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Hydrazine derivatives of ring-substituted tetracarbonyl-*h*^{5}-cyclopentadienylvanadium complexes

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Abstract

The complexes h^5-Cp′V(CO)$_3$(hydrazine′) (Cp′ = C_5H_5, C_5Me_5, 1,2- and 1,3-C_5H_3(Me)cetyl, $C_5H_4SiMe_3$, and indenyl; hydrazine′ = N_2H_4, N_2H_3Me, H_2NMe_2, H(Me)NN(Me)H, and N_2H_3Ph), containing the hydrazine′ ligand in the mono-hapto mode, have been prepared via the precursors Cp′V(CO)$_3$(thf) and characterized by their IR, ^1H, and ^{51}V NMR spectra. The V-hydrazine′ moiety is rigid on the NMR time scale. Coordination of the NH_2 group is preferred, but for Cp′ = $C_5H_4SiMe_3$ and C_5H_3(Me)cetyl, and hydrazine′ = H_2NNHPh, the ligand bonds to about equal extents through NH_2 and NHPh. $\delta(^{51}V)$ values, typically between −620 and −690 ppm (relative to $VOCl_3$) lie between those for amine and nitrile derivatives, reflecting the intermediate basicity of the hydrazines.

Introduction

A variety of carbonyl-hydrazine complexes of the transition metals following the elements of the vanadium triad have been described previously, among them $M(CO)_5N_2H_4$ (M = Cr, Mo, W) [1], $C_5H_5M'(CO)_2N_2H_4$ (M′ = Mn, Re) [1,2] and $[M(CO)_5]_2$-μ-N_2H_4 [3,4]. Hydrazine complexes are of interest in respect of oxidation and reduction reactions, which yield respectively, dinitrogen complexes and complexes containing the NH_3 ligand. Examples of oxidation products are $C_5H_5Mn(CO)_2N_2$ (from $C_5H_5Mn(CO)_2N_2H_3Me$ [4]) and $[Cr(CO)_5]_2$-μ-N_2H_2 (from the dinuclear N_2H_4 precursor [5]). The complete redox series has been reported for the complexes $C_5H_5Re(CO)_2L$ with L = N_2, N_2H_2, and NH_3 [6]. Hydrazine is a probable intermediate in the in vivo reduction of N_2 to NH_3 in nitrogen fixation; hydrazine complexes may therefore be regarded as models for some of the functional aspects of the cofactor in nitrogenase, as exemplified by the various functional models which have been established for the molybdenum nitrogenase and which contain molybdenum in a low oxidation state. Since the discovery of the role of vanadium in nitrogen fixation [7], and the isolation of a vanadium-dependent

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nitrogenase from special strains of *Azotobacter chroococcum* and *A. vinelandii* [8], only two complexes of low-valent vanadium relevant to the problem of N_2 reduction have been reported, viz. $[V(CO)_5L]^-$, where $L = NH_3$ [9,10] and h^1-N_2 [11].

In this first account of the previously unknown hydrazine complexes $Cp'V(CO)_3$(hydrazine′), we focus on the preparation and characterization of these half-sandwich complexes, with special attention to achieving optimal stability at room temperature through variations in the hydrazine′ and cyclopentadienyl ligands. We have shown earlier that the complexes $C_5H_5V(CO)_4\{N\}$ are thermolabile if $\{N\}$ is a monodentate amine [12].

Results and discussion

The precursors $Cp'V(CO)_3thf$

These were obtained by UV irradiation of $Cp'V(CO)_4$ at dry-ice temperature (a general high yield synthesis for the tetracarbonyls has recently been described [13,14]). The green solutions decompose at elevated temperature, i.e. the complexes are less stable than the well known $C_5H_5Nb(CO)_3thf$ and $C_5H_5Ta(CO)_3thf$ [15], and $C_5H_5V(CO)_3$(tetrahydrothiophene) [16], but more stable than the parent compound $C_5H_5V(CO)_3thf$ [12,17]. Decomposition temperatures, together with CO stretching frequencies and $\delta(^{51}V)$ values for selected examples, are given in Table 1a and 1b. The decomposition products are $Cp'_2V_2(CO)_5$ and $Cp'V(CO)_4$, and the typical change in the IR spectrum as the temperature is gradually increased is shown for $C_5Me_5V(CO)_3$(2-Me-thf) and its decomposition products in Fig. 1. The 2-methyltetrahydrofuran derivatives of all of the other cyclopentadienyl complexes are very unstable, and have not been characterized even at 195 K. No complexation is observed when $C_5Me_5V(CO)_4$ is irradiated in 2,5-dimethyltetrahydrofuran.

The hydrazine′ complexes

The tricarbonylhydrazine′ complexes of vanadium were prepared by addition of an excess of the hydrazine′ to thf solutions of the thf-containing precursors in the cold. The thf/hydrazine′ exchange, which takes place at ca. 240–250 K, is accompanied by a colour change from green to dark-red. The solutions of the complexes decompose during several days even at low temperature; the red powders ($C_5Me_5V(CO)_3$hydrazine′) or oils ([1,2-/1,3-C_5H_3(Me)-cetyl]$V(CO)_3$(hydrazine′)),

Table 1a

Data for selected complexes $Cp'V(CO)_3thf$

Complex	Decomposition above [a]	$\nu(CO)$ [b] (cm^{-1})
$C_5H_5V(CO)_3thf$	220	1950 1835
$C_5Me_5V(CO)_3$(2-Me-thf) [c]	230	1940 1830
$IndV(CO)_3thf$	250	1955 1850
$C_5H_4SiMe_3V(CO)_3thf$	260	1960 1855
C_5H_3Me(cetyl)$V(CO)_3thf$	260	1945 1835
$C_5Me_5V(CO)_3thf$	270	1937 1820

[a] Approximate decomposition temperature (K); by IR. [b] The first band ($A'^{(1)}$) is m-s, the second band ($A'^{(2)} + A''$) vs and broad. [c] Cf. also Fig. 1.

Table 1b

$\delta(^{51}V)$ values (ppm relative to $VOCl_3$) for $C_5Me_5V(CO)_3$ solv and its decomposition products

Complex	Solvent			
	thf	2-Me-thf	2,5-Me_2-thf	n-hexane
$C_5Me_5V(CO)_3$solv	−317	−297	–	–
$C_5Me_5V(CO)_4$	−1525	−1518	−1512	−1478
$(C_5Me_5)_2V_2(CO)_5$	−1826	−1807	[a]	−1797

[a] Not observed.

which can be isolated by precipitation with heptane or by cooling the solutions to 195 K, are stable for several weeks when stored under argon in the cold. The maximum stability is observed for hydrazine′ = N_2H_4, and Cp′ = C_5Me_5 or C_5H_3(Me)cetyl. IndenylV$(CO)_4$ and $C_5H_5V(CO)_4$ do not form stable hydrazine′ complexes, and the presence of N_2H_3Ph also leads to substantial instability. 1,1-Diphenylhydrazine does not react at all. Spectral data of the complexes are collated in Tables 2 (IR) and 3 (NMR).

The IR spectra in solution exhibit two bands in the CO stretching region which are assigned to the $A'^{(1)}$ (ca. 1935 cm^{-1}) and the $A'^{(2)} + A''$ mode (ca. 1830 cm^{-1}). In Nujol, the latter is split (cf. Table 2). For hydrazines ligands containing an NH_2 moiety, a typical $\delta(NH_2)$ near 1600 cm^{-1} is observed. The NH stretching region (3400 to 3100) is comparable to that of hydrazine itself [18], and hydrazine complexes of other transition metals such as $C_5H_5Mn(CO)_2$(hydrazine) [1,19].

The ^1H NMR spectra show one (H_2N–NMe_2) or two typically broadened (^{14}N relaxation) and usually unstructured resonances for the hydrazine protons, with a deshielding of 1.5 to 1.9 ppm for the signal belonging to the HN coordinated to vanadium. The exchange between the inequivalent protons observed in unsymmetrically substituted free hydrazines [20] is suppressed by complexation. In the case of methylhydrazine and 1,1-dimethylhydrazine, the ^1H NMR pattern clearly shows that coordination occurs via the NH_2 moiety, a conclusion supported by the ^{51}V NMR spectra (vide infra). This mode of coordination has also been verified by an

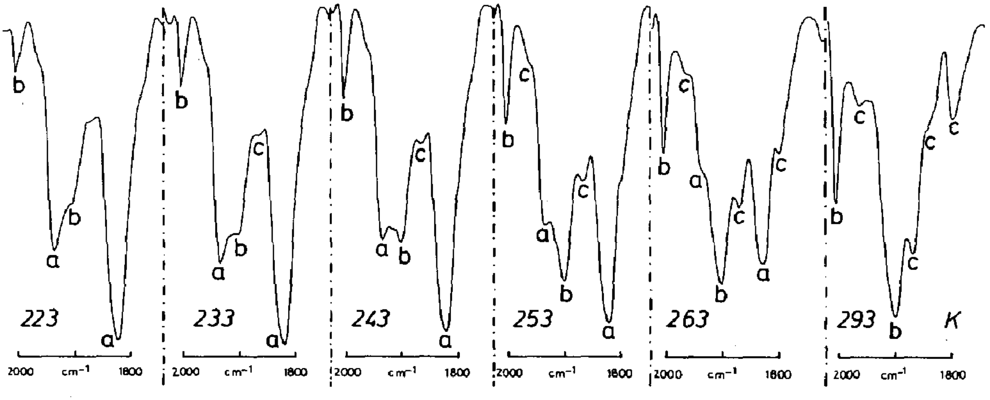

Fig. 1. The change in the CO stretching region in the IR spectrum of $C_5Me_5V(CO)_3$(2-Me-thf) (a) with increase in temperature, showing the formation of the decomposition products $C_5Me_5V(CO)_4$ (b) and $(C_5Me_5)_2V_2(CO)_5$ (c).

Table 2

IR data for selected complexes $Cp'V(CO)_3$(hydrazine')

Complex		ν(CO)/THF (cm^{-1}) [a]	IR data/nujol (cm^{-1})		
Cp'	Hydrazine'		ν(CO) [b]	ν(NH) [c]	$\delta(NH_2)$
C_5Me_5	N_2H_4 [d]	1933 1825	1938 1832 1805	3375 3320 3240 3170	1595
	N_2H_3Me	1934 1825	1929 1824 18032	3355 3280 3165	1601
	NH_2NMe_2	1935 1855	1936 1850 1832	3315 3125	1585
	NHMeNHMe	1933 1827	1932 1852 1837	3340 3210	
	N_2H_3Ph	1936 1833			
Indenyl	N_2H_4	1953 1857 [e]			
C_5MeH_3cetyl	N_2H_4	1945 1835			
$C_5(SiMe_3)H_4$	N_2H_4	1950 1840			

[a] The relative intensities are m-s and vs. [b] Intensities (from left to right): s, vs, vs. [c] Intensities (from left to right): m, s, w, m for $C_5Me_5V(CO)_3N_2H_4$; fairly similar intensities for the other hydrazine' complexes. [d] Compare N_2H_4 (from ref. 18): 3350, 3325, 3314 and 3280 cm^{-1} (in the gaseous phase). [e] Shoulder at 1845 cm^{-1}.

Table 3

NMR data on the complexes $Cp'V(CO)_3$(hydrazine')

Complex		^{51}V NMR		^1H
Cp'	Hydrazine'	δ [a] (ppm)	$W_{1/2}$ (Hz)	δ [b] (ppm)
C_5Me_5	N_2H_4	−680	160	4.45(VN*H*) 2.93(N*H*) 1.82(C*H*)
	N_2H_3Me	−687	170	4.35(VN*H*) 2.51(N*H*) 2.44(NC*H*) 1.81(CC*H*)
	NH_2NMe_2	−623	185	4.11(VN*H*) 2.26(NC*H*) 1.79(CC*H*)
	NHMeNHMe	−570	170	4.45(VN*H*) 2.70(N*H*) 1.83(CC*H*) 2.42 [c](VNC*H*) 2.31 [d](NNC*H*)
	N_2H_3Ph	−649	240	
Indenyl	N_2H_3Me	−507	160	
C_5MeH_3cetyl [e]	N_2H_4	−676, −679	300	
	N_2H_3Me	−680, −684	300	
	N_2H_3Ph [f]	−640, −649	400	
		−713, −716	200	
$C_5(SiMe_3)H_4$	N_2H_4	−661	300	4.54(VN*H*) 3.03(N*H*) 0.10(SiC*H*) 5.50/4.91 (Cp-*H*)
	N_2H_3Me	−664	250	
	N_2H_3Ph [f]	−620	300	
		−692	150	
C_5H_5	N_2H_4	−679	160	
	N_2H_3Me	−682	160	
	N_2H_3Ph	−641	250	

[a] Relative to $VOCl_3$ at 300 to 303 K in THF solution. [b] All signals appear as singlets (broad resonances for the hydrogens attached to N), except for $C_5Me_5V(CO)_3$NHMeNHMe, for which the methyl protons of the hydrazine ligand are doublets (footnotes c and d and Fig. 2). [c] Coupling constant $^3J(CH{-}NH)$ 6.0 Hz. [d] $^3J(CH{-}NH)$ 5.4 Hz. [e] The first (low-field) δ value is for the 1,2-, the second for the 1,3-isomer. [f] The broader low-field signals are tentatively assigned to the NH_2-bound isomer(s) (see text).

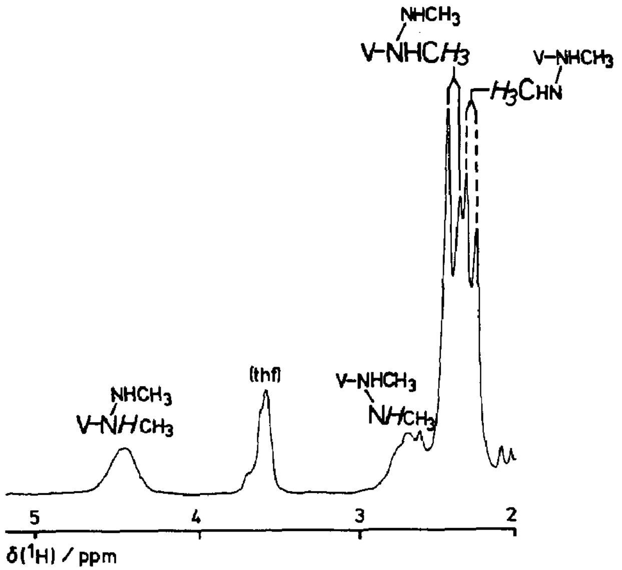

Fig. 2. Signals from the hydrazine′ ligand in the 80 MHz ^{1}H NMR spectrum of $C_5Me_5V(CO)_3$ NHMeNHMe (thf-d_8, 260 K).

X-ray structure study of $[Ru(PPh_3)(dibenzotetrathiadecane)NH_2NHMe]^{2-}$ [21]. $C_5Me_5V(CO)_3NHMeNHMe$ is a special case in as far as the ^{1}H resonance for the NHMe not coordinated to vanadium shows a partly resolved coupling of the proton on nitrogen to the methyl protons (Fig. 2). The two methyl groups are represented in the spectrum by doublets; the coupling constants $^3J(^1HN-^1HC)$ (5.4 and 6.0 Hz) are fairly similar to those for $W(CO)_5NHMeNHPh$ [22].

^{51}V NMR spectra

The ^{51}V NMR signals of all of the hydrazine complexes are surprisingly sharp for a complex of local C_s symmetry containing a sterically demanding cyclopentadienyl ligand, and this behaviour is in common with the parent tetracarbonyl complexes $Cp'V(CO)_4$ [13]. Akitt [23] has shown that the field gradient at a quadrupolar nucleus such as vanadium (nuclear spin = 7/2, quadrupole moment = -0.052×10^{-28}) vanishes, if the two ligand systems (C_5H_5 and $(CO)_4$) are arranged in such a way that their cone angles at the vanadium centre are equal to the magic angle. Electronic imbalances in the ligand systems, e.g. those generated by the replacement of a CO for a nitrogen ligand, can be counteracted by deviations from this geometry. A field gradient close to zero drastically diminishes the otherwise very effective quadrupole relaxation. Effective quadrupole relaxation, and hence rather broad lines, are observed in the ^{51}V NMR spectra of the thf precursors (Table 1b).

The shielding of the ^{51}V nucleus, and hence the chemical shift $\delta(^{51}V)$, are mainly determined by direct electronic effects, viz. the basicity (polarizability, electronegativity) and π-acidity of the ligands [24,25]. Secondary (electronic and steric) effects arise from substituents on the ligands [24,26]. In the d^4-systems investigated here, both hard ligands and bulky ligands give rise to deshielding effects. Thus, the $\delta(^{51}V)$ values for $Cp'V(CO)_3thf$ are near −300 ppm (Table 1b; $\delta[C_5H_5V(CO)_4]$ −1534 ppm). For $C_5H_5V(CO)_3\{N\}$, values of −430 (aliphatic amines), −496 (aniline), −520 (pyridine), −650 (imidazoles), −700 (NCS-) and −725 (nitriles) have been reported [12]. The $\delta(^{51}V)$ values for {N} = hydrazine′ (−641 to −682, Table 3) lie in the expected range between the better σ-donating amines and the better π-accepting nitriles. This is also the case for the hydrazine′ derivatives of the ring-substituted Cp′V(CO)$_4$, while the ^{51}V nucleus is substantially deshielded in indenyl-V(CO)$_3$N$_2$H$_3$Me (δ −507 ppm) as a consequence of the electron-withdrawing effect of the anellated six-membered ring, and in accord with the difference in shielding between $C_5H_5V(CO)_4$ and indenyl-V(CO)$_4$ [13].

The similarity of the $\delta(^{51}V)$ values of, e.g. the complexes $C_5Me_5V(CO)_3N_2H_4$ and $C_5Me_5V(CO)_3N_2H_3Me$, suggests coordination via the NH_2 group of the latter, the coordination mode already postulated on the basis of the proton NMR spectra. The increase in the basicity of the hydrazine caused by a second methyl substituent plus the increased steric crowding at the metal centre in $C_5H_5V(CO)_3NHMeNHMe$ induce a deshielding of 110 ppm. The decrease of shielding in $C_5Me_5V(CO)_3N_2H_3Ph$ appears to reflect a more distant steric effect produced by the phenyl group. In the case of the complexes C_5H_3(Me)cetyl-V(CO)$_3$N$_2$H$_3$Ph, the ^{51}V resonances are doublets, indicating the presence of virtually equal amounts of the 1,2- and 1,3-isomers of the Cp′ ligand (cf. Fig. 3), with the sterically more demanding 1,2-isomer probably giving the low-field component(s). When the H_2N–NHPh is present, two doublets (Fig. 3) arise from the isomers in which either the NH_2 or the NHPh centres are coordinated. Following the above arguments, the highfield signal, which accounts for about 40% of the overall intensity, is assigned to the isomer in which coordination is through the less basic nitrogen bearing the phenyl group. Similarly, we assign the two signals observed for the cyclopentadienylsilyl complexes to the NH_2 (−620 ppm) and the NHPh-bound isomer (−692 ppm; 20% of the integral intensity).

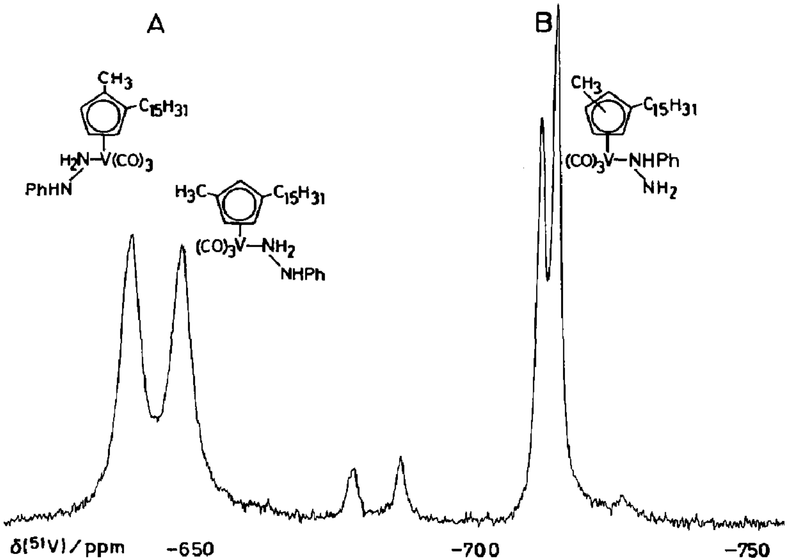

Fig. 3. 94.7 MHz ^{51}V NMR spectrum of the various isomers of C_5H_3(Me)cetyl-V(CO)$_3$NH$_2$NHPh (thf/thf-d_8 2/1, 303 K). Assignments are tentative (see the discussion in the text). The ratio A/B is 1.7/1. The origins of the small signals at −678 and −686 ppm are unknown.

Experimental

General and spectra

All operations were carried out in highly purified, oxygen-free solvents under argon. UV irradiations were carried out with a high pressure mercury lamp (Philips HPK 125) fitted into a cooled immersion well (Solidex glass ware; Mangels, Bonn) and placed close to the Duran vessel (cooled by a dry-ice/ethanol mixture) containing the reactants. Effective cooling of the lamp was achieved with methylcyclohexane from a cryostat. Commercially available hydrazine chlorides were converted into the free hydrazines by treatment with NH_3 in ether suspension and used after removal of the ether in vacuo. N_2H_4 was employed in the form of its hydrate. The starting compounds $Cp'V(CO)_4$ were prepared from $V(CO)_6$ and $Cp'H$ as descibed in the literature ([13] and, for $Cp' = Me_3SiC_5H_4V(CO)_4$) as in ref. 14). The silyl complex contains varying amounts of $C_5H_5V(CO)_4$.

IR spectra were recorded on a Perkin–Elmer 325 spectrometer in Nujol mulls, or as ca. 0.02 *M* solutions in 0.1 mm KBr cuvettes. For low-temperature spectra, a low temperature unit Beckmann VLT-2 RIIC fitted with internal ZnS (Intran) and external electrically-heated NaCl windows was employed; this allows charging of the cell under an inert gas atmosphere after cooling with dry-ice/ethanol, and subsequent gradual warming-up with cell heating. Temperatures were measured with a thermocouple. ^1H NMR spectra were recorded for thf-d_8 solutions on a Bruker WP 80 spectrometer, and shifts are relative to internal TMS. ^{51}V NMR spectra were recorded at 94.7 MHz on a Bruker AM 360 spectrometer by use of 10 mm diameter vials containing solutions in thf/thf-d_8 2/1. Typical measuring parameters: Pulse angle 45°, sweep width 100 kHz, 16 K data set (digital resolution 12.2 Hz/point), number of scans 2000, line broadening factor 10 Hz. All shifts, $\delta(^{51}V)$, are relative to external $VOCl_3/CDCl_3$, and were corrected for thf-d_8/$CDCl_3$. The spectra were recorded at 300 ± 1 K (the temperature was thermostatically controlled to avoid line broadening due to temperature fluctuation: the shift-temperature gradient for this type of complexes is -0.6 to -1.0 ppm/deg [27]).

Preparation of complexes

In a typical experiment, a solution of 400 mg (1.34 mmol) of $C_5Me_5V(CO)_4$ dissolved in 20 ml of thf was irradiated at 195 K (dry-ice/ethanol) for 90 min. The dark-green thf solution of $C_5Me_5V(CO)_3$thf thus generated was treated at 195 K with 0.12 ml (2.7 mmol) of methylhydrazine (N_2H_3Me), and the mixture was kept at 250 K for 12 h. The red solution, containing the hydrazine complex $C_5Me_5V(CO)_3N_2H_3Me$, was then concentrated to 1 ml at 273 K and treated with 70 ml of n-hexane. During this treatment, the product began to separate out, and precipitation was completed by cooling the reaction mixture to 195 K. The precipitate was filtered off, washed four times with 5 ml portions of pre-cooled (195 K) n-hexane, and dried for 2 h under high vacuum. Yield 200 mg (47%) of a light-red, micro-crystalline powder. Analysis: Found: C, 52.9; H, 7.1; N, 8.8; V, 16.3. $C_{14}H_{21}N_2O_3V$ (316.27) calcd.: C, 53.17; H, 6.69; N, 8.86; V, 16.11%.

Other complexes were prepared similarly in yields of ca. 50%. $C_5Me_5V(CO)_3N_2H_4$ and $C_5Me_5V(CO)_3NH_2NMe_2$ were obtained as red-violet powders, and C_5Me_5V-$(CO)_3$NHMeNHMe was almost black. The complexes with $Cp' = 1,2$- or $1,3$-C_5H_3-

(Me)cetyl were isolated as red viscous oils. The complexes indenyl-V(CO)$_3$(hydrazine′) and $C_5H_5V(CO)_3$(hydrazine′) were not isolated owing to their lability even in the cold. $C_5H_4SiMe_3V(CO)_3$(hydrazine) was obtained as a red powder.

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