Cyclopentadienylization of pentafulvenes with stannyl- and nitrosyl-carbonylvanadium complexes

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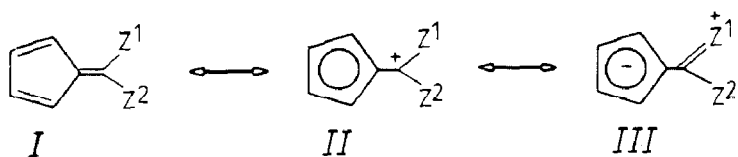*Institut für Anorganische und Angewandte Chemie der Universität, D-2000 Hamburg 13 (F.R.G.)*

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Abstract

The complexes $R_3SnV(CO)_5PPh_3$ and $R_3SnV(CO)_6$ (R = Ph, Et, n-Bu, CH_2Ph), for which an improved synthesis is described, react with pentafulvenes $C_5H_4CZ_2$ to give ring-substituted cyclopentadienyl (Cp) or fulvene (Fv) complexes. Less polar fulvenes form alkyl-Cp complexes ($Z_2 = Ph_2$ and (p-substituted Ph)$_2$) or alkenyl-Cp complexes ($Z_2 = Me_2$, $(CH_2)_4$, $(CH_2)_5$) with the elimination of the stannyl ligand, while the reaction with polar fulvenes ($Z_2 = H$, NMe_2; $(NMe_2)_2$ and $S(CH_2)_2S$) gives the Fv complexes $C_5H_4CZ_2V(CO)_3SnR_3$ with the stannyl ligand still coordinated to vanadium. A Fv complex, $V(NO)(CO)_2C_5H_4CHNMe_2$, is also obtained from the reaction of $V(NO)(CO)_5$ with dimethylaminofulvene. The IR, ^1H, ^{13}C and ^{51}V NMR data show that the dipolar (i.e. the h^5-cyclopentadienyloidal) resonance structure predominates in all but the dimercaptofulvene complex.

Introduction

Fulvenes may use all of their six π electrons in coordination to a transition metal, and function either as a triene (I, in Scheme 1) or as a cyclopentadienyl ligand (II). The dipolar form II is stabilized if the substituent Z on the exocyclic carbon is a group such as NMe_2 (III, in Scheme 1). The h^5- and the h^6-mode of coordination derived from both the non-polar and the polar resonance structures of the fulvene have been described for inter alia, the metals of the group 6 triad [1,2], but until now fulvene complexes of vanadium were unknown. In the present work, the reaction of fulvenes $C_5H_4CZ^1Z^2$ with different polarities (cf. Scheme 1 and ref. 3) towards $R_3SnV(CO)_6$ (**1**), $R_3SnV(CO)_5PPh_3$ (**2**) and $V(CO)_5NO$ (**3**) are described. The stannyl ligand may be lost or retained during the reaction. Unlike in the reaction between pentafulvenes and the neutral seven-coordinate hydrido complexes

$$I \longleftrightarrow II \longleftrightarrow III$$

| Z^1 / Z^2		μ (D)
Me / Me	a	1.44
$-(CH_2)_5-$	b	
$-(CH_2)_6-$	c	
Ph / Ph	d	1.1
$p\text{-MeOC}_6H_4 / p\text{-MeOC}_6H_4$	e	2.47
$p\text{-Me}_2NC_6H_4 / p\text{-Me}_2NC_6H_4$	f	
$p\text{-ClC}_6H_4 / p\text{-ClC}_6H_4$	g	0.0
NMe_2 / H	h	4.48
NMe_2 / NMe_2	i	5.4
$-SCH_2CH_2S-$	j	3.75
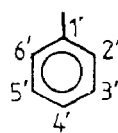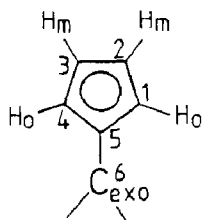
Scheme 1

HV(CO)$_4$(diphos), where the hydride is transferred to the exocyclic carbon [4], a transfer of the stannyl group is not observed.

Results and discussion
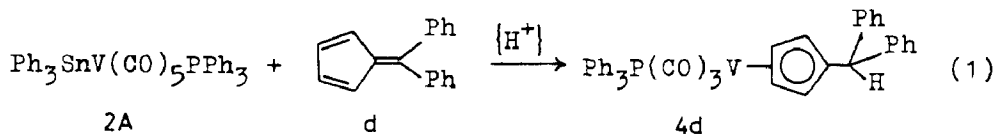
The numbering scheme for the complexes described here and in the experimental section is summarized in Scheme 2.

4	5	6	7

See Scheme I for Z^1 and Z^2

	Ph	A
	Et	B
R =	n–Bu	C
	PhCH$_2$	D

$$8$$

$$9$$
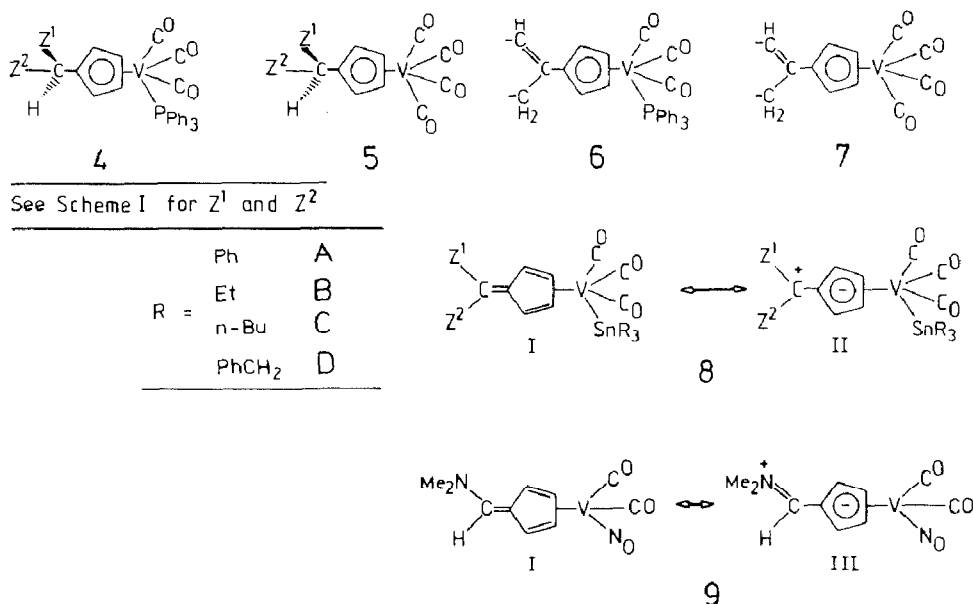
Scheme 2

Reactions with bis(aryl)fulvenes

The reaction between $Ph_3SnV(CO)_5PPh_3$ (**2A**) and 6,6′-diphenylfulvene (**d**) in THF (eq. 1) leads, with the elimination of the stannyl group and transfer of a proton from the solvent and/or surplus fulvene to the exocyclic carbon, to the ring-substituted, phosphine-stabilized complex h^5-$\{C_5H_4CHPh_2\}V(CO)_3PPh_3$ (**4d**). Corresponding reactions (to give less stable products) are observed with the trial-

$$Ph_3SnV(CO)_5PPh_3 \quad + \quad \overset{Ph}{\underset{Ph}{\diagup}} \quad \xrightarrow{\{H^+\}} \quad Ph_3P(CO)_3V - \overset{Ph}{\underset{H}{\diagup\diagdown Ph}} \quad (1)$$

$$\text{2A} \qquad\qquad \text{d} \qquad\qquad\qquad\qquad \text{4d}$$

kyltin derivatives $R_3SnV(CO)_5PPh_3$ (R = Et: **2B**, n-Bu: **2C** and $PhCH_2$: **2D**) on the one hand, and between **2A** and the bis(aryl)fulvenes **e**, **f** and **g** on the other hand. The phosphine-free complexes $Cp'V(CO)_4$ (**5**) are also obtained as by-products. A complex of type **5** is also the product of reaction between $Ph_3SnV(CO)_6$ (**1**) and **d** in THF/CH_2Cl_2. In THF, **1** undergoes heterolytic dissociation into $[SnPh_3]^+$ and $[V(CO)_6]^-$ [5], which is unreactive towards fulvenes; the reaction is, however, inhibited in CH_2Cl_2.

The solution IR spectra (Table 1) show two bands due to CO stretching modes around 1945 and 1850 (**4**), and 2025 and 1910 cm^{-1} (**5**), respectively. In KBr, the low-frequency band splits, in agreement with observations on many other aryl-group 15 derivatives of $CpV(CO)_4$ [6]. The ^{51}V chemical shifts $\delta(^{51}V)$ (Table 1), of the Cp compounds **4** and **5** are similar to those for the parent unsubstituted Cp complexes,

Table 1

IR and ^{51}V NMR data for complexes **4** and **5**

Complex		$\nu(CO)$ [a] (cm^{-1})			Phase	$\delta(^{51}V)(ppm)$ [b]
4d	1946s	1648s,br			THF	−1308
	1946s	1857s	1837s		KBr	
4e	1944	1847br			THF	−1312
	1946	1855	1837		KBr	
4f	1947	1850br			THF	−1303
	1948	1855	1841		KBr	
4g	1947	1850br			THF	−1304
	1943	1860	1848		KBr	
5d [c]	2030m	1949w,sh	1928s,sh	1918vs	heptane	−1518
5e	2022m	1910vs			THF	−1522
5f	2025	1905			THF	[d]
5g [c]	2030m	1950w,sh	1930s,sh	1918vs	heptane	−1513

[a] Compare $C_5H_5V(CO)_3PPh_3$ (1955vs, 1862vs,br; in THF) and $C_5H_5V(CO)_4$ (2030m and 1933vs cm^{-1}; in hexane). [b] In acetone-d_6, relative to $VOCl_3$. Compare $C_5H_5V(CO)_3PPh_3$ (−1316, in THF) and $C_5H_5V(CO)_4$ (−1534 ppm, in THF). Line widths at half-height are ca. 450 Hz (**4**) and ca. 50 Hz (**5**). [c] The weak shoulder at 1850 cm^{-1} is assigned to the IR-forbidden B_1 mode, which is more intense if the Cp ligand is sterically demanding [23]; for the same reason, the E mode is split. These effects are not observed for solutions in THF, where the bands are considerably broadened. [d] Not determined.
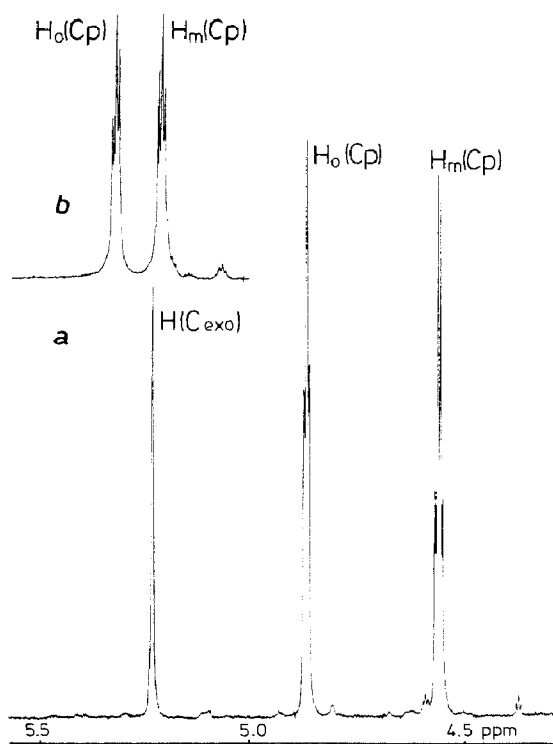
Fig. 1. ^{1}H NMR spectra (expansions for the Cp/fulvene regions) of the complexes **4f** (a; 360 MHz) and **8Ah** (b; 300 MHz). The signal from the proton on the C_{exo} of **8Ah** (8.27 ppm) is not shown. The triplet at lower field comes from the *ortho* hydrogens (H_o) and the quartet a higher field from the *meta* hydrogens (H_m); cf. Scheme 1. For discussion see text.

with a tendency (more evident in the case of **5**) for deshielding of the vanadium nucleus *.

The two sets of ring protons, which for conveniency we note by o and m (cf. Scheme 1), in the complexes **4** and **5** give rise to only one multiplet or broad singlet in the ^{1}H NMR spectrum (Table 2), indicative of very similar ν_o and ν_m. The resonance is located at ca. 4.8 ppm, which is typical of a cyclopentadienyl proton. In the case of **4f**, however, two signals are observed (Fig. 1a): the o protons give rise to a pseudo-triplet (virtual coupling constant J 2.2 Hz) and the m protons to a pseudo-quartet ($J(^1H-^{31}P)$ 2.2 Hz). Differing coupling behaviour of the o and m protons is also observed for the $^1H-^{103}Rh$ coupling in cyclopentadienylrhodium complexes [7], and for the $^1H-^{31}P$ coupling in h^3-allylV(CO)$_3$diphos [6]. In all type **4** and **5** complexes, the hydrogen attached to the exocyclic carbon resonates near 5 ppm. ^{13}C NMR spectral data for the compounds, which are listed in Table 2, are consistent with their formulation as h^5-cyclopentadienyl complexes.

Reactions with bis(alkyl)fulvenes

Reaction between **2A** and 6,6-tetramethylenefulvene (**b**) followed by separation of the products on silica gel leads to low yields of a product which we formulate as

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* The interpretation of the ^{51}V NMR spectra of carbonylvanadium half-sandwich complexes will be discussed in a forthcoming paper.

Table 2

^{1}H ^{a} and ^{13}C ^{b} NMR data for complexes **4**, **5** and two related molybdenum and manganese complexes

^{1}H NMR

Complex (solvent)	Cp-protons	H(C$_{exo}$)	Others
4d (acetone)	4.83(m,4H)	5.03(s,1H)	7.26(m,10H): Ph 7.32, 7.43(m,15H): PPh$_3$
4e (acetone)	4.79(m,4H)	4.93(s,1H)	6.81, 7.13(m,8H): C$_6$H$_4$ 7.33, 7.43(m,15H): PPh$_3$ 2.52(s,12H): Me
4f (toluene)	4.53(q,2H) ^{c,d} 4.85(t,2H) ^{c}	5.22(s,1H)	6.54, 7.27(m,8H): C$_6$H$_4$ 6.98, 7.42(m,15H): PPh$_3$ 2.52(s,12H): Me
4g (acetone)	4.87(n,4H)	5.04(s,1H)	7.25, 7.32(m,8H): C$_6$H$_4$ 7.32, 7.43(m,15H): PPh$_3$
5d (acetone)	5.25(s,4H)	5.06(s,1H)	7.26(m,10H): Ph
5g (acetone)	5.27(s,4H)	5.11(s,1H)	7.25–7.32(m,8H): Ph
Mo(CO)$_3$-**e** ^{e} CDCl$_3$	5.15(s,4H)	5.02(s,1H)	6.75–7.10(m,8H): C$_6$H$_4$
Mn(CO)$_3$-**d** ^{f} C$_6$D$_6$	4.12(t,2H) 3.86(t,2H)	4.82(s,1H)	7.10(m,10H): Ph

^{13}C NMR

Complex	C(1) to C(4)	C(5)	C(6)	Phenyl-C ^{g}
4d	91.7, 92.5	^{h}	51.3	126.2, 128.1, 128.6, 144.4
4e	91.7, 92.3	^{h}	49.6	113.4, 129.4, 136.9, ^{h,i}
4g	91.4, 93.0	114.2	49.9	128.2, 130.2, 131.8, 142.9
Mo(CO)$_3$-**e** ^{e}	91.3, 94.6	116.9	49.1	113.7, 129.2, 135.8, 158.2 ^{i}

^{a} δ(^{1}H). Multiplicity and normalized integral intensities in parentheses. In the case of **4f** and Mn(CO)$_3$-**d**, the low-field resonance corresponds to H$_o$, the high-field resonance to H$_m$ (cf. Scheme 1); see also Fig. 1,a for **4f**. Abbreviations: m = multiplet, s = singlet, t = triplet, q = quartet. ^{b} δ(^{13}C); for the numbering of the C-atoms see Scheme 1. ^{c} Virtual ^{1}H–^{1}H coupling constant 2.2 Hz. ^{d} J(^{1}H–^{31}P) 2.2 Hz. ^{e} The complex is dimeric; data from ref. 24. ^{f} From ref. 25. ^{g} The most deshielded carbon is the quaternary C of the phenyl on C$_{exo}$. Data for the carbons of the triphenylphosphine ligand are as follows: 128.3 (d, ^3J(C–P) 9 Hz): C(3′), C(5′); 132.8 (d, ^2J(C–P) 11 Hz): C(2′), C(8′); 130.0(s): C(4′). C(1′) is not observed. ^{h} Not observed. ^{i} The methyl groups resonate at 54.5 (**4e**) and 55.1 ppm [Mo(CO)$_3$-**e**], respectively.

an alkenyl-substituted cyclopentadienyl complex (**6b**: ν(CO) 1945 and 1850 cm^{-1}; eq. 2). The main argument for this formulation comes from the δ(^{51}V) value of

$$Ph_3SnV(CO)_5PPh_3 \quad + \quad \text{(2A)} \quad \text{(b)} \longrightarrow Ph_3P(CO)_3V\text{—(6b)} \qquad (2)$$
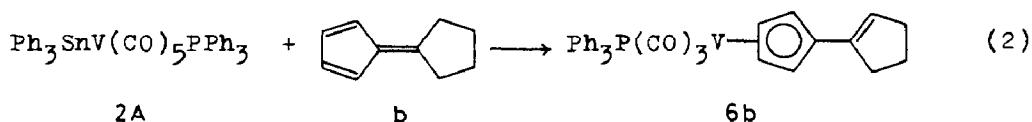
−1245 ppm, representing a deshielding of the vanadium nucleus by 71 ppm with respect to C$_5$H$_5$V(CO)$_3$PPh$_3$ (δ −1316 ppm). This deshielding contribution cannot be explained simply in terms of the influence of a sterically demanding substituent (which gives rise to deshieldings of 10 to 20 ppm; Table 1 and [9]). Large deshielding effects have been observed for h^5-indenylV(CO)$_4$ relative to CpV(CO)$_4$

(indene can be looked at as an alkenylCp) [9], and in ferrocenes carrying a sp^2 carbon as a substituent relative to alkyl-substituted ferrocenes [10]. Hydrogen abstraction from the fulvene and the concomitant formation of an alkenylCpV(CO)$_4$ have also been observed in the reactions of V(CO)$_6$ with 6,6-dialkylfulvenes [11]. 6,6-Pentamethylenefulvene (c), and 6,6-dimethylfulvene (a) show a reaction pattern similar to that of **b** ($\delta(^{51}V)$: **6c** -1284, **6a** -1272 ppm).

Similar to **4f** (vide supra), **6b** exhibits, in the ^{1}H NMR, two pseudo-triplets for the ring-protons at 4.77 (*m*) and 5.13 ppm (*o*) which are further split by ^{1}H–^{31}P coupling (*m*: pseudo-quartet, J(HP) 2.2 Hz; *o*: triplet of doublets, J(HP) 0.8 Hz).

Ph$_3$SnV(CO)$_6$ (**1**) reacts with **c** to yield two main species, which can be separated by chromatography on magnesium silicate. One of the compounds is the previously known [11] alkenylCpV(CO)$_4$ (**7c**, $\delta(^{51}V)$ -1494, compare CpV(CO)$_4$: -1552 ppm, ν(CO) 2022 and 1908 cm^{-1}), which also exhibits an intense, characteristic ν(C=C) band at 1635 cm^{-1}. The second product is a fulvene complex containing the V(CO)$_3$SnPh$_3$ moiety (**8Ac**; $\delta(^{51}V)$ -1592 ppm; ν(CO) 1946, 1903 and 1871 cm^{-1}; $\delta(^1H_o)$ 5.85, $\delta(^1H_m)$ 4.67 ppm; for a comprehensive discussion of the stannyl complexes see next section).

Reactions with amino- and thio-fulvenes

When the polar fulvenes 6-dimethylaminofulvene (**h**), 6,6-bis(dimethylamino)fulvene (**i**) and 6,6-dithioethylenefulvene (**j**) are treated with Ph$_3$SnV(CO)$_5$PPh$_3$, the triphenylphosphine ligand is eliminated and the stannyl group remains attached to the vanadium centre (eq. 3a and 3b, Scheme 3). IR and NMR data for the new complexes, which can be isolated from the THF solutions in the form of wine-red (**8Ah**), vermilion (**8Ai**), or deep-blue (**8Aj**) powders and in yields between 40 and 60%, are summarized in Tables 3 and 4. The reaction times (ca. 24 h) can be reduced, but with a loss in yield, by UV radiation.

In contrast to the reactions described in the two preceding sections, neither hydrogen abstraction from the fulvene nor hydrogen transfer to the exocyclic carbon is involved, and the compounds **8A** may therefore be regarded as genuine fulvene vanadium complexes, comparable to the isoelectronic complexes Cr(CO)$_3$(fulvene). X-ray data for the latter have revealed a dominance of the polar cyclopentadienyloidal resonance form III in eq. 3a in the case of fulvene = **h** [12], and approximately equivalent contributions from the fulvenoidal and cyclo-

Table 3

IR data for the complexes **8**

Complex	ν(CO) (cm^{-1})			ν(C=N) (cm^{-1})	
8Ah	1902vs	1840vs,sh	1820vs,br	1620s	THF
	1898vs	1819vs,br	1793vs,br	1627s	KBr
8Ai	1903vs	1830vs	1805vs	a	THF
	1893vs	1808s	1784vs	1583m 1528m	KBr
8Aj	1919vs	1865vs,sh	1852vs,br		THF
	1907vs	1850vs,br	1843vs,br		KBr
8Bh	1890	1830		1622	THF
8Ch	1892	1813		1622	THF
8Dh	1895	1813		1620	THF

a Not assigned unambiguously.
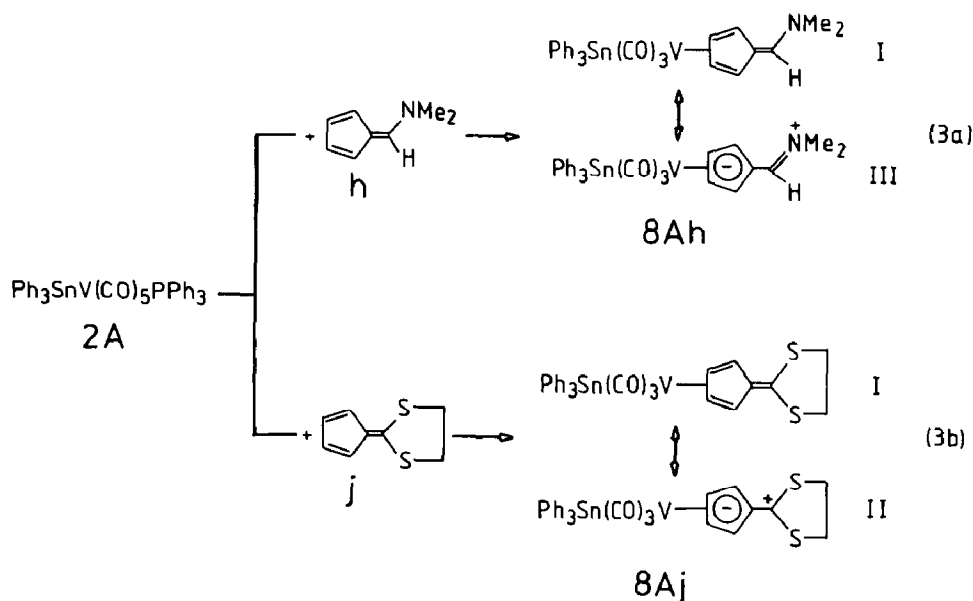
Scheme 3

pentadienoidal structures I and III (eq. 3b), in the case of fulvene $=$ **j** [1]. The triolefinic h^6-coordination is achieved with dialkyl- or diaryl fulvenes and the $Cr(CO)_3$ moiety [13].

The spectroscopic data for **8Ah** and **8Ai** clearly show that in our carbonyl-vanadium complexes, the fulvene ligand is almost completely in the cyclopentadienyl form: A strong $\nu(C=N)$ indicates that the resonance structure III (eq. 3a) is very effectively stabilized by delocalization of the positive charge onto the nitrogen of the dimethylamino group. The sulfur functions in **8Aj** do less effectively delocalize positive charge from the exo-carbon, and this leads to an interaction between the π-system of the five-ring and C_{exo}. As a consequence, the vanadium centre is relieved of some of the electron density of the carbocyclic ligand, and π back-donation into antibonding CO orbitals is reduced with respect to **8Ah** and **8Ai** (compare the high-frequency shift of the $\nu(CO)$ for **8Aj** in Table 3).

The proton NMR spectra (Table 4) exhibit, for all three complexes, two virtual triplets (shifted to high field with respect to the free fulvenes) in the region characteristic of cyclopentadienyl ligands (see Fig. 1,b, for **8Ah**). The singlet for the hydrogen on C_{exo} of **8Ah** appears at 8.27 ppm; the low-field shift relative to the uncoordinated fulvene **h** amounts to 1.06 ppm, and is again indicative of an increased positive charge on the exocyclic carbon in the complex. Owing to the hindered rotation about the C–N bond, the two methyl groups of the dimethylamino substituent in **8Ah** give rise to two distinct resonances even at room temperature.

Further insight into the bonding interaction between vanadium and the fulvene ligand comes from the ^{13}C NMR spectra (Table 4 and, for **8Ah**, Fig. 2), with a key role played by the resonance of C_{exo}. Coordination of a carbon to a metal centre generally leads to an additional shielding of the ^{13}C nucleus with respect to the uncoordinated ligand [14]. Hence, if C_{exo} participates in coordination, an upfield shift of its resonance should be observed. On the other hand, if there is no

Table 4

^{1}H and ^{13}C NMR data for complexes **8** and corresponding chromium compounds ^{a}

^{1}H NMR: $\delta(^1\text{H})$(ppm) and [Δ] ^{b} (ppm)

Complex	H$_{ortho}$ ^{c}	H$_{meta}$ ^{c}	H(C$_{exo}$)	Other
8Ah ^{k}	5.32(t)	5.21(t)	8.27(s)	3.37 and 3.61(s): NMe$_2$
	[1.1]	[1.0]	[−1.08]	7.24 and 7.59(m): Ph
Cr(CO)$_3$-**h**	5.07(s)	5.07(s)	7.74(s)	3.36(s): NMe$_2$ ^{d}
	[1.3]	[1.1]	[−0.74]	
8Ch	5.22	5.14(br)	8.14(s)	3.39 and 3.63(s): NMe$_2$ ^{e}
8Dh	4.72(t)	4.58(t)	8.18(s)	3.26 and 3.64(s): NMe$_2$ ^{e}
8Ai ^{f}	5.28(t)	4.92(t)		3.34(s): NMe$_2$
	[0.88]	[1.05]		7.18 and 7.61(m): Ph
8Aj	4.95(t)	5.60(t)		4.04(s): CH$_2$
	[1.44]	[0.79]		7.30 and 7.56(m): Ph
Cr(CO)$_3$-**j**	4.98(t)	5.43t		3.56(s): CH$_2$
	[1.41]	[0.96]		

^{13}C NMR: $\delta(^{13}\text{C})$ and [$\Delta\delta$] ^{g} (ppm)

Complex	C(1), C(4)	C(2), C(3)	C(5)	C(6)	Other
8Ah ^{l}	92.4	97.8	87.0	164.0	42.2 and 49.5: NMe$_2$; ^{h}
	[24.2	26.8	30.2	−15.2]	
Cr(CO)$_3$-**h**	90.1	90.1	81.2	154.7	41.0 and 47.8: NMe$_2$
	[26.5	34.5	36.0	−5.9]	
8Ai ^{i}	95.9	97.6	94.9	^{j}	47.7: NMe$_2$; ^{h}
8Aj	88.9	100.3	^{j}	155.0	41.9: CH$_2$; ^{h}
	[31.7	28.8		5.8]	
Cr(CO)$_3$-**j**	87.5	93.2	93.6	158.2	41.2: CH$_2$
	[33.1	35.9	39.4	2.4]	
8Dh	90.8	95.7	87.8	162.8	41.8 and 48.8: NMe$_2$; ^{h}

^{a} From ref. 1. ^{b} In acetone-d_6, except where otherwise noted. Δ is the difference between the $\delta(^1\text{H})$ values of the free fulvene and the coordinated ligand. ^{c} Cf. Scheme 1. ^{d} At 335 K; at room temperature, there are two singlets. ^{e} Additional data: **8Ch**: 0.90(t, Me), 1.29 and 1.38(m, CH$_2$), 1.68(t, CH$_2$Sn); **8Dh**: 2.39(s, CH$_2$), 6.93 and 7.12(m, Ph). ^{f} In acetone-d_6/THF-d_8. ^{g} In acetone-d_6 if not noted otherwise. $\Delta\delta$ is the difference between the $\delta(^{13}\text{C})$ values of the free and the coordinated fulvene (a positive sign for $\Delta\delta$ indicates an upfield shift in the complex). Cf. Scheme 1 for the numbering of the C-atoms. ^{h} Additional data: **8Ah**: 128.3(C(4′)), 128.8(C(3′), C(5′)), 138.3(C(2′), C(8′)) and 149.3(C(1′)); **8Ai**: 131.2, 131.7, 140.7 and 152.0; **8Aj**: 128.9, 129.1, 138.0 and 147.6; **8Dh**: 128.4, 128.3, 128.8 and 146.3 (all belonging to the Ph substituents of the benzyl groups), and 25.3(CH$_2$). ^{i} In dmso-d_6. ^{j} Not observed. ^{k} See also Fig. 1,b. ^{l} See also Fig. 2.

involvement of C_{exo}, its positivation on being coordinated should result in a deshielding. Behrens et al. [1] and Panosyan et al. [14] have shown that there is an approximate linear correlation between the coordination shift $\Delta\delta = \delta[C_{exo}$(free ligand)] − $\delta[C_{exo}$(coordinated ligand)] in Cr(CO)$_3$fulvene. While the $\Delta\delta$ value of −15.2 for **8Ah** again supports the predominance of the dipolar structure III in eq. 3a, the high-field shift ($\Delta\delta + 5.6$ ppm) in the case of **8Aj** is indicative of sizable contributions of the triolefinic structure I (eq. 3b) to the resonance hybride. $\delta(^{51}\text{V})$ values scatter unsystematicaly around the resonance for C$_5$H$_5$V(CO)$_4$ (−1534 ppm): **8Ah** −1560, **8Ai** −1510, **8Aj** −1414 ppm.

Type **8** complexes have also been obtained with **h** and trialkyltin ligands attached to vanadium, reflecting the same reaction pattern as that shown in eq. 3a (Scheme 3). The products are considerably less stable, and have not been isolated analytically
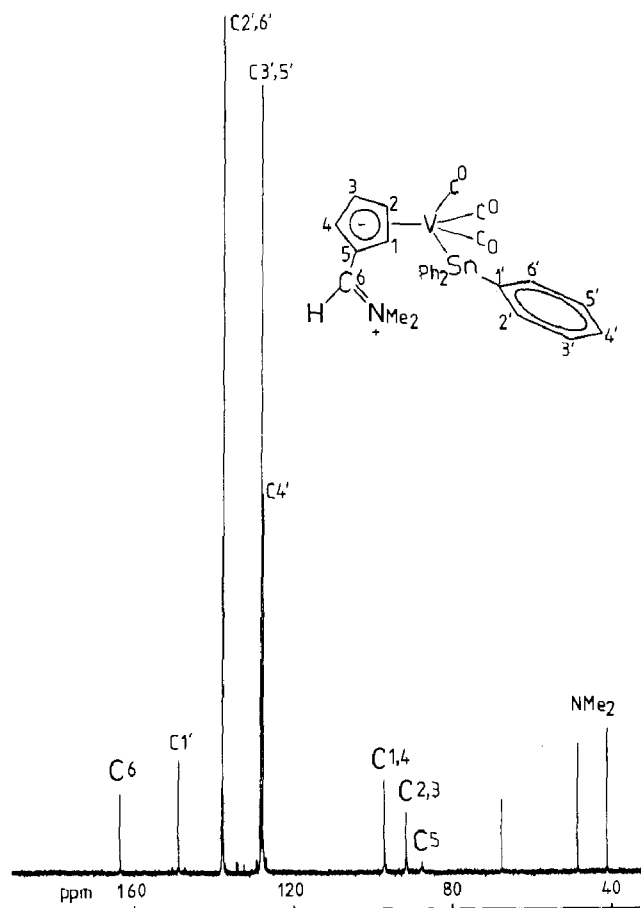
Fig. 2. 75.5 MHz ^{13}C NMR spectrum of **8Ah**.

pure. The stability decreases in the series **8A** > **8D** > **8C** > **8B** (cf. Scheme 2). Some of the spectroscopic data are shown in Tables 3 and 4. The ^{51}V chemical shifts are: **8Bh** −1599, **8Ch** −1594 and **8Dh** −1558 ppm.

$V(NO)(CO)_5$ (3) and 8-dimethylaminofulvene (h)

Complex **3** is expected to form complexes similar to those obtained with the isosteric hexacarbonylchromium [1,15]. Direct reaction of thermolabile **3** at 220 K with the fulvene **h** in THF or CH_2Cl_2 yields the fulvene complex $V(NO)(CO)_2(C_6 H_4CHNMe_2)$ (**9**; eq. 4), which can be isolated as a violet-black,
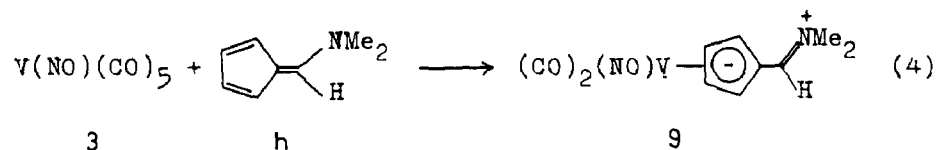
micro-crystalline powder. The same product is obtained from $V(NO)(CO)_4PPh_3$. The IR spectrum exhibits bands at 1921vs, 1853s ($\nu(CO)$), 1615m ($\nu(C=N)$) and 1570s cm^{-1} ($\nu(NO)$). The signals from the ring protons in **9** ($\delta(^1H)$ 5.52 and 5.31 ppm, broadened singlets) are shifted to high field, while that for the hydrogen

attached to C_{exo} (8.04 ppm) is deshielded with respect to the uncoordinated fulvene. For the methyl protons of the NMe_2 substituent, a broad singlet at 3.39 ppm is observed. The IR and NMR results are again consistent with the dipolar cyclopentadienyloid formulation of **9** shown in eq. 4. The chemical shift of the ^{51}V NMR signal (-1293 ppm) is similar to those reported for other dicarbonylnitrosylvanadium complexes (e.g. $V(NO)(CO)_2$triphos, -1238 to -1331 ppm [16]). The resonance is split into a $1/1/1$ triplet by coupling of the ^{51}V nucleus with the nucleus ^{14}N (nuclear spin $= 1$); the one-bond coupling constant is 90 Hz, and hence comparable to the $^1J(^{51}V-^{14}N)$ values for the $V(5+)$ complexes $(Me_3SiO)_3V=N$-t-Bu (95 Hz [17]) and $O=V(NEt_2)(O$-i-Pr$)_2$ (110 Hz [18]).

Experimental

General and physical measurements

All operations were carried out under inert gas, in oxygen-free, highly-purified solvents. The UV source was a high pressure mercury lamp (Philips HPK 125) with a water-cooled quartz immersion well, fitted into a reaction vessel that allowed passage of N_2 to take off CO liberated during the photo-reaction. Carrier for column chromatography (Kieselgel [silicagel] 60, 70–230 mesh ASTM; Florisil (magnesium silicate), 150–200 mesh ASTM; Merck) were activated under high vacuum for 3 h and treated with N_2 before use. Starting materials were obtained from commercial sources or prepared by published procedures: $[Et_4N][V(CO)_6]$, $[Et_4N][V(CO)_5PPh_3]$ and $[Na(diglyme)_2][V(CO)_5PPh_3]$ [19], $Ph_3SnV(CO)_6$ [5], $V(NO)(CO)_5$ and $V(NO)(CO)_4PPh_3$ [20], pentafulvenes [3b–d, 21].

IR spectra were recorded with Perkin–Elmer instruments (557 and 325) for 0.01–0.02 M solutions in 0.1 mm KBr cells. ^1H NMR: Bruker WP 80 and AM 360 for samples in dry, oxygen-free, deuterated solvents. ^{13}C NMR: Bruker WP 80 (20.15 MHz) and AM 360 (90.56 MHz) for samples in 10 mm vials. In some cases, a 0.02 M acetone-d_6 or dmso-d_6 solution of tris(acetylacetonato) chromium was added as a relaxation agent. The standard used for the ^1H and ^{13}C NMR spectra was TMS. ^{51}V NMR: Bruker WH 90 (23.66 MHz) in 10 mm vials, acetone-d_6. External standard was $VOCl_3$ in $CDCl_3$ or $VOCl_3$ neat with D_2O as external lock. All $\delta(^{51}V)$ values are corrected for the change in solvent (5.2 ppm for acetone-d_6/$CDCl_3$, 2.8 ppm for acetone-d_6/D_2O. The ^{51}V NMR spectra were recorded at a controlled fixed temperature (300 ± 1 K) to avoid shift effects due to temperature effects (the temperature gradient for this type of cyclopentadienylvanadium compounds amounts to ca. 0.5 ppm/deg. [22]).

Preparation of complexes

$(C_6H_5)_3SnV(CO)_5P(C_6H_5)_3$ (**2A**). The literature procedures for the preparation of **2A** give a maximum yield of 35% [5]. If the starting materials are $[Et_4N][V(CO)_5PPh_3]$ and Ph_3SnCl, **2A** is contaminated with $[Et_4N]Cl$. The following procedure enables the preparation of pure **2A** in yields of 70%:

A solution of 1.57 g (3.08 mmol) of $[Na(diglyme)_2][V(CO)_6]$ and 0.31 g (3.10 mmol) of PPh_3 in 100 ml of THF was irradiated for 2.5 h. After evaporation of the solvent, the red $[Na(diglyme)_2][V(CO)_5PPh_3]$ was redissolved in 80 ml of CH_2Cl_2 and treated with 1.19 g (3.08 mmol) of Ph_3SnCl. After about 1 h of stirring, the

ν(CO) bands typical of the [V(CO)$_5$PPh$_3$]$^-$ anion (1963w, 1823s, 1790sh cm^{-1} [19]) had disappeared. The resulting yellow solution was washed four times with 30 ml portions of oxygen-free water. The yellow-brown CH$_2$Cl$_2$ layer was separated off and residual water frozen out at $-60°$C. Filtration through 1 cm of silica gel gave an orange solution from which the solvent was removed at room temperature to leave an orange powder. This was redissolved in 15 ml CH$_2$Cl$_2$/heptane 4/1 and recrystallized by cautious concentration. Yield 1.73 g (2.16 mmol) 70%.

(C$_2$H$_5$)$_3$SnV(CO)$_5$PPh$_3$ (2B), (n-C$_4$H$_9$)$_3$SnV(CO)$_5$PPh$_3$ (2C), and (C$_6$H$_5$CH$_2$)$_3$-SnV(CO)$_5$PPh$_3$ (2D). These compounds were prepared from [Na(diglyme)$_2$][V-(CO)$_5$PPh$_3$] (740 mg; 1.0 mmol) and an equimolar amount of R$_3$SnCl, as described for **2A**, but filtration was carried out at $-60°$C and without silica gel to avoid decomposition. The complexes were isolated as spectroscopically pure, orange oils (yields: 45% (**2B**), 20% (**2C**) and 15% (**2D**), and used without further purification.

h^5-(C$_5$H$_4$CHZ$_2$)V(CO)$_3$PPh$_3$ (Z = C$_6$H$_5$ (4d), p-CH$_3$OC$_6$H$_4$ (4b), p-(CH$_3$)$_2$NC$_6$H$_4$ (4f) and p-ClC$_6$H$_4$ (4g), and h^5-(C$_5$H$_4$CHZ$_2$)V(CO)$_4$ (Z = C$_6$H$_5$) (5d) and p-ClC$_6$H$_4$ (5g). A: A solution of 660 mg (0.82 mmol) of **2A** and an equimolar amount of the fulvene C$_5$H$_4$CZ$_2$ in 50 ml of THF was stirred for 24 h, during which the colour changed from orange to red-brown and finally to dark-brown. After concentration to a few ml, the mixture of **4** and **5** was chromatographed on silica gel (column dimensions: 6 × 25 cm; elutant: THF/n-heptane 1/4). In the case of **4d**/**5d** and **4g**/**5g**, a yellow fraction containing the tetracarbonyls was eluted as the first fraction, from which small amounts of **5d** and **5g** were isolated as orange light-sensitive oils. The second, orange-red fraction contained **4d** or **4g**. This fraction was evaporated to dryness and the residue was taken in 30 ml of THF/heptane 1/1. Crystallization by slow concentration in vacuo yielded the orange (**4d**) or orange-brown (**4g**) as micro-crystalline powders.

In the case of **4e**/**5e** and **4f**/**5f**, only a single, broad, orange-coloured fraction was obtained, which contained the tricarbonyls **4** and small amounts of the tetracarbonyls **5**: After removal of the solvent, the residue was kept for ca. 7 days (during which the tetracarbonyls **5e** and **5f** decompose) then dissolved in 30 ml of THF/heptane 1/1. Filtration and slow evaporation of the solution yielded a pure orange-brown powder of **4e** or **4f**. Yields: 48% (**4d**), 26% (**4e**), 15% (**4f**), 28% (**4g**).

B: **5d** can also be prepared in the following manner: A solution of 980 mg (1.72 mmol) of Ph$_3$SnV(CO)$_6$ (**1**) and 397 mg (1.72 mmol) of **d** in 50 ml of CH$_2$Cl$_2$/THF 100/1 was stirred for 24 h, at room temperature to yield a mixture of [V(CO)$_6$]$^-$ and **5d**. Vacuum evaporation of the solvent left a brown residue, from which **5d** was extracted with five 40 ml portions of n-pentane. Removal of the pentane yielded 100 mg (15%) of a viscous orange oil, which decomposed on standing at room temperature for several days.

The reactions between Ph$_3$SnV(CO)$_5$L (L = PPh$_3$: 2A, L = CO: 1) and dialkylfulvenes. Treatment of **2A** in THF with the fulvene **b** yielded a mixture of the alkenylcyclopentadienyl complex **6b**, the alkylcyclopentadienyl complex **4b**, and [V(CO)$_5$PPh$_3$]$^-$. Separation on silica gel led to partial decomposition; a small amount of **4b** was eluted with THF (2nd fraction), and isolated as a red oil after removal of the solvent followed by redissolution in THF/heptane 2/1 and gradual concentration. The main product of reaction between **2A** and the fulvenes **a** and **c**, respectively, are the alkenyl derivatives **6a** and **6c**. These labile compound could not be purified.

Reaction of **1** with **c** in heptane for 10 days gave a dark-brown solution containing the tetracarbonylalkenylcyclopentadienyl complex **7c** and the fulvene complex **8Ac**. After precipitation of unchanged **1** with THF, filtration and evaporation of the solution left a brown oil, which was redissolved in hexane/THF 15/1 and chromatographed on Florisil (column dimensions 2.5 × 25 cm; elutant hexane/THF 15/1). Small amounts of **7c** (orange oil) and **8Ac** (red-brown oil) were isolated from the 2nd and 3rd fractions, respectively, by evaporation of the solvent (**7c**) or precipitation with heptane from the concentrated solution (**8Ac**).

h-{C$_5$H$_4$CHN(CH$_3$)$_2$}V(CO)$_3$Sn(C$_6$H$_5$)$_3$ (8Ah), h-{C$_5$H$_4$C[N(CH$_3$)$_2$]$_2$}V(CO)$_3$-Sn(C$_6$H$_5$)$_3$ (8Ai), and h-{C$_5$H$_4$C(SCH$_2$CH$_2$S)}V(CO)$_3$Sn(C$_6$H$_5$)$_3$ (8Aj). 530 mg (0.66 mmol) of **2A** and an equimolar amount of the fulvene were stirred in THF for 24 h (room temperature), during which the orange solutions turned wine-red (**8Ah**), cinnabar-red (**8Ai**), or deep-blue (**8Aj**). After filtration of the solutions and concentration to about 20 ml, the complexes were precipitated with pentane as intensely coloured powders. The products were filtered off, washed twice with 10 ml portions of pentane and dried for 2 h under high vacuum to yield 370 mg (60%) of dark-red **8Ah**, 230 mg (40%) of rose-tinted, light-brown **8Ai** and 360 mg (55%) of dark-blue **8Aj**. Analysis of **8Ah**: Found: C, 57.79; H, 4.62; N, 2.29; Sn, 19.5; V, 8.11. C$_{29}$H$_{28}$NO$_3$VSn (M = 606.17) calcd.: C, 57.46; H, 4.32; N, 2.31; Sn, 19.58; V, 8.40%.

*The reaction between the fulvene **h** and the stannyl complexes R$_3$SnV(CO)$_5$L (L = PPh$_3$; R = Et, n-Bu, PhCH$_2$. L = CO; R = Ph).* A solution of 0.20 mmol of the vanadium compounds **2** and an equimolar amount of the fulvene **h** in 30 ml of THF was stirred for 24 h, then 5 ml of heptane were added and the solution was filtered. Evaporation of the solvent yielded the fulvene complexes as a red-brown (**8Bj**), red (**8Cj**), or wine-red (**8Dj**) oil. Repeated reprecipitation from THF/heptane gave a spectroscopically pure product in the case of **8Dj** only.

Small amounts of the fulvene complex **8Aj** are produced as **1** and **j** react in suspension in heptane. A THF solution of the pasty precipitate obtained from this reaction gave IR and [51]V NMR spectra which showed the pattern of **8Aj** along with [V(CO)$_6$]$^-$ as the main product.

h-{C$_5$H$_4$CHN(CH$_3$)$_2$}V(NO)(CO)$_2$ (9). A: 335 mg (0.96 mmol) of [Et$_4$N][V-(CO)$_6$] and 132 mg (1.13 mmol) of NO[BF$_4$] were allowed to react in 20 ml of CH$_2$Cl$_2$ at −78°C, and the V(NO)(CO)$_5$ (**3**) isolated as described in ref. 20. Complex **3** was redissolved in 20 ml of cold (−70°C) THF, and a cold solution of 116 mg (0.96 mmol) of **h** in 10 ml of THF was added dropwise. The (originally violet, but now orange-brown) solution was allowed to warm with stirring to 10°C during 24 h, and became violet again. Dissolution with 5 ml of pentane followed by filtration of the solution at room temperature and vacuum evaporation of the solvent gave a black residue, which was redissolved in 20 ml of THF. From this solution, **9** was precipitated with heptane at room temperature as a dark-violet to black powder contaminated with small amounts of **h**, which could not be removed by reprecipitation. The dry compound can be stored under nitrogen in the dark at −20°C for several weeks without substantial decomposition. At room temperature, **9** rapidly decomposes with the evolution of nitric oxides.

B: A solution of 122 mg (0.27 mmol) and V(NO)(CO)$_4$PPh$_3$ in 20 ml of THF and 36 mg (0.30 mmol) of **h** in 10 ml of THF were mixed at 0°C. The mixture was allowed to warm during 12 h to 10°C. The black, powdery **9** was isolated from the

dark-violet solution by adding 10 ml of heptane, then filtering and concentrating the solution to ca. 10 ml. The stabilizing ligand PPh$_3$ is completely removed from the complex in this reaction.

Acknowledgement

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