}C_6Me_6)$. On a vacuum line, 1.195 mmol of 2-butyne was condensed into a mixture of **1** (0.197 g, 0.58 mmol) and 0.4 g of Mg turnings (excess) in 10 mL of THF. The mixture was thawed out and stirred at 2 °C for 18 h, after which an orange-brown solution had formed. The solvent was pumped off and the oily residue extracted with 20 mL of pentane. Concentrating and cooling the extract yielded, after repeated washings with cold (−80 °C) pentane to remove a brown oil, 49 mg (0.18 mmol, 30% based on V, 45% based on 2-butyne) of brown-red crystalline $CpV(\eta^6\text{-}C_6Me_6)$. MS (percentages in parentheses): *m/e* 278 (1.3, M^+), 181 (7.2, Cp_2V^+), 162 (74, $C_6Me_6^+$), 147 (100, $C_6Me_5^+$). IR: 3085 (vw), 2720 (vw), 1412 (vw), 1277 (w), 1100 (m), 1058 (mw), 999 (s), 771 (vs) cm^{-1}. ^{1}H NMR (90 MHz, benzene-d_6, 25 °C): δ 35.3 ($\Delta\nu_{1/2}$ = 440 Hz, Ar Me). When the solution is heated to 90 °C, hexamethylbenzene (δ 2.14 ppm) is liberated and green crystalline CpV(μ-arene)VCp[9a] is formed.

CpV(η^4-2,3-dimethyl-1,3-butadiene)PMe$_3$. 1 (0.65 g, 1.93 mmol) was stirred with magnesium turnings (0.4 g, excess) and 0.4 mL (3.5 mmol) of 2,3-dimethyl-1,3-butadiene in 15 mL of THF at room temperature for 20 h. The solution changed from purple-blue to green. The solvent was removed in vacuo, and residual THF was removed by stirring with 10 mL of pentane, which was subsequently pumped off. The mixture was extracted with 20 mL of pentane. Concentrating and gradually cooling the extract to −80 °C yielded 0.25 g (0.91 mmol, 47%) of green crystalline CpV(C$_6$H$_{10}$)PMe$_3$. The IR and ^{1}H NMR spectra of the product were identical with those reported in ref 13a.

CpV(σ-η^3-C$_2$Ph$_2$C$_4$H$_6$)PMe$_3$ (9). A solution of 4 (0.24 g, 0.54 mmol) in 10 mL of toluene was frozen in liquid nitrogen and evacuated. After the mixture was thawed out, 1 atm of 1,3-butadiene was admitted, and the mixture was stirred at room temperature for 16 h. The solution changed from deep cherry red to red-brown. The solvent was pumped off and the residual solid recrystallized from pentane to yield 0.17 g (0.39 mmol, 72%) of red-brown crystalline 9. Anal. Calcd for C$_{26}$H$_{30}$PV: C, 73.58; H, 7.12; V, 12.00. Found: C, 73.47; H, 7.28; V, 11.91. IR: 3060 (w), 3015 (w), 2815 (w), 1585 (m), 1525 (mw), 1438 (m), 1296 (vw), 1277 (mw), 1245 (vw), 1222 (w), 1182 (vw), 1072 (w), 1012 (mw), 953 (s), 938 (sh), 849 (mw), 835 (w), 793 (vs), 760 (m), 731 (m), 702 (vs), 658 (vw), 533 (vw) cm^{-1}.

CpV[η^4-CH$_2$=CHC(Ph)=C(Ph)Et]PMe$_3$ (10). A solution of 4 (0.29 g, 0.65 mmol) in 10 mL of toluene was frozen in liquid nitrogen and evacuated. After the mixture was thawed out, 1 atm of ethene was admitted. The mixture was stirred for 16 h at room temperature, and the color changed from cherry red to brown. The solvent was pumped off and the brown residue extracted with 10 mL of pentane. Concentrating and cooling the extract to −30 °C yielded 0.12 g (0.28 mmol, 43%) of brown crystalline 10. Anal. Calcd for C$_{26}$H$_{32}$PV: C, 73.23; H, 7.56; V, 11.94. Found: C, 73.02; H, 7.53; V, 12.00. IR: 3055 (vw), 3038 (w), 1583 (s), 1475 (s), 1433 (m), 1360 (m), 1298 (mw), 1280 (m), 1220 (w), 1200 (vw), 1067 (mw), 1012 (mw), 1000 (mw), 950 (vs), 935 (mw), 895 (w), 802 (vs), 780 (m), 763 (vs), 721 (mw), 706 (vs), 644 (w), 552 (mw), 485 (w) cm^{-1}.

In a Töpler pump reaction (on a 0.25-mmol scale) under otherwise similar conditions, an uptake of 2.0 mol of ethene/mol of 4 was observed.

Reaction of 10 with CO. An NMR tube containing a solution of 10 in benzene-d_6 was sealed under 0.7 atm of CO. When it was thawed out, the solution instantly became orange-brown. ^{1}H NMR spectroscopy showed that a mixture of CpV(CO)$_4$ (δ (Cp) 4.20, s), CpV(CO)$_3$PMe$_3$ (4.43, d, J_{PH} = 1.5 Hz), *cis*-CpV(CO)$_2$(PMe$_3$)$_2$ (4.46, t, J_{PH} = 1.8 Hz), and *trans*-CpV(CO)$_2$(PMe$_3$)$_2$ (4.53, t, J_{PH} = 1.2 Hz) had formed, together with free 3,4-(*E*)-diphenyl-1,3-hexadiene. ^{1}H NMR (300 MHz, 20 °C): δ 7.3–7.1 (m, Ph), 6.77 (dd, 17.3 Hz, 10.8 Hz, 1 H, -CH=), 4.92 (dd, 10.8 Hz, 1.9 Hz, 1 H, syn =CH$_2$), 4.76 (dd, 17.3 Hz, 1.9 Hz, 1 H, anti =CH$_2$), 2.25 (q, 7.5 Hz, 2 H, -CH$_2$-), 0.79 (t, 7.6 Hz, 3 H, Me).

CpV(C$_4$Me$_2$Ph$_2$)PMe$_3$ (14). Into a solution of 4 (0.42 g, 0.94 mmol) in 8 mL of toluene 0.95 mmol of 2-butyne was condensed. After it was warmed to room temperature, the mixture was stirred for 2 h, the color of the solution changing from cherry red to brown (formation of 13). The mixture was then stirred at 45 °C for 3.5 h, after which a green solution had formed. The solvent was removed in vacuo and the residual solid recrystallized from diethyl ether. After two pentane washings, green crystals of 14 (0.233 g, 0.53 mmol, 56%) were isolated. Anal. Calcd for C$_{26}$H$_{30}$PV: C, 73.58; H, 7.12; V, 12.00. Found: C, 73.46; H, 7.18; V, 12.02. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz): δ 7.6–6.8 (m, 10 H, Ph), 5.30 (d, J_{PH} = 4.4 Hz, 5 H, Cp), 3.16 (d, J_{PH} = 10.3 Hz, 3 H, V=CC*H*$_3$), 1.90 (s, 3 H, C=CC*H*$_3$), 0.40 (d, J_{PH} = 8.8 Hz, 9 H, PMe$_3$). ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 17.94 (q, 127.0 Hz, d, J_{PC} = 6.9 Hz, Me), 19.21 (q, 128.5 Hz, d, J_{PC} = 22.1 Hz, PMe$_3$), 28.80 (q, 125.7 Hz, d, J_{PC} = 6.9 Hz, Me), 80.80 (d, J_{PC} = 6.9 Hz, C=C), 88.71 (d, J_{PC} = 6.9 Hz, C=*C*), 99.27 (d, 171.3 Hz, Cp), 124.22, 124.87, 127.58, 128.06, 130.38, 132.38 (all d, Ph *C*H), 143.93 (d, J_{PC} = 11.1 Hz, Ph C), 145.41 (d, J_{PC} = 5.5 Hz, Ph C), 257, 273 (very br, V=*C*). ^{51}V NMR (78.9 MHz, benzene-d_6, 21 °C): δ −487 ($\Delta\nu_{1/2}$ = 850 Hz). IR: 3060 (vw), 3045 (w), 3015 (w), 1590 (s), 1585 (s), 1478 (s), 1432 (m), 1408 (w), 1297 (w), 1280 (m), 1069 (mw), 1012 (mw), 1000 (mw), 946 (vs), 938 (sh), 805 (s), 793 (vs), 760 (m), 732 (s), 698 (vs), 644 (mw), 600 (vw), 533 (w), 425 (vw) cm^{-1}.

CpV(C$_4$Ph$_4$)PMe$_3$ can be prepared similarly from 4 and diphenylethyne. However, heating to 60 °C for 4 h was necessary for the reaction to be completed. No intermediate bis(alkyne) adduct was observed. The compound crystallizes rather poorly, but an NMR-tube experiment showed the reaction to be quantitative. ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 18.01 (q, 128.5 Hz, d, J_{PC} = 23.0 Hz, PMe$_3$), 91.23 (d, J_{PC} = 5.1 Hz, C=C), 100.15 (d, 172.3 Hz, Cp), 125.04, 166.78, 127.96, 129.86, 129.92, 132.39 (all d, Ph *C*H), 143.10 (d, J_{PC} = 6.1 Hz, Ph C), 144.60 (d, J_{PC} = 8.4 Hz, Ph C), 264.1 (d, J_{PC} = 63 Hz, V=*C*).

NMR Experiment: Reaction of 4 with 2-Butyne. On a vacuum line 2-butyne (0.16 mmol) was condensed into an NMR tube containing 4 (70 mg, 0.16 mmol) in 0.4 mL of benzene-d_6, after which the tube was sealed under vacuum. After 6 h at 20 °C a brown solution had formed, containing the bis(alkyne) complex 13 and 14 in a 2.5:1 ratio. After the mixture was heated to 50 °C, the reaction proceeded to give 14 quantitatively. 13: ^{1}H NMR (300 MHz, 20 °C) δ 7.8–6.8 (m, Ph), 4.97 (d, J_{PH} = 2.2 Hz, 5 H, Cp), 2.56 (s, 6 H, Me), 1.21 (d, J_{PH} = 8.3 Hz, 9 H, PMe$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C): δ 19.56 (Me), 20.10 (d, J_{PC} = 18.0 Hz, PMe$_3$), 97.71 (Cp), 165 (br, ≡*C*Ph), 179 (very br, ≡*C*Me), 191 (br, ≡*C*Ph), Ph resonances are broadened and were not individually assigned; ^{13}C{^{1}H} NMR (75.4 MHz, −50 °C, toluene-d_8) δ 157.87 (d, J_{PC} = 43.7 Hz, ≡*C*Me), 164.52 (d, J_{PC} = 40.3 Hz, ≡*C*Ph), 190.10 (d, J_{PC} = 10.1 Hz, ≡*C*Ph), 198.49 (d, J_{PC} = 12.8 Hz, ≡*C*Me).

CpV[C$_4$Me$_2$(CH$_2$)$_n$]PMe$_3$ (n = 3 (15), 4 (16)). 1 (0.85 g, 2.52 mmol) was stirred with magnesium turnings (0.5 g, excess) and 0.4 mL (2.5 mmol) of 2,7-nonadiyne in 15 mL of THF for 1 h at room temperature. The solution changed from purple-blue to green. The solvent was pumped off and residual THF removed by stirring with 5 mL of pentane, which was subsequently pumped off. The mixture was dried in vacuo and extracted with 35 mL of pentane. The extract was concentrated and cooled to −80 °C. After several days green 15 slowly crystallized. The mother liquor was decanted and the product washed with pentane at −80 °C, dried, and isolated; yield 0.24 g (0.78 mmol, 31%) of green crystalline 15. The yield appears to be limited by the extreme solubility of the product. Anal. Calcd for C$_{17}$H$_{26}$VP: C, 65.38; H, 8.39; V, 16.31. Found: C, 65.53; H, 8.31; V, 16.41. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz): δ 5.14 (d, J_{PH} = 3.7 Hz, 5 H, Cp), 3.26 (d, J_{PH} = 11.7 Hz, 6 H, Me), 3.08 (m, 2 H, =C—C*H*H), 2.61 (m, 1 H, -C*H*H-), 2.28 (m, 1 H, -CH*H*-), 1.39 (m, 2 H, =C—CH*H*), 0.44 (d, J_{PH} = 8.1 Hz, 9 H, PMe$_3$). ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 19.76 (q, 127.3 Hz, d, J_{PC} = 20.9 Hz, PMe$_3$), 29.05 (br q, 126 Hz, Me), 29.84 (t, 129 Hz, -CH$_2$-), 32.39 (t, 129 Hz, d, J_{PC} = 4.8 Hz, =C—CH$_2$), 87.90 (d, J_{PC} = 6.4 Hz, C=C), 98.67 (d, 170.8 Hz, Cp), 259.6 (br, $\Delta\nu_{1/2}$ = 195 Hz, V=*C*). IR: 3090 (w), 2910 (vs), 2815 (m), 2680 (vw), 1459 (mw), 1292 (w), 1272 (m), 1260 (w), 1162 (w), 1043 (vw), 1010 (mw), 942 (vs), 930 (sh), 779 (vs), 721 (mw), 709 (mw), 665 (m), 612 (vw), 542 (w), 441 (vw), 400 (w) cm^{-1}.

16 was prepared similarly with use of 2,8-decadiyne. It is an oil, however, and could not be crystallized. Removal of the solvent from the extract in vacuo yielded 73% of crude green 16 (>90% pure by NMR). ^{1}H NMR (benzene-d_6, 45 °C, 300 MHz): δ 5.07 (d, J_{PH} = 2.9 Hz, 5 H, Cp), 3.17 (d, J_{PH} = 10.3 Hz, 6 H, Me), 0.62 (d, J_{PH} = 8.0 Hz, 9 H, PMe$_3$); CH$_2$ resonances between 3.1 and 1.3 ppm, not individually assigned. ^{13}C NMR (benzene-d_6, 45 °C, 75.4 MHz): δ 20.23 (q, 127.3 Hz, d, J_{PC} = 21.0 Hz, PMe$_3$), 24.69 (t, 125.7 Hz, -CH$_2$-), 27.70 (q, 124.1 Hz, Me), 28.17 (t, 124.1 Hz, d, J_{PC} = 6.4 Hz, =C—CH$_2$), 77.40 (d, J_{PC} = 8.1 Hz, C=C), 98.12 (d, 170.8 Hz, Cp), 263.4 (very br, $\Delta\nu_{1/2}$ = 272 Hz, V=*C*). IR (neat): 3090 (w), 2915 (vs), 2850 (s), 2825 (s), 2680 (vw), 1432 (m), 1415 (m), 1257 (w), 1300 (mw), 1281 (s), 1012 (m), 947 (vs), 935 (sh), 800 (sh), 788 (vs), 708 (mw), 663 (m), 420 (mw) cm^{-1}.

Reaction of 16 with CO. An NMR tube with a solution of 16 in benzene-d_6 was sealed under 0.7 atm of CO. When it was thawed out, the green solution turned red-brown instantly. 16 was completely converted into CpV[η^4-O=CC$_4$Me$_2$(CH$_2$)$_4$](PMe$_3$)CO (17). After 1 day 60% of 17 was converted into

Table VI. Crystallographic Data for 2, 4, 10, and 14

	2	**4**	**10**	**14**
formula	$C_{13}H_{27}P_2V$	$C_{25}H_{33}P_2V$	$C_{26}H_{32}PV$	$C_{26}H_{30}PV$
fw	296.25	446.42	426.46	424.4
cryst syst	orthorhombic	monoclinic	triclinic	orthorhombic
space group	*Pbca*	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a, Å	12.351 (3)	8.249 (2)	8.875 (3)	12.957 (3)
b, Å	15.526 (4)	17.619 (2)	9.589 (2)	19.205 (5)
c, Å	16.948 (3)	16.278 (2)	15.081 (6)	9.155 (2)
α, deg	90.0	90.0	90.95 (3)	90.0
β, deg	90.0	100.61 (2)	91.54 (3)	90.0
γ, deg	90.0	90.0	117.44 (2)	90.0
V, Å^3	3250 (1)	2325.4 (7)	1138 (1)	2278 (1)
Z	8	4	2	4
d_{calcd}, g cm^{-3}	1.211	1.275	1.24	1.24
$F(000)$, e	1264	944	452	896
μ(Mo Kα), cm^{-1}	7.6	5.6	4.99	4.98
cryst size, mm	0.25 × 0.30 × 0.40	0.10 × 0.13 × 0.25	0.30 × 0.30 × 0.20	0.26 × 0.33 × 0.39
T, K	130	130	130	170
2θ limits, deg	$2.4 < 2\theta < 52$	$2.32 < 2\theta < 52.0$	$2 < 2\theta < 54$	$3.5 < 2\theta < 55$
data collected	$+h,+k,+l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,+l$
no. of unique data	3180	4550	4950	2973
no. of rflns obsd	2474 ($I > 2.5\sigma(I)$)	3536 ($I > 2.5\sigma(I)$)	3072 ($I > 3\sigma(I)$)	2603 ($I > 3\sigma(I)$)
no. of params refined	254	387	336	363
$R(F)$	0.035	0.032	0.050	0.032
$R_w(F)$	0.041	0.035	0.056	0.029
w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	1	$1/[\sigma^2(F_o) + 0.00015(F_o)^2]$

$CpV[\eta^4\text{-}O{=}CC_4Me_2(CH_2)_4](CO)_2$ (18). 17: ^{1}H NMR (300 MHz, 25 °C) δ 4.08 (d, J_{PH} = 2.9 Hz, 5 H, Cp), 2.02 (d, J_{PH} = 2.2 Hz, 3 H, Me), 1.56 (s, 3 H, Me), 1.05 (d, $^2J_{PH}$ = 8.2 Hz, PMe_3), CH_2 resonances not individually assigned; ^{13}C NMR (75.4 MHz, 25 °C) δ 16.4 (br q, Me), 16.68 (q, 129 Hz, d, J_{PC} = 19.3 Hz, PMe_3), 22.19, 22.54, 23.68, 24.69 (all t, 128 Hz, CH_2), 76.96 (s, C), 90.04 (s, C), 92.16 (d, 176 Hz, Cp), 169.22 (d, J_{PC} = 6.4 Hz, C=O). 18: ^{1}H NMR (300 MHz, 25 °C) δ 4.23 (s, 5 H, Cp), 1.54 (s, 6 H, Me), CH_2 resonances not individually assigned; ^{13}C NMR (75.4 MHz, 25 °C): δ 8.83 (q, 127 Hz, Me), 21.95 (t, 128 Hz, CH_2), 23.28 (t, 128 Hz, CH_2), 88.37 (s, C), 96.59 (d, 179 Hz, Cp), 105.72 (s, C), 172.97 (s, C=O); IR ν(C=O) 1590 cm^{-1}.

X-ray Structure Determinations of 2, 4, 10, and 14. Pertinent crystal data and data collection parameters can be found in Table VI. Crystals were either transferred by inert-atmosphere handling techniques into the cold nitrogen stream of the low-temperature unit mounted on an Enraf-Nonius CAD4F diffractometer (2, 4, 10, determined at the Rijksuniversiteit Groningen) or sealed in a thin-walled capillary and mounted on a Syntex $P2_1$ diffractometer (14, determined at the Chalmers University of Technology).

For 2, the lattice parameters were determined from the angular settings of 25 reflections (6.68° < θ < 16.23°). The space group was determined from the observed systematic absences and checked for the presence of higher metrical symmetry.[58] The monitoring of three standard reflections during data collection showed no significant decay of the crystal. The net intensities of the data were corrected for Lorentz and polarization effects. Isotropic secondary extinction[59] correction was applied. The structure was solved by direct methods (SHELXS86[60]). All hydrogen atoms were located on a Fourier difference map and refined isotropically. In the final Fourier difference map, one peak of height 0.803 e Å^{-3} was located at 2.60 Å from V(1), most likely due to a minute amount of cocrystallized $CpVBr(PMe_3)_2$ in the crystal.

For 4, the lattice parameters were derived from the angular settings of 22 reflections (13.22° < θ < 19.22°). The space group was derived from the observed systematic absences and checked for the presence of higher metrical symmetry.[58] The monitoring of three standard reflections during data collection showed no significant decay of the crystal. The net intensities of the data were corrected for Lorentz and polarization effects. An isotropic secondary extinction[59] correction was applied. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86[60]). All hydrogen atoms were located on a Fourier difference map and refined isotropically. A final Fourier difference map did not show residual peaks greater than ±0.42 e Å^{-3}.

For 10, the lattice parameters were derived from the angular settings of 25 reflections (7.4° < θ < 20.7°). The monitoring of three standard reflections during data collection showed no significant decay of the crystal. All hydrogen atoms were located on a Fourier difference map and refined with isotropic-fixed thermal parameters (B = 4 Å^2). The hydrogen atoms on C(1)–C(7) were refined individually, while the others were refined restrained at 0.96 Å from their carrier atoms. In the final Fourier difference map, two peaks, of heights 1.20 and 1.05 e Å^{-3}, were located within 0.85 Å of V and P, respectively.

For 14, the lattice parameters were obtained from the angular settings of 15 reflections. The monitoring of two standard reflections during data collection showed no significant decay of the crystal. Intensity data were corrected for Lorentz and polarization effects, and a Gaussian correction was made for absorption with use of ABSORB[61] (maximum and minimum transmission factors 0.899, 0.882). The structure was solved by direct methods (MITHRIL[62]). All hydrogen atoms were located from a Fourier difference map and refined isotropically. The isotropic thermal parameters for the phenyl hydrogen atoms were held invariant at B = 1.5 Å^2. A final difference map showed maximum and minimum residual densities of 0.30 and –0.28 e Å^{-3}, respectively.

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Registry No. 1, 88622-66-6; 2, 115162-64-6; 3, 61160-66-5; 4, 115162-66-8; 5, 115162-67-9; 6, 115162-68-0; 7, 125754-82-7; 8, 125754-83-8; 9, 126927-93-3; 10, 126927-94-4; 13, 125778-62-3; 14, 125754-84-9; 15, 125778-63-4; 16, 125778-64-5; 17, 126948-98-9; 18, 126948-99-0; $Cp(V(\eta^6\text{-}C_6Me_6)$, 126948-97-8; $[CpV(\mu\text{-}SPh)_2]_2$, 59487-44-4; $BrMg(CH_2)_4MgBr$, 23708-47-6; $Cp^*{}_2TiCl$, 73348-99-9; $ClMg(CH_2)_4MgCl$, 22758-42-5; PhC≡CPh, 501-65-5; PhSSPh, 882-33-7; $VCl_3\cdot 3THF$, 19559-06-9; Cp_2Mg, 1284-72-6; $CpV(\eta^4$-2,3-dimethyl-1,3-butadiene)PMe_3, 110174-54-4; $CpV(\mu$-hexamethylbenzene)VCp, 126927-95-5; $CpV(CO)_4$, 12108-04-2; CpV-

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(58) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(59) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

(60) Sheldrick, G. M. SHELXS86, Program for Crystal Structure Solution; Universität Göttingen: Göttingen, FRG, 1986.

(61) DeTitta, G. T. *J. Appl. Crystallogr.* **1985**, *18*, 75.

(62) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

$(CO)_3PMe_3$, 12276-38-9; *cis*-$CpV(CO)_2(PMe_3)_2$, 62414-52-2; *trans*-$CpV(CO)_2(PMe_3)_2$, 62414-53-3; $CpV(C_4Ph_4)PMe_3$, 126949-00-6; 3,4-(*E*)-diphenyl-1,3-hexadiene, 126948-96-7; 1-hexene, 592-41-6; 2-butyl-1-methyl-1-heptene, 37549-88-5; 7-methyl-5-undecene, 126927-92-2; 2-butyl-1-octene, 5698-48-6; hexamethylbenzene, 87-85-4.

Supplementary Material Available: Full details of structure determinations and tables of positional and thermal parameters and bond distances and angles for **2**, **4**, **10**, and **14** (45 pages); listings of observed and calculated structure factors for **2**, **4**, **10**, and **14** (63 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Secondary Carbene Complexes of Manganese and Rhenium

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Reactions of *mer,trans*-$M(CO)_3(PPh_3)_2CHO$ (M = Mn, Re) with protonic acids or methylating agents lead to isolation of rare secondary hydroxy- and methoxycarbene complexes in high yields. The compounds have been characterized by IR and ^1H and ^{13}C NMR spectroscopy; the methoxycarbene *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$ has also been characterized by X-ray crystallography (space group *Pbca*, $a = 18.934$ (4) Å, $b = 19.810$ (6) Å, $c = 23.436$ (5) Å, $Z = 8$, $d_c = 1.42$ g cm^{-3}, and $R = 0.068$). Aminolysis of the methoxycarbene complexes with benzylamine produces the corresponding aminocarbene complexes in high yields. One of these, *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3^-$, has been characterized by X-ray crystallography (space group $P2_1/n$, $a = 14.268$ (2) Å, $b = 16.107$ (2) Å, $c = 22.264$ (3) Å, $\beta = 104.62$ (2)°, $Z = 4$, $d_c = 1.35$ g cm^{-3}, and $R = 0.061$). Deprotonation of the aminocarbene complexes yields the corresponding iminomethyl (formimidoyl) complexes.

Introduction

Hydroxy- and alkoxycarbene complexes, M=CHOR (R = H, alkyl), are of interest because of their proposed intermediacy in catalytic reductions of CO that lead to oxygenates.[1] Few complexes of the first type have been isolated,[2] particularly those involving first-row transition elements;[3] in other cases, more labile hydroxycarbene complexes have been spectroscopically observed at low temperatures.[4] The alkoxycarbene compounds can sometimes be prepared by α-hydride abstraction from the corresponding ether complexes, $M-CH_2-OR$, although ether cleavage is frequently the competing or exclusive pathway.[5] One potentially general route to either type of compound would involve electrophilic additions to neutral metal formyl complexes. However, this method has shown only limited success,[2-4] in part because the initial electrophilic addition is often followed by rapid hydride transfer from a second molecule of the neutral formyl. We have isolated and characterized hydroxy- and methoxycarbene cationic complexes of the general formula *mer,trans*-$M(CO)_3(PPh_3)_2(CHOR)^+$ (M = Mn, Re; R = H, CH_3) by direct electrophilic additions to the corresponding neutral formyls. Also reported are the first aminolysis reactions of secondary methoxycarbene cationic complexes which lead to aminocarbene derivatives (see Chart I). Finally, deprotonations of the aminocarbene complexes afforded the corresponding iminomethyl derivatives. Structures of the manganese methoxycarbene and (benzylamino)carbene complexes have been established by X-ray crystallography.

Chart I. Secondary Carbene Complexes

mer,trans-$M(CO)_3(PPh_3)_2(CHOH)^+X^-$
1a: M = Mn, X = *p*-$CH_3C_6H_4SO_3$
b: M = Mn, X = BF_4
c: M = Re, X = *p*-$CH_3C_6H_4SO_3$

mer,trans-$M(CO)_3(PPh_3)_2(CHOCH_3)^+X^-$
2a: M = Mn, X = CF_3SO_3
b: M = Mn, X = BF_4
c: M = Re, X = CF_3SO_3

mer,trans-$M(CO)_3(PPh_3)_2(CHNHCH_2C_6H_5)^+X^-$
3a: M = Mn, X = CF_3SO_3
b: M = Mn, X = BF_4
c: M = Re, X = CF_3SO_3

Results and Discussion

Hydroxycarbene Complexes. Direct protonation of *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$ was accomplished by either *p*-toluenesulfonic acid or $HBF_4\cdot(CH_3)_2O$; only the former was used with the corresponding rhenium complex.[6] It was necessary to prepare the manganese complex **1b** at low temperature because of its high lability; compounds **1a** and **1c** could be prepared at room temperature. All reactions were complete after a few minutes, and the complexes were isolated in better than 90% yields. The

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[1] (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

[2] (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Lilga, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590. (c) Barratt, D. S.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1986**, *306*, C41.

[3] A preliminary account of some of this work has been published: Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1987**, *6*, 2624.

[4] (a) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663. (b) Asdar, A.; Lapinte, C. *J. Organomet. Chem.* **1987**, *327*, C33. (c) Asdar, A.; Lapinte, C.; Toupet, L. *Organometallics* **1989**, *8*, 2708.

[5] (a) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (c) Guerchais, V.; Lapinte, C.; Thepot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604.

[6] For the preparations of the formyl complexes, see: Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.

0276-7333/90/2309-1936$02.50/0