

The 1,4- and 2,3-diazadiene complexes of carbonylvanadium. Their ^{51}V NMR properties, and the crystal structure of *cis*- $[\eta^5\text{-C}_5\text{Me}_5\text{V}(\text{CO})_2]^1\text{PrN}=\text{CHCH}=\text{N}^1\text{Pr}]$

Claus Woitha, Ulrich Behrens, Vassilios Vergopoulos and Dieter Rehder *

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

(Received February 19th, 1990)

Abstract

The reaction between $\text{Cp}'\text{V}(\text{CO})_3\text{THF}$ ($\text{Cp}' = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{SiMe}_3$, C_5Me_5) or $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{THF}]$ and diazadienes ($\text{RN}=\text{CHCH}=\text{NR}(\text{dad})$, $\text{R}'\text{HC}=\text{NN}=\text{CHR}'(\text{azine})$; L) at low temperature yields the complexes *cis*- $[\text{Cp}'\text{V}(\text{CO})_2\text{L}]$ ($\text{R} = n\text{-C}_5\text{H}_{11}$, ^1Pr , ^tBu , Ph , $4\text{-MeOC}_6\text{H}_4$; $\text{R}' = p\text{-Tol}$, $4\text{-HOC}_6\text{H}_4$, $4\text{-MeOC}_6\text{H}_4$) or *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{L}]$ ($\text{R} = p\text{-Tol}$, $4\text{-MeOC}_6\text{H}_4$, $\text{R}' = \text{Ph}$). In some cases ($\text{R} = n\text{-C}_5\text{H}_{11}$, ^1Pr ; $\text{R}' = \text{Ph}$), direct irradiation of $\text{C}_5\text{Me}_5\text{V}(\text{CO})_4$ in the presence of L leads to the same complexes. With $\text{R}' = \text{Me}$, the mono-substituted complexes $\text{Cp}'\text{V}(\text{CO})_3\text{L}$ or $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{L}]$ are formed. The $\delta(^{51}\text{V})$ values of *cis*- $[\text{Cp}'\text{V}(\text{CO})_2\text{L}]$ (-346 to -498 ppm for $\text{L} = \text{dad}$, -300 to -393 ppm for $\text{L} = \text{azine}$; relative to VOCl_3) indicate that the ligands are comparable in overall ligand strength to amines. The crystal structure has been determined for *cis*- $[\text{C}_5\text{Me}_5\text{V}(\text{CO})_2]^1\text{PrN}=\text{CHCH}=\text{N}^1\text{Pr}]$ (**4b**). The ^1Pr -dad ligand in **4b** forms a chelate-5 ring ($d(\text{VN}) = 206.7(2)$ pm) in the envelope conformation and exhibits partial enediamine coordination ($d(\text{CC}) = 137.2(7)$ pm). Structure information has also been obtained for *cis*- $[\text{C}_5\text{Me}_5\text{V}(\text{CO})_2\text{PhHC}=\text{NN}=\text{CHPh}]$ (**4g**): Benzaldazine in **4g** is coordinated in the $\eta^2\text{-(NN)}$ mode (perpendicular to the mirror plane of the molecule) with $d(\text{VN}) = 201.9(5)$ and $d(\text{NN}) = 140.0(12)$ pm.

Introduction

Ligands containing nitrogen donors do not commonly form stable complexes with metals in their low oxidation states, although several complexes of vanadium have been known for some time, such as $[\text{V}(\text{bipy})(\text{terpy})\text{NCMe}]^+$ [1], $[\text{V}(\text{NCMe})_6]^+$ [2] $[\text{V}(\text{dipy})_3]$ and $[\text{V}(\text{dipy})_3]^-$ [3], and $[\text{CpV}(\text{CO})_n\text{L}]$ with L a bifunctional *N*-ligand forming chelate-5 ring structures [4–6] or coordinating in the monodentate fashion (hydrazines) [7]. Diazadiene complexes of low-valent vanadium have been mentioned only sporadically. Examples are the V^{-1} complexes $\text{Na}[\text{VL}_2(\text{THF})_4]$ ($\text{L} =$

$\text{PhN}=\text{CPhCPh}=\text{NPh}$) [8] and $[\text{VL}'_4(\text{NO})_2]\text{Br}$ ($\text{L}' = \text{RN}=\text{CHCH}=\text{NR}$; $\text{R} = {}^i\text{Pr}$, Tol) [9]. However, none of these has been structurally characterized. The examples given here demonstrate that *N*-donors may form stable complexes with vanadium in its oxidation states $-I$, 0 and $+I$, provided that the ligand system can accommodate π electron density-delocalized towards the coordination sphere by the metal centre. This is the case with diazadienes, which contain an unsaturated carbon-nitrogen backbone.

We have for some years been interested in quantifying the ligand strength of a ligand (its σ -donor plus π -acceptor capacity) by an intrinsic quantity, viz. the shielding of the metal nucleus embedded in the coordination sphere, and we have established a magnetochemical series [9–12] for the ligand strengths on the basis of ^{51}V shielding data. The present work was aimed at structural characterization of diazadiene complexes of V^{+I} and V^{-I} and to classify these ligands in relation to other *N*-donors.

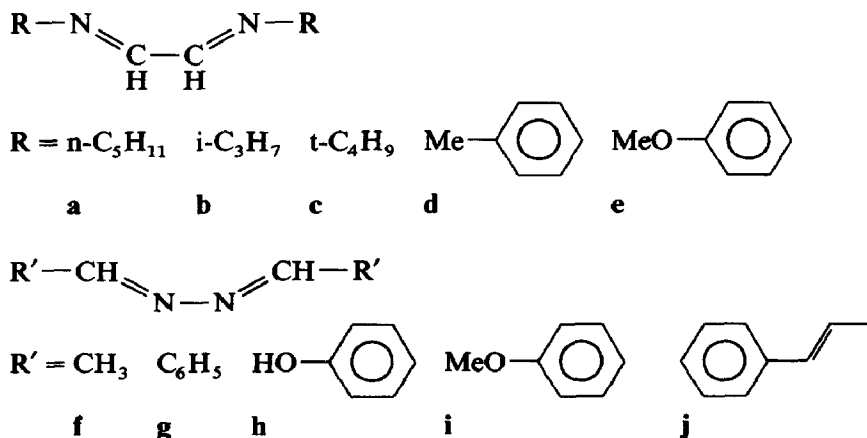
1,4-Diazadienes (dad) coordinated to late transition metals have become increasingly important as ligands in various catalytically assisted processes [13,14], but their use as ancillary ligands in early transition metal complexes remains unexplored. Very little is known of the coordination behaviour of 2,3-diazadienes (azines). Only a singular report exists on azine complexes of vanadium, in its oxidation state $+V$ ($[\text{VO}(\text{azine})\text{Cl}]$, with the functionalized azine acting as a tridentate ligand and the complex ascribed the structure of a trigonal bipyramid [15]).

Results and discussion

Preparation and spectroscopic characterization

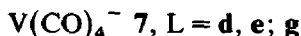
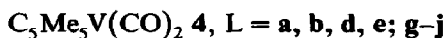
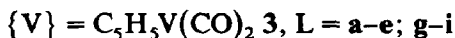
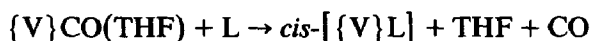
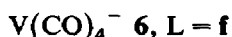
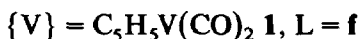
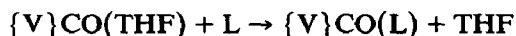
The ligands used are shown in Scheme 1.

Although some of these ligands react slowly with $\text{CpV}(\text{CO})_4$ at room temperature in the diffuse daylight, this is not a convenient route for the synthesis of the complexes, because in solution they are labile and decompose within a few hours. In several cases involving the complexes **4** (for numbering see below), acceleration of the reaction by UV irradiation leads to reasonable yields. Most of the compounds



Scheme 1

are, however, light-sensitive. We therefore employed the dark reaction between the THF complexes $\{V\}CO(THF)$, where $\{V\}$ stands for $C_5H_5V(CO)_2$, $C_5Me_5V(CO)_2$, $C_5H_4SiMe_3V(CO)_2$ and $V(CO)_4^-$. These compounds can be generated by UV irradiation of the parent carbonyls $\{V\}(CO)_2$ in THF solution at dry-ice temperature. They are stable up to 260 K ($C_5Me_5V(CO)_3THF$ [7,16]), 240 K ($C_5H_5V(CO)_3THF$ [7,17]) and 220 K ($[Et_4N][V(CO)_5THF]$ [10,18]), and readily react when treated with dad or azine at 195 K and warmed up to the decomposition temperature of $\{V\}CO(THF)$ to form mono- and (in most cases) *cis*-disubstituted products:



The THF solutions of the complexes are red (1; 2; 3a-e; 4a, b, d, e; 5; 6; 7) or deep blue (all disubstituted cyclopentadienyl complexes with azines, i.e. 3g-i; 4g-j; 7g), and more or less labile even when kept under an inert gas, with exclusion of light, and at low temperature. Complexes containing the pentamethylcyclopentadienyl ring are more stable. However, in the case of ^tBu-dad (c), steric hindrance prevents the formation of a complex. Generally, the stabilities of the complexes 3, 4 and 5 decrease in the sequence $a > b > c > d, e$ and $g > h, i > j$, i.e. the more stable complexes in the case of dad ligands (a-e) are those with non-bulky alkyls on the nitrogens, while azines (f-j) with alkyl substituents on the carbons do not form disubstituted complexes at all. The anionic complexes 6 and 7g are even more labile. In 7d and 7e, aryl substituents on dad impart some stability, indicating that the ability of aryls to delocalize π electron density becomes a stabilizing factor in V^{-1} complexes, whereas V^{+1} compounds are destabilized. In addition to this stabilizing effect in the anionic complexes, the low solubility of $[Et_4N]-7e$ in THF aided its isolation.

The IR pattern in the $\nu(CO)$ region (Table 1) is consistent with the assignments of 1, 2 and 6 to mono-, and 3, 4, 5 and 7 to disubstitution products. As far as the tricarbonyl complexes are concerned, the positions of the CO stretching bands are similar to those observed for $CpV(CO)_3(\text{hydrazine})$ [7]. In the dicarbonyl complexes, the bands are quite significantly shifted to higher wave numbers than those for other complexes of composition *cis*- $[C_5H_5V(CO)_2NN]$ ($NN = Me(H)PhCN=C$ (σ -py): 1901 and 1834 cm^{-1} [4]; $NN = \text{bipyridyl}$: 1843 and 1780 cm^{-1} [5]). For the ligand arrangements we assume the structures depicted below (A and B), which are supported by the structures found for the molecules 4b and 4g in the crystalline solid state (vide infra) and also, in the case of B, by the value $\delta(^1H)$ of 8.88 ppm for

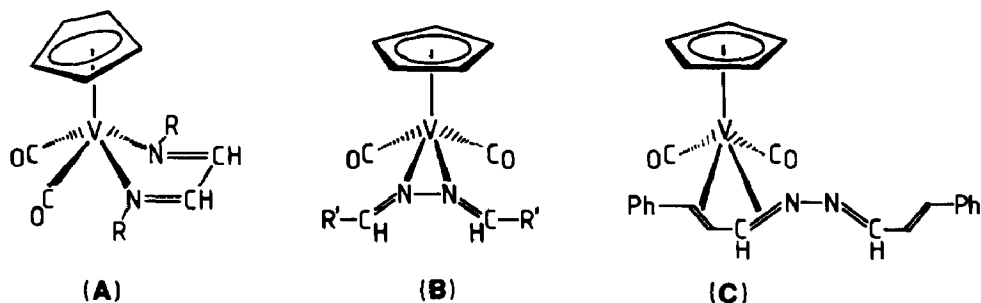
Table 1

IR (CO stretching region) and ^{51}V NMR data in THF

Complex	$\nu(\text{CO})$ (cm^{-1})		δ (ppm)	$W_{1/2}^a$ (Hz)
$\text{C}_5\text{H}_5\text{V}(\text{CO})_3\text{L}$ (1)				
L = f	1952s	1895vs	-372	
$\text{C}_5\text{Me}_5\text{V}(\text{CO})_3\text{L}$ (2)				
L = f	1835s	1830vs	-430	
<i>cis</i> - $[\text{C}_5\text{H}_5\text{V}(\text{CO})_2\text{L}]$ (3)				
L = a	1925vs	1860s	-431	490
b	1925vs	1860s	-415	240
c	1940s	1840s	-431	
d	1945vs	1885s	-346	570
e	1946s	1890s		
g	1930vs	1865s	-325	370
h	1938vs	1849s	-300	520
i	1933vs	1850s	-308	520
<i>cis</i> - $[\text{C}_5\text{Me}_5\text{V}(\text{CO})_2\text{L}]$ (4)				
L = a	1920vs	1850s	-498	760
b	1910vs	1845s	-424	375
d	1920vs	1857s		
e	1915vs	1857s		
g	1917vs	1856s	-383	
h	1905vs	1835s	-374	850
i	1900vs	1860s	-379	720
j	1922vs	1860s	-393	620
<i>cis</i> - $[\text{C}_5\text{H}_4\text{SiMe}_3\text{V}(\text{CO})_2\text{L}]$ (5)				
L = g			-310	
h			-292	
i			-278	
$[\text{V}(\text{CO})_5\text{L}]^-$ (6)				
L = f			-1501	580
<i>cis</i> - $[\text{V}(\text{CO})_4\text{L}]^-$ (7)				
L = d	1938s	1830vs ^b	-927	540
e	1943s	1835vs ^{b,c}	-940	340
g			-1019 ^d	330
<i>cis</i> - $[\text{CpV}(\text{CO})_2\text{L}]$, L = j (8) ^e				
Cp = C_5H_5	1960vs	1875s	-803	520
Cp = $\text{C}_5\text{H}_4\text{SiMe}_3$			-771	

^a Width of the resonance signal at half-height. Not determined (owing to unfavorable signal-to-noise ratio) if not indicated. ^b Broad band with a shoulder at ca. 1820 cm^{-1} . ^c In pyridine; Nujol: 1941s, 1860s, 1817s, 1798sh. ^d At 230 K. ^e Tentative formulation; see C in Scheme 2.

the methyne hydrogen of **4g**, which is only slight (0.17 ppm) to low field of the resonance for the free ligand and indicates the absence of involvement of the methyne carbons in coordination. The complex obtained from the reaction between cinnamic azine (j) and $\text{C}_5\text{H}_5\text{V}(\text{CO})_3$ THF exhibits an IR pattern similar to that observed for the complexes 3, and is assigned *cis*- $[\text{C}_5\text{H}_5\text{V}(\text{CO})_2\text{L}]$ for this reason. The different color (red, instead of blue for other azine complexes of this composition) and the largely deviating $\delta(^{51}\text{V})$ value (-803 ppm instead of ca. -310 ppm) suggests a different bonding mode. C in Scheme 2 is a tentative formulation,



Scheme 2

supported by the existence of alkene and alkyne complexes $\text{CpV(CO)}_2\text{L}'$ with $\text{L}' = \text{cyclo-C}_4\text{R}_4$ [19], $\eta^4\text{-C}_3\text{Ph}_3\text{H(CO)}$ [20] or $\eta^2\text{-tolane}$ [19,21].

⁵¹V NMR spectra

$\delta(^{51}\text{V})$ values for the diazadiene complexes are listed (in italics) in Table 2 together with $\delta(^{51}\text{V})$ values for carbonylvanadium complexes containing other, mainly *N*-ligands. The following features are noted:

(1) There is an increase in ⁵¹V shielding on going from cyclopentadienyl to pentamethylcyclopentadienyl complexes, in accord with trends observed for other ligands such as THF or hydrazines [7], but in contrast to those observed for alkyne complexes [21,24] and the parent carbonyls (Table 2).

(2) There is the usual marked down-field shift when one CO is replaced by a less powerful π acceptor (more effective σ donor). There is a similar effect as a second CO is replaced, but the effect is substantially less pronounced in diazadiene complexes than, e.g., in phosphine and amine complexes.

(3) Dad and azine ligands induce large deshielding of the ⁵¹V nucleus, especially azines. In the monosubstituted Cp complexes, the signals are at the end of the low-field (high-frequency) range for *N* ligands, and for the other complexes, the deshielding effect is similar to that of amines.

A qualitative explanation for these effects can be derived on the basis of a simplified approach to the parameters responsible for variations in shielding, which are related to the paramagnetic deshielding contribution of the overall shielding, $\sigma' = \sigma'(\text{dia}) + \sigma'(\text{para})$. $\sigma'(\text{dia})$ is practically constant for a series of similar complexes [25]. $\sigma'(\text{para})$ is inversely proportional to the HOMO–LUMO gap and the cube of the expansion of the 3*d* cloud, and directly proportional to the square of the 3*d* LCAO coefficient of the MO's relevant for electronic transitions:

$$\sigma'(\text{para}) = \text{const} \Delta E^{-1} \langle r^{-3} \rangle_{3d} C_{3d}^2$$

The validity of this relation in interpreting ⁵¹V NMR data has been confirmed for a large number of ligands in the complex series $[\text{V(CO)}_5\text{L}]^-$ [10]. ΔE is influenced by the overall strength of the ligand field, and changes in this quantity straightforwardly explain variation of σ' when a strong π -accepting ligand such as CO (which effectively stabilizes a complex containing a low-valent metal center) is replaced by a ligand with poorer acceptor ability. The values $\langle r^{-3} \rangle$ and C^2 , which correlate with the nephelauxetic effect and the covalency of the metal–ligand bond, are less obviously involved in variations of shielding. Generally, however, we can assume

Table 2

 $\delta(^{51}\text{V})$ values (ppm), relative to VOCl_3

Compound	δ	Ref.
$\text{Cp}'\text{V}(\text{CO})_4$		
$\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$	-1542	22
C_5H_5	-1534	6b,c
C_5Me_5	-1492 ^a ; -1525 ^b	6b,c;7
$\text{Cp}'\text{V}(\text{CO})_2\text{dad}$		
$\text{Cp}' = \text{C}_5\text{Me}_5$ (4)	-424 to -498	
C_5H_5 (3)	-346 to -431	
$\text{Cp}'\text{V}(\text{CO})_2\text{azine}$		
$\text{Cp}' = \text{C}_5\text{Me}_5$ (4)	-374 to -393	
C_5H_5 (3)	-300 to -325	
$\text{C}_5\text{H}_4\text{SiMe}_3$ (5)	-278 to -310	
$\text{C}_5\text{H}_5\text{V}(\text{CO})_3\text{L}$		
$\text{L} = \text{PMe}_2\text{Ph}$	-1396	16
NCMe	-719	16
N_2H_4	-679	7
imidazole	-659	16
NH_2R ^c	-615 to -649	6a,b
pyridine	-519	16
azine (1)	-372	
THF	-136	7,16
$\text{C}_5\text{H}_5\text{V}(\text{CO})_2\text{L}$		
$\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	-1110	23
cinammic azine (8)	-803	
alkynes	-598 to -626	24
<i>dad</i> (3)	-346 to -431	
amines ^c	-302 to -345	6a,b
azine (3)	-300 to -325	
Schiff base ^d	-194/-213 ^e	6a
bipyridyl	-63	16
$[\text{V}(\text{CO})_6]^-$	-1952	23
$[\text{V}(\text{CO})_5\text{L}]^-$		
$\text{L} = \text{PMe}_2\text{Ph}$	-1855	23b
N_2	-1671	10,18
1-hexyne	-1636	10,18
N_2H_4	-1557	^f
NCMe	-1601	10,18
azine (6)	-1501	
pyridine	-1461	10,18
THF	-1367	10,18
$[\text{V}(\text{CO})_4\text{L}]^-$		
$\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	-1790	23
azine (7)	-1019	
<i>dad</i> (7)	-927 to -940	

^a In CDCl_3 . ^b In THF. ^c Aliphatic. ^d The Schiff base originating from 2-formylpyridine and 1'-amino-1'-methyltoluene. ^e Two diastereomers. ^f Unpublished.

that a ligand function which is more easily polarized (less electronegative), e.g. *C* in CO vs. *N* in amines and diazadienes, gives rise to an expansion of the *d*-electron cloud (decrease of $\langle r^{-3} \rangle$) and an increase in covalency (decrease in C^2), and hence a decrease in $\sigma'(\text{para})$, which acts in the same direction as the decrease in $\sigma'(\text{para})$

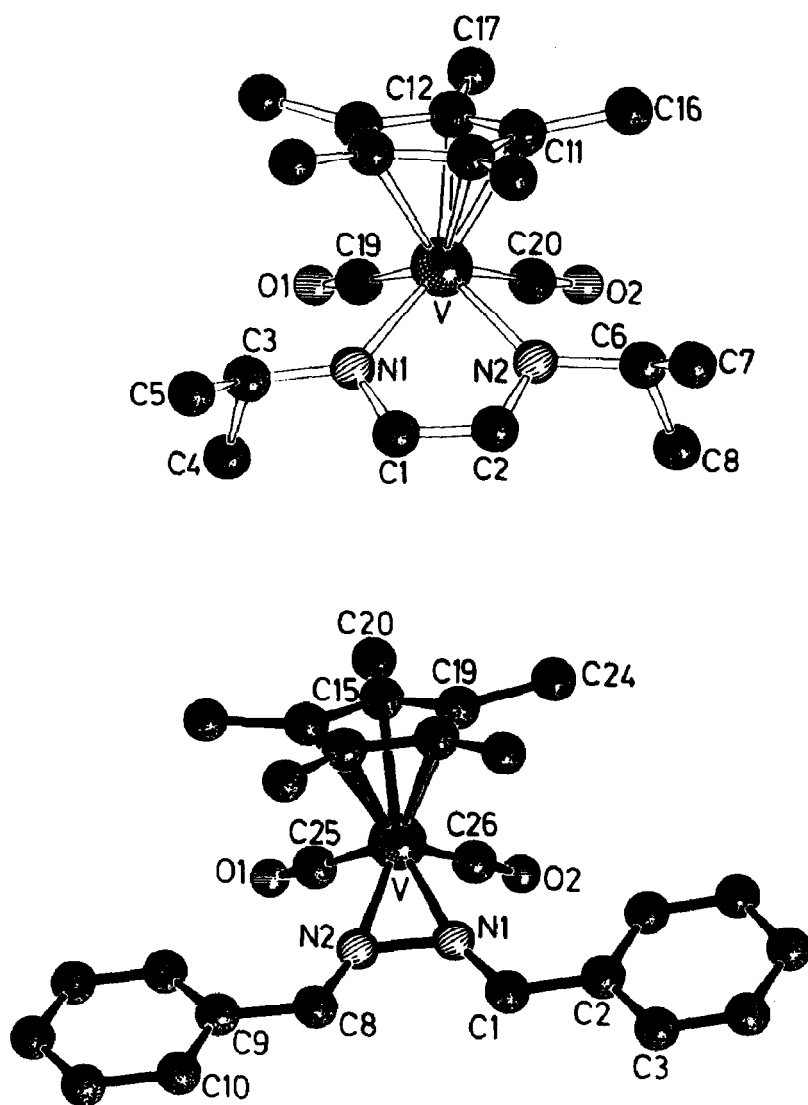


Fig. 1. SCHAKAL plots and numbering schemes for the molecules 4b (top; hydrogen atoms have been omitted for clarity) and 4g.

owing to an increase of ΔE . A smaller paramagnetic deshielding term in turn gives rise to enhanced overall shielding σ' . Consequently, high metal shielding in low-valent compounds is commonly observed with strong π acceptors (CO, CNR, PF_3) and highly polarizable ligands (stibines, thio ethers, iodide) [10,12,23,25–26].

On this basis, dad and azine, in the complexes $\text{cis-}[\text{CpV}(\text{CO})_2\text{L}]$, for which a reliable amount of data has been collected, are weak ligands, comparable with (aliphatic) amines in their electronic behaviour, but stronger than pyridine derivatives such as bipyridyl or the Schiff base $\text{Me}(\text{H})\text{PhCN}=\text{C}(\text{o-py})$ containing an amine and a pyridine *N*. Diazadienes must thus be placed between alkynes on the one hand, and pyridines and ligands coordinating via oxygen (THF) on the other. The sequence in Table 2 may be taken as reflecting their relative positions on a

Table 3

Selected bond lengths (pm) and bond angles (°) for the complexes **4b** and **4g**

4b ^a		4g ^a	
V–N	206.7(2)	V–N	201.9(5)
V–CO	191.9(2)	V–CO	190.0(11)
V–C(CMe ₅)	228.5	V–C(C ₅ Me ₅)	227.1(8)
C–O	116.6(6)	C–O	118.2(15)
C1–C2	137.2(7)	N1–N2	140.0(12)
N–CH	133.0(5)	N–CH	129.2(8)
N–C(ⁱ Pr)	148.4(7)	HC–C(phenyl)	144.0(9)
V–Cp(center)	194.6	V–Cp(center)	192.8
N1–V–N2	75.4(2)	N1–V–N2	41.7(4)
OC–V–CO	77.3(2)	OC–V–CO	76.1(6)
N–V–CO	82.4	N–V–CO	118.5(5)
O–C–V	174.1(2)	O–C–V	176.0(13)
V–N–CH	116.3(3)	V–N–N	69.7(6)
V–N–C(ⁱ Pr)	128.1(3)	V–N–CH	164.6(9)
C(H)–N–C(ⁱ Pr)	115.5(6)	N–C(H)–C(Ph)	122.3(12)

^a Averaged for the molecular mirror plane.

magnetochemical scale of overall ligand strengths, with a larger $|\delta|$ value indicating the stronger ligand.

Crystal structures

SCHAKAL plots of the complexes **4b** and **4g**^{*} are displayed in Fig. 1, selected bond lengths and bond angles in Table 3, fractional coordinates for in Table 4.

Compound **4b** crystallizes in the monoclinic space group $P2_1/n$ [27a*]. The molecule has an idealized mirror plane bisecting the OC–V–CO angle and the chelate-5 ring which is formed as the ligand ⁱPr-dad is coordinated through the two nitrogen functions. The 5-membered ring is in the envelope conformation, folded along the N1–N2 axis. The almost ideal plane spanned by N1, N2, C1 and C2 points away from the two CO groups. Vanadium deviates from this plane by 15.8 pm. The bond distances $d(\text{N1–C1})$ (133.6(6) pm) and $d(\text{N2–C2})$ (132.6(6) pm) are only slightly longer than those in $\text{Fe}(\text{CO})\chi^i\text{Pr-dad}(2,3\text{-Me}_2\text{C}_4\text{H}_4)$ (131.7(2) pm), in which dad functions as a pure bidentate *N*-donor [28]. The carbon–carbon bond length $d(\text{C1–C2})$ (137.2(7) pm) is, however, rather short, and is comparable to the $d(\text{CC})$ value of 137.5(7) pm in $[\text{C}_5\text{Me}_5\text{Hf}^i\text{Pr-dad}(\mu\text{-H})]_2$ [29], indicating partial enediamine character for the coordinated ⁱPr-dad in **4b** (cf. A in Scheme 2). The distance between vanadium and the centre of the cyclopentadienyl ring (194.6 pm) is very similar to that observed in other $\eta^5\text{-Cp}$ complexes of vanadium [30*]. The V–N1–N2–(CO)₂ moiety is tetragonal-pyramidal.

* Thwarted by a persistent twinning problem, we were only able to refine the structure of **4g** to an *R*-value of 9%. For this reason, the cell and structure parameters may not be wholly reliable. Further in addition to the standard deviations for bond distances and angles indicated in Table 3, these parameters may involve an additional systematic error. From the chemical point of view, however, the molecular structure of **4g** as illustrated in Fig. 1 is reliable in all its aspects.

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

In **4g** (space group $P2_1/n$) [**27b***], the ligand benzaldazine is coordinated through the two nitrogen atoms in a symmetrical side-on fashion. The molecule by itself has a mirror plane, containing the vanadium atom and the carbon atoms C15 and C20 of the cyclopentadienyl unit, and bisecting the azine ligand and the angle between the two carbonyl groups. This is different from the ligand arrangement in *cis*- $[\eta^5\text{-indenylV(CO)}_2\eta^2\text{-C}_2\text{HPh}]$, where the C–C linkage of the side-on coordinating acetylene lies in the mirror plane [21]. The linkage between the methyne and phenyl carbons has partial double bond character, showing that the π electron system is delocalized throughout the coordinating ligand. This view is emphasized by the fact that all atoms in the ligand back-bone (N1–N2–C1–C8–C2–C9) are nearly co-planar. The distance between vanadium and the centre of the $\eta^5\text{-C}_5\text{Me}_5$ system is 192.8 pm.

Experimental

General procedure and spectra

All operations were carried out under argon and in highly purified solvents. Starting materials were prepared by procedures as described previously: $(\text{C}_3\text{H}_5\text{V(CO)}_4)$ and $\text{C}_5\text{Me}_5\text{V(CO)}_4$ [6b,c], $\text{C}_3\text{H}_4\text{SiMe}_3\text{V(CO)}_4$ [22*], $[\text{Et}_4\text{N}][\text{V(CO)}_6]$ [31]; **b**, **c** and **d** [32], **e** [33]; **f** [34]. Analogous procedures were used for the preparation of **a** [32] and **g–j** [34]).

IR spectra were obtained on a Perkin Elmer 577 spectrometer as ca. 0.02 *M* THF solutions in 0.1 mm KBr cells. $^{51}\text{V}\{^1\text{H}\}$ NMR spectra were scanned at 298(1) K on a Bruker AM 360 spectrometer at 94.7 MHz as ca. 0.02 *M* solutions in THF/THF- d_8 2/1 contained in rotating 10 mm diameter vials. The samples were thermostated to prevent shifts of the resonance signals due to the temperature changes (temperature gradients for the compounds under investigation are around 1 ppm/deg [35]). Typical measuring parameters: Pulse angle 60°, sweep width 50 kHz, 8 K data set (digital resolution 6 Hz/point), scan number 2500. Generally, the spectra were obtained without applying delay time and line broadening. All spectra were referenced against $\text{VOCl}_3/\text{CDCl}_3$ and the $\delta(^{51}\text{V})$ values corrected for lock shift.

X-Ray diffraction study

Crystals of **4b** (crystal dimensions: $0.51 \times 0.31 \times 0.09\text{ mm}^3$) were obtained by adding a large excess of methanol to a concentrated solution of **4b** in hexane and keeping the solution for one week at 195 K. Data were collected at room temperature on an Enraf Nonius CAD 4 diffractometer using graphite monochromator Cu-K_α irradiation. Collection of the reflections was carried out in the $\theta/2\theta$ scan mode in the scan range $5^\circ < 2\theta < 120^\circ$. From the observed 3507 reflections, 1959 significant ones ($F > 4\sigma(F)$) were used in the structure solution and refinement. Refinements were carried out with 228 parameters to a final *R* value of 0.057. A numerical absorption correction was applied; the maximum and minimum transmission factors were 0.7322 and 0.3647, respectively. H atoms were refined as rotors riding on the pivot C atoms with a common isotropic thermal factor for all H atoms. The structure was solved and refined by the use of the programs SHELXS-86 and SHELX-76 [36]. Crystals of **4g** were grown at 195 K in the boundary layer of a THF solution of the complex layered with n-hexane. Data were collected at room temperature on a Syntex $P2_1$ diffractometer using graphite monochromator Mo-K_α

Table 4

Fractional coordinates and isotropic temperature factors for **4b** and **4g**

Atom	x	y	z	U(eq)
4b				
V	0.62210(9)	0.72562(5)	0.64422(7)	0.0370(9)
N1	0.7566(4)	0.6396(3)	0.6024(3)	0.042(5)
N2	0.6268(4)	0.6286(3)	0.7497(3)	0.043(5)
C1	0.7635(6)	0.5671(3)	0.6547(5)	0.055(7)
C2	0.6864(6)	0.5411(3)	0.7337(5)	0.055(7)
C3	0.8499(5)	0.6501(3)	0.5253(5)	0.048(6)
C4	0.9874(6)	0.6664(4)	0.5818(5)	0.075(8)
C5	0.8508(6)	0.5769(3)	0.4485(5)	0.065(7)
C6	0.5470(6)	0.6250(4)	0.8442(4)	0.055(7)
C7	0.4544(7)	0.5498(4)	0.8459(5)	0.083(9)
C8	0.6441(7)	0.6284(5)	0.9438(5)	0.085(9)
C9	0.4962(6)	0.7115(3)	0.4804(5)	0.046(6)
C10	0.4193(5)	0.6894(3)	0.5594(5)	0.043(6)
C11	0.4063(5)	0.7607(3)	0.6231(4)	0.041(6)
C12	0.4793(6)	0.8260(3)	0.5833(5)	0.047(6)
C13	0.5321(6)	0.7957(3)	0.4932(5)	0.049(6)
C14	0.5182(7)	0.6564(4)	0.3898(5)	0.071(8)
C15	0.3541(6)	0.6056(3)	0.5670(5)	0.068(8)
C16	0.3141(6)	0.7703(4)	0.7038(5)	0.066(7)
C17	0.4786(7)	0.9170(3)	0.6151(5)	0.066(8)
C18	0.5967(7)	0.8465(4)	0.4155(5)	0.077(9)
C19	0.7600(6)	0.8038(3)	0.6275(5)	0.052(7)
O1	0.8365(5)	0.8567(3)	0.6205(4)	0.081(6)
C20	0.6334(6)	0.7908(4)	0.7705(5)	0.053(6)
O2	0.6407(5)	0.8363(3)	0.8421(3)	0.079(6)
4g				
<i>Molecule 1</i>				
V1	0.0836(1)	0.2061(1)	0.0321(1)	0.053(2)
N1	0.2078(6)	0.2547(4)	0.0976(6)	0.050(9)
N2	0.2265(6)	0.1886(5)	0.1137(6)	0.060(10)
C1	0.2748(8)	0.2977(6)	0.1366(7)	0.066(12)
C2	0.2498(10)	0.3625(6)	0.1203(9)	0.076(14)
C3	0.3249(11)	0.4072(6)	0.1748(10)	0.083(16)
C4	0.3040(18)	0.4699(8)	0.1655(16)	0.136(29)
C5	0.2099(27)	0.4902(12)	0.1034(23)	0.211(50)
C6	0.1358(13)	0.4478(9)	0.0501(12)	0.104(22)
C7	0.1571(10)	0.3852(7)	0.0576(11)	0.091(18)
C8	0.3106(8)	0.1669(6)	0.1722(9)	0.060(13)
C9	0.3268(9)	0.0998(5)	0.1859(8)	0.064(13)
C10	0.4168(11)	0.0814(7)	0.2538(10)	0.088(17)
C11	0.4374(18)	0.0163(10)	0.2686(15)	0.148(30)
C12	0.3661(17)	−0.0274(9)	0.2109(13)	0.113(25)
C13	0.2802(12)	−0.0061(8)	0.1447(15)	0.103(23)
C14	0.2591(11)	0.0557(7)	0.1283(12)	0.096(19)
C15	−0.0692(7)	0.1889(6)	0.0019(7)	0.055(11)
C16	−0.0078(9)	0.1448(6)	0.0741(8)	0.072(13)
C17	0.0546(9)	0.1817(6)	0.1561(8)	0.070(13)
C18	0.0309(7)	0.2437(5)	0.1336(7)	0.053(11)
C19	−0.0434(8)	0.2479(6)	0.0425(9)	0.067(13)
C20	−0.1531(11)	0.1723(8)	−0.0952(11)	0.099(19)
C21	−0.0151(12)	0.0724(6)	0.0619(13)	0.110(20)

Table 4 (continued)

Atom	x	y	z	U(eq)
4g				
<i>Molecule 1</i>				
C22	0.1325(11)	0.1512(9)	0.2505(10)	0.104(20)
C23	0.0794(9)	0.2993(7)	0.2066(9)	0.086(16)
C24	−0.0999(10)	0.3085(5)	−0.0154(12)	0.093(18)
C25	0.0678(9)	0.1382(8)	−0.0553(9)	0.085(16)
O1	0.0520(70)	0.0999(5)	−0.1123(8)	0.101(13)
C26	0.0436(8)	0.2472(6)	−0.0882(9)	0.068(13)
O2	0.0182(7)	0.2711(6)	−0.1617(7)	0.100(13)
<i>Molecule 2</i>				
V2	0.5241(1)	0.7876(1)	0.0743(1)	0.047(2)
N1	0.5895(6)	0.7426(4)	0.2011(5)	0.048(8)
N2	0.6046(7)	0.8055(4)	0.2160(6)	0.061(10)
C1	0.6261(7)	0.6977(5)	0.2621(8)	0.058(11)
C2	0.6075(8)	0.6324(5)	0.2448(9)	0.0709(13)
C3	0.6640(11)	0.5904(7)	0.3191(10)	0.089(17)
C4	0.6521(15)	0.5243(9)	0.3044(21)	0.150(33)
C5	0.5831(19)	0.5042(9)	0.2124(22)	0.140(34)
C6	0.5306(13)	0.5443(8)	0.1381(14)	0.112(23)
C7	0.5424(10)	0.6080(6)	0.1553(9)	0.074(14)
C8	0.6612(7)	0.8295(5)	0.2978(7)	0.050(11)
C9	0.6750(7)	0.8973(5)	0.3098(8)	0.056(11)
C10	0.7394(10)	0.9232(7)	0.3988(11)	0.081(17)
C11	0.7549(12)	0.9871(9)	0.4085(13)	0.107(22)
C12	0.7137(11)	1.0275(7)	0.3263(14)	0.092(19)
C13	0.6471(14)	1.0028(7)	0.2382(13)	0.107(22)
C14	0.6310(10)	0.9377(6)	0.2291(11)	0.082(16)
C15	0.4960(8)	0.8052(6)	−0.0769(6)	0.056(12)
C16	0.5680(8)	0.8466(5)	−0.0151(7)	0.057(11)
C17	0.6528(8)	0.8099(5)	0.0474(7)	0.061(12)
C18	0.6246(9)	0.7434(5)	0.0234(7)	0.060(12)
C19	0.5354(7)	0.7426(4)	−0.0495(7)	0.050(10)
C20	0.4011(10)	0.8211(7)	−0.1586(9)	0.079(15)
C21	0.5658(11)	0.9159(7)	−0.0235(11)	0.091(18)
C22	0.7465(8)	0.8374(9)	0.1212(9)	0.095(20)
C23	0.6982(10)	0.6926(6)	0.0741(8)	0.074(14)
C24	0.4777(11)	0.6795(5)	−0.1005(10)	0.084(16)
C25	0.4382(9)	0.8540(7)	0.0580(9)	0.076(16)
O1	0.3797(7)	0.8948(5)	0.0428(7)	0.099(13)
C26	0.4075(7)	0.7465(6)	0.0363(8)	0.055(11)
O2	0.3278(7)	0.7251(6)	0.0106(7)	0.096(13)

irradiation. Collection of reflections was carried out in the scan range $5^\circ < 2\theta < 50^\circ$. From the observed 5234 reflections, 3412 significant ones ($F > 6\sigma(F)$) were used. Refinement was carried out with 559 parameters to a final R value of 0.093 (see the comment in the first footnote on p. 104).

Preparation of complexes

The same general procedure was employed for the synthesis of all of the complexes, most of which, owing to their lability, were not isolated. **4b**, **4g**–**i** and **7e**

were obtained in the form of micro-crystalline powders and gave satisfactory elemental analyses. A solution of 1 mmol of the parent carbonyl $\text{Cp}'\text{V}(\text{CO})_4$ in 15 ml of THF (orange solution) was cooled in dry ice/ethanol and irradiated for 1 h to generate green $\text{Cp}'\text{V}(\text{CO})_3\text{THF}$. For the irradiation, a high pressure mercury lamp (Philips HPK 125) in a water-cooled quartz immersion-well was used. The lamp was placed in the immediate proximity of a Duran (borosilicate) vessel containing the reaction mixture. The carbon monoxide released during irradiation was pumped off from time to time. A precooled solution of two-fold molar excess of diazadiene in 3 ml of THF was then added, the mixture warmed to the decomposition temperature of the THF complex (240 K for $\text{Cp}' = \text{C}_5\text{H}_5$ and $\text{C}_5\text{H}_4\text{SiMe}_3$, 260–270 K for C_5Me_5) and stirred for several hours to yield red (**1f**; **2f**; **3a–c**; **3e**; **4a**, **b**, **d**, **e**; **1f**; **2f**; **8**), red-violet (**3d**), green (**4j**) or blue (**3g–i**, **4g–i**, **5g–i**) solutions containing the complexes. The solutions were characterized spectroscopically immediately after preparation. They decompose, even when kept at low temperature, within hours to days. For several 1,4-diazadiene complexes, decomposition products can be detected in the ^{51}V NMR by relatively sharp resonances ($W_{1/2}$ ca. 120 Hz) between -338 and -474 ppm.

$\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ and **b** also react directly in the diffuse daylight and at room temperature to form, after several days, **3b**. For the isolation of **4b**, direct irradiation (at 260 K) of a solution in THF of $\text{C}_5\text{Me}_5\text{V}(\text{CO})_4$ and the ligand in a 1/2 molar ratio is the more convenient route, since it gives better yields. The compounds are isolated from the concentrated THF solution by removal of the unchanged parent carbonyl and most of the dad through precipitation with heptane at 195 K, filtration, concentration of the filtrate to a few ml and addition of methanol, again at 195 K. The excess of the ligand remains in the supernatant methanol. Complexes, **4g–i** were obtained similarly by irradiation of $\text{C}_5\text{Me}_5\text{V}(\text{CO})_4$ in the presence of the azine, in the molar ratio 2/1. Treatment with heptane at 245 K selectively precipitated the azine complex in yields of ca. 45%. Use of direct irradiation is restricted to the examples noted here. Analysis: **4b** Found: C, 62.7; H, 8.3; N, 7.1; V, 13.3. $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}_2\text{V}$ (382.42) calcd.: C, 62.82; H, 8.17; N, 7.33; V, 13.32%. **4g** Found: C, 69.7; H, 6.0; N, 7.1; V, 11.2. $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_2\text{V}$ (450.46) calcd.: C, 69.33; H, 6.04; N, 6.22; V, 11.31%.

A procedure analogous to that described for the cyclopentadienyl complexes was applied to the preparation of the complexes derived from $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$. Irradiation of the yellow solution yielded the red $[\text{Et}_4\text{N}][\text{V}(\text{CO})_5\text{THF}]$, which reacts with diazadienes at 200–210 K to form red (**7d**, **e**, **6f**) or blue (**7g**) complexes. In the case of **7e**, red $[\text{Et}_4\text{N}]\text{-7e}$ begins to separate out during the reaction. The mixture was kept overnight at 270 K and the product then filtered off, washed with three 2 ml portions of THF, and recrystallized from pyridine/diethylether as red needles. Yield: 35%. Analysis: Found: C, 59.6; H, 6.5; N, 7.6; V, 9.1. $\text{C}_{28}\text{H}_{36}\text{N}_3\text{O}_6\text{V}$ (561.55) calcd.: C, 59.89; H, 6.46; N, 7.48; V, 9.07%.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (grant Re 431/6-3) and the Fonds der Chemischen Industrie.

References

- 1 J.C. Dobson and H. Taube, *Inorg. Chem.*, 28 (1989) 1310.
- 2 P. Chandrasekhar and P.H. Bird, *Inorg. Chim. Acta*, 97 (1985) L31.
- 3 S. Herzog and R. Taube, *Naturwissenschaften*, 43 (1956) 349.
- 4 H. Brunner and W.A. Herrmann, *Z. Naturforsch.*, 26b (1973) 606.
- 5 S. Gambarotta, A. Chiesi-Villa, and C. Guastine, *Inorg. Chem.*, 27 (1988) 99.
- 6 (a) M. Hoch and D. Rehder, *Inorg. Chem. Acta* 115 (1986) L24. (b) *Chem. Ber.*, 121 (1988) 1541. (c) M. Hoch, A. Duch and D. Rehder, *Inorg. Chem.*, 25 (1986) 2907.
- 7 C. Woitha and D. Rehder, *J. Organomet. Chem.*, 353 (1988) 315.
- 8 G. Kreisel and W. Seidel, *Z. Chem.*, 25 (1985) 101.
- 9 F. Nümann and D. Rehder, *Z. Naturforsch.*, 39b (1984) 1654.
- 10 K. Ihmels and D. Rehder, *Organometallics*, 4 (1985) 1340.
- 11 F.J. Wells, G. Wilkinson, M. Montevalli, and M.B. Hursthouse, *Polyhedron*, 6 (1987) 1351.
- 12 J. Mason, *Chem. Rev.*, 87 (1987) 1299.
- 13 (a) H. tom Dieck, C. Munz, and J. Ehlers, in H. Werner and E. Erker (Eds.), *Organometallics in Organic Synthesis 2*, Springer-Verlag, Berlin, 1989, p. 21. (b) M. Brockmann, H. tom Dieck, and I. Kleinwächter, *J. Organomet. Chem.*, 309 (1986) 345. (c) H. tom Dieck, A.M. Lauer, L. Stamp, and R. Diercks, *J. Molec. Catal.*, 35 (1986) 317. (d) M. Mallien, E.T.K. Haupt, and H. tom Dieck, *Angew. Chem.*, 100 (1988) 1091; *Angew. Chem. Int. Ed. Engl.* 27 (1988) 1062. (e) H. tom Dieck, M. Mallien, and R. Diercks, *J. Molec. Catal.*, 51 (1989) 53.
- 14 (a) K. Vrieze, *J. Organomet. Chem.* 300 (1986) 307. (b) G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 21 (1982) 151.
- 15 M.N. Mookerjee, R.V. Singh, and J.P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, 15 (1985) 13.
- 16 M. Hoch and D. Rehder, *J. Organomet. Chem.*, 288 (1985) C25.
- 17 L.N. Lewis and K.G. Caulton, *Inorg. Chem.*, 19 (1990) 1840.
- 18 K. Ihmels and D. Rehder, *Chem. Ber.*, 118 (1985) 895.
- 19 L.N. Lewis and K.G. Caulton, *J. Organomet. Chem.*, 252 (1983) 57.
- 20 K.-J. Jens and E. Weiss, *Chem. Ber.*, 117 (1984) 2469.
- 21 H.G. Alt, H.E. Engelhardt, A. Razavi, M.D. Rausch, and R.D. Rogers, *Z. Naturforsch.*, 43b (1988) 438.
- 22 A. Duch, M. Hoch, and D. Rehder, *Chimia*, 42 (1988) 179. The reaction between $\text{Me}_3\text{SiC}_5\text{H}_5$ and $\text{V}(\text{CO})_6$ yields an approximately equimolar mixture of $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ and $\text{Me}_3\text{SiC}_5\text{H}_4\text{V}(\text{CO})_4$. $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ can be removed almost quantitatively by fractional recrystallization from THF/heptane at ca. 200 K.
- 23 (a) D. Rehder, *J. Magn. Reson.*, 38 (1980) 419; (b) *idem*, *Magn. Reson. Rev.*, 9 (1984) 125.
- 24 H.G. Alt and H.E. Engelhardt, *Z. Naturforsch.*, 40b (1965) 1134.
- 25 (a) D. Rehder, in J. Mason (Ed.), *Multinuclear NMR*, Plenum Press, New York 1987, ch. 19. (b) D. Rehder, *Chimia* 40 (1986) 186.
- 26 (a) D. Wenke, K. Ihmels, P. Oltmanns, and D. Rehder, *Inorg. Chim. Acta*, 100 (1985) L11. (b) R. Talay and D. Rehder, *ibid.*, 77 (1983) L175.
- 27 (a) Additional data for **4b**: $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}_2\text{V}$, $M = 38.42$ g/mol; $a = 1025.1(1)$, $b = 1599.2(1)$, $c = 1283.2(1)$ pm, $\beta = 97.86(1)^\circ$, $Z = 4$, $V = 2083.8 \times 10^6$ pm³, $\rho(\text{calcd}) = 1.22$ kg/l, $\mu = 40$ cm⁻¹. (b) Additional data for **4g**: $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_2\text{V}$, $M = 450.45$ g/mol, $a = 1577.9(8)$, $b = 2131.6(9)$, $c = 1585.4(8)$ pm, $\beta = 118.46(4)^\circ$, $Z = 8$, $V = 4688.0 \times 10^6$ pm³, $\rho(\text{calcd}) = 1.28$ kg/l, $\mu = 4$ cm⁻¹.
- 28 H.W. Frühauf and G. Wolnershäuser, *Chem. Ber.*, 115 (1982) 1070.
- 29 B. Hessen, J.E. Bol, J.L. de Boer, A. Meetsma, and J.H. Teuben, *J. Chem. Soc., Chem. Commun.*, (1989) 1276.
- 30 For examples, see Refs. 5, 6b and 21, and references cited therein.
- 31 F. Calderazzo and G. Pampaloni, *J. Organomet. Chem.*, 250 (1983) C33.
- 32 H. tom Dieck and I.W. Renk, *Chem. Ber.*, 104 (1971) 92.
- 33 M. Kliegmann and R.K. Barnes, *J. Org. Chem.*, 35 (1970) 3140.
- 34 E. Müller (Ed.), *Methoden der Organischen Chemie*, vol. 10/2, Georg Thieme Verlag, Stuttgart, 1967, p. 91.
- 35 C.J. Jameson, D. Rehder, and M. Hoch, *J. Am. Chem. Soc.*, 109 (1987) 2589.
- 36 (a) G.M. Sheldrick, *Program for Crystal Structure Determination*, Cambridge, 1976. (b) *Program for Crystal Structure Solutions*, Göttingen, 1986.