Reactivity of bis(η⁶-arene) derivatives of titanium, vanadium and niobium with fulvenes bearing electron-withdrawing substituents

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Abstract

The reaction of $M(\eta^6\text{-arene})_2$ (M = Ti, arene = MeC_6H_5; M = V, Nb, arene = $1,3,5\text{-Me}_3C_6H_3$) with "pentacarbomethoxycyclopentadiene" (pcmcpH), 1-benzoyl-6-hydroxy-6-phenyl fulvene (dbcpH), and 1-benzoyl-3-nitro-6-hydroxy-6-phenyl fulvene (dbncpH) proceeds with evolution of dihydrogen and oxidation of the metal to coordination compounds containing O,O'-coordinated cyclopentadienyl anions, i.e., $[pcmcp]^-$, $[dbcp]^-$, and $[dbncp]^-$, respectively. Complexes of general formula $M(O,O'\text{-anion})_3$, where the metal is in the +III oxidation state, have been isolated for titanium and niobium. In the case of vanadium, different compounds have been obtained depending on the fulvene and the reaction conditions. In particular, solvated derivatives of vanadium(II) of general formula $V(O,O'\text{-anion})_2(THF)_2$ have been prepared in THF whereas $V(O,O'\text{-anion})_2$ complexes have been isolated in toluene even in the presence of excess fulvene.
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1. Introduction

Since many years, cyclopentadienyl chemistry has been keeping a leading role in synthetic organometallic chemistry, one of the reasons being probably the fact that the C_5 ring can achieve different coordination modes (η^5, η^4, η^3, η^1) adapting itself to the electronic situation of the metal; its electronic and steric properties can be modulated by suitable tuning of the ring substituents. In particular, the proton acidity of the parent diene can be varied in a very broad span [1], up to reaching the extreme case in which the proton is no longer on the ring system. As a matter of fact, if the substituents carry one or more oxygen atoms, the proton can be located on the oxygen atoms themselves, thus actually transforming the cyclopentadiene into a fulvene derivative (Chart 1). The proton acidity reaches its maximum when the proton is no more bonded to any carbon atom (Chart 2). Moreover, the loss of the hydroxyl proton (as either H^+ or H_2) causes a rearrangement of the fulvene to an aromatic five-membered π-system with a cyclopentadienyl core (Chart 3), the acidic and the oxidizing properties of the fulvene will be enhanced.

Literature shows that $[pcmcp]^-$, the anion of the so-called "pentacarbomethoxycyclopentadiene" (Chart 3), has been widely used as a ligand for many elements of the Periodic Table [2,6], but the synthetic routes mainly consist of metathetical reactions, see the following equation:

$$MX_n + n\, M'(pcmcp) \rightarrow M(pcmcp)_n + n\, M'X \quad (1)$$
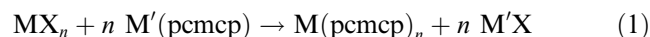
* Corresponding author. Tel.: +39 50 2219 219; fax: +39 50 2219 246.
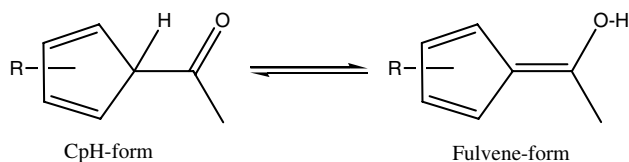*E-mail address:* pampa@dcci.unipi.it (G. Pampaloni).

Chart 1. Equilibrium between the cyclopentadiene and the fulvene forms of an oxygen-containing group substituted cyclopentadiene.
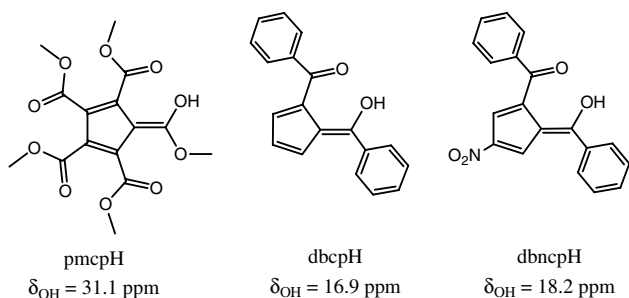

pmcpH
$\delta_{OH} = 31.1$ ppm

dbcpH
$\delta_{OH} = 16.9$ ppm

dbncpH
$\delta_{OH} = 18.2$ ppm

Chart 2. Chemical structures and ^{1}H NMR chemical shifts (δ_H) of the hydroxyl protons of pcmcpH [2,3], dbcpH [4] and dbncpH [5] in CCl$_4$.

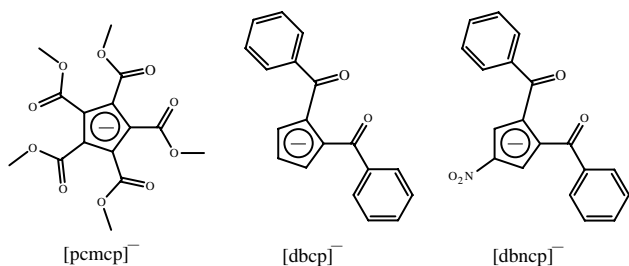

[pcmcp]$^-$

[dbcp]$^-$

[dbncp]$^-$

Chart 3. Cyclopentadienyl anions derived from pcmcpH, dbcpH and dbncpH by loss of the oxygen-bonded proton.

where M is the transition or main groups elements; X = [C$_5$H$_5$]$^-$, [C$_5$Me$_5$]$^-$, OH$^-$, acetate, carbonate; and M′ = H, K, Tl.

Redox processes have been observed in the reaction of [RuCpH(PPh$_3$)$_2$] with pcmcpH to give the ruthenium(IV) dihydride [RuCp(H)$_2$(PPh$_3$)$_2$][pcmcp] [6g], via a H$^+ \rightarrow$ H$^-$ two-electron reduction. A M(II) $\rightarrow$ M(III) oxidation with H$_2$ evolution is observed in the reaction of M$_2$(CH$_3$COO)$_4$, M = Cr, Rh, with pcmcpH, the products being Cr(pcmcp)$_3$ [6c] or the rhodium(III) sandwich derivative [Rh(η^5-C$_5$H$_2$(COOMe)$_3$)$_2$][pcmcp] [6i].

As far as the other fulvenes reported in Chart 1 are concerned, virtually no chemistry is reported in the literature, except for their synthesis [4] and the crystal structures of both the toluoyl analogue of dbcpH [7] and the nitro substituted derivative dbncpH [5]. Only one metal complex is known with these ligands namely, the ruthenium(II) derivative Ru(η^5-C$_5$Me$_5$)(η^5-dbcp) [8].

The recent isolation of Group 6 species of general formula [M(η^6-MeC$_6$H$_5$)$_2$][Anion] (M = Cr, Anion = [pcmcp]$^-$, [dbcp]$^-$, [dbncp]$^-$ [9]; M = Mo, Anion =
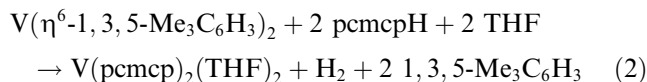
[pcmcp]$^-$ [10]) by reaction of M(η^6-MeC$_6$H$_5$)$_2$ with the fulvenes reported in Chart 1, prompted us to extend our research to the elements of Groups 4 and 5. Elements of these groups show higher lability of the metal-bonded arene ligands and higher oxophilicity with respect to the Group 6 analogues; hence, a redox reaction with arene displacement was expected. In this paper we will confirm this hypothesis with the isolation and characterization of species of general formulae ML$_n$, M = Ti, V, Nb; L = [pcmcp]$^-$, [dbcp]$^-$, [dbncp]$^-$ anions.

2. Results and discussion

2.1. Synthesis and characterization

2.1.1. "Pentacarbomethoxycyclopentadiene" (pcmcpH)

The reaction between V(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ and pcmcpH in THF is fast. Due to the limited solubility of the product in THF a slight cloudiness is observed about 15 min after reagents mixing. Oxidation of the metal substrate does not go beyond the +II state and the final result is a brick-red vanadium(II) derivative which analyzes correctly for the bis-O,O'-chelate V(pcmcp)$_2$(THF)$_2$, see the following equation:

$$V(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2 + 2 \text{ pcmcpH} + 2 \text{ THF}$$
$$\rightarrow V(\text{pcmcp})_2(\text{THF})_2 + H_2 + 2 \ 1,3,5\text{-}Me_3C_6H_3 \quad (2)$$

The IR spectrum of the compound shows absorption bands typical of the O,O'-bidentate coordination of the [pcmcp]$^-$ ligand (Table 1), with strong signals due to the stretching of the C=O and C–OMe bonds of the coordinated and uncoordinated ester functionalities. The presence of coordinated THF is indicated by the absorptions at 1045 and 903 cm^{-1}, which are not observed for the compound obtained when the reaction is carried out in toluene, vide infra. Coordination at vanadium occurs by means of four oxygen atoms from two pairs of chelating ester groups of two [pcmcp]$^-$ anions and two oxygen atoms from THF, which most likely adopt a *trans* disposition as reported for MeOH in the structurally characterized M(pcmcp)$_2$(MeOH)$_2$, M = Fe, Cu [6f].

When the reaction between V(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ and pcmcpH was carried out in toluene the unsolvated vanadium(II) derivative V(pcmcp)$_2$ was obtained.

X-band EPR spectroscopy of V(pcmcp)$_2$(THF)$_2$ and V(pcmcp)$_2$ in either fluid or frozen THF solution did not reveal signals ascribable to V(II) species, but spectra typical of mononuclear VO^{2+} complexes [11] present as impurities were observed. Analogous spectra were also observed for other V(III) and V(II) complexes synthesized in this work (vide infra), indicating that these species are quite sensitive to residual oxygen and moisture present during the preparation and subsequent handling of the samples [12]. Representative spectra are shown in

Table 1

IR spectra (Nujol mull) of ester CO absorptions in M(pcmcp)$_2$L$_2$ and M(pcmcp)$_3$ complexes

M(pcmcp)$_2$L$_2$				
M	L	$\tilde{v}_{C=O}$ (cm^{-1})	$\tilde{v}_{C-OMe}$ (cm^{-1})	Ref.
Mn	–	1725 s,1705 m, 1680 m, 1648 vs,	1312 s, 1285 s, 1250 vs, 1205 s	[6f]
Fe	MeOH	1725 s, 1700 m, 1677 s, 1645 s	1312 s, 1280 s, 1245 s, 1200 s	[6f]
Co	H$_2$O	1745 m, 1703 vs, 1655 vs	1325 s, 1275 m, 1235 vs, 1200 vs, 1175 s	[6f]
Ni	–	1745 s, 1706 s, 1656 s	1310 s, 1270 m, 1230 s	[6f]
Cu	MeOH	1740 s, 1700 s, 1630 s	1327 s, 1242 s, 1225 s, 1198 s	[6f]
V	THF	1742 s, 1721 vs, 1694 s, 1645 vs	1328 s, 1218 vs, 1166 m	This work
M(pcmcp)$_3$				
M		$\tilde{v}_{C=O}$ (cm^{-1})	$\tilde{v}_{C-OMe}$ (cm^{-1})	Ref.
Ti		1735, 1712, 1683(br)	1342, 1212(br)	This work
V		1729, 1712, 1585	1338, 1228	This work
Nb		1736, 1712, 1615	1376, 1358, 1337, 1219	This work
Cr		1725, 1695, 1640	1365, 1320, 1240, 1225, 1210	[6c]

Fig. 1. In isotropic solution, eight-line EPR spectra are obtained arising from the 3d^1 unpaired electron ($S = 1/2$) of V(IV) interacting with the nuclear spin of ^{51}V ($I = 7/2$, natural abundance ca. 100%); these spectra exhibit the typical variation in linewidth with M$_I$ observed for VO^{2+} species in solution [11a,13]. In frozen solution and in polycrystalline solids, nearly axial EPR spectra, typical of vanadyl complexes with distorted square-pyramidal geometry ($g_z < g_x \neq g_y$, $A_z > A_x \neq A_y$ with z along the V=O bond) [14] are observed; g and hyperfine coupling parameters obtained from the analysis of EPR spectra are reported in Table 2.

In order to get some insight into the nature of vanadyl impurities, a suspension of V(pcmcp)$_2$(THF)$_2$ was exposed to dioxygen in a gas volumetric apparatus. A fast O$_2$ absorption was noticed with several color changes of the reaction mixture (from pale brown to violet, orange and green). As the final O$_2$/V molar ratio was 7.8 it is most likely that the ligand too was involved in the reaction. We therefore decided to repeat the oxidation by using a O$_2$/V molar ratio of 0.5 as for Eq. (3) and by slowly adding oxygen to a suspension of V(pcmcp)$_2$(THF)$_2$ kept under an argon atmosphere in order to reduce the partial pressure of dioxygen.

$$V(pcmcp)_2(THF)_2 + 1/2\ O_2 \rightarrow VO(pcmcp)_2 + 2\ THF \quad (3)$$
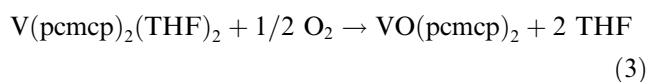
By operating under these conditions [15], red-violet microcrystalline VO(pcmcp)$_2$ was isolated and characterized by IR and EPR spectroscopies. Its IR spectrum shows an absorption of medium intensity at 981 cm^{-1} attributed to a V=O stretching vibration [16] and bands attributed to metal bonded and uncoordinated ester groups of the [pcmcp]$^-$ anion. The EPR spectra in fluid and frozen THF solution are almost superimposable to those recorded on powder and solution samples of V(II) and V(III) complexes (see Table 2), indicating that small

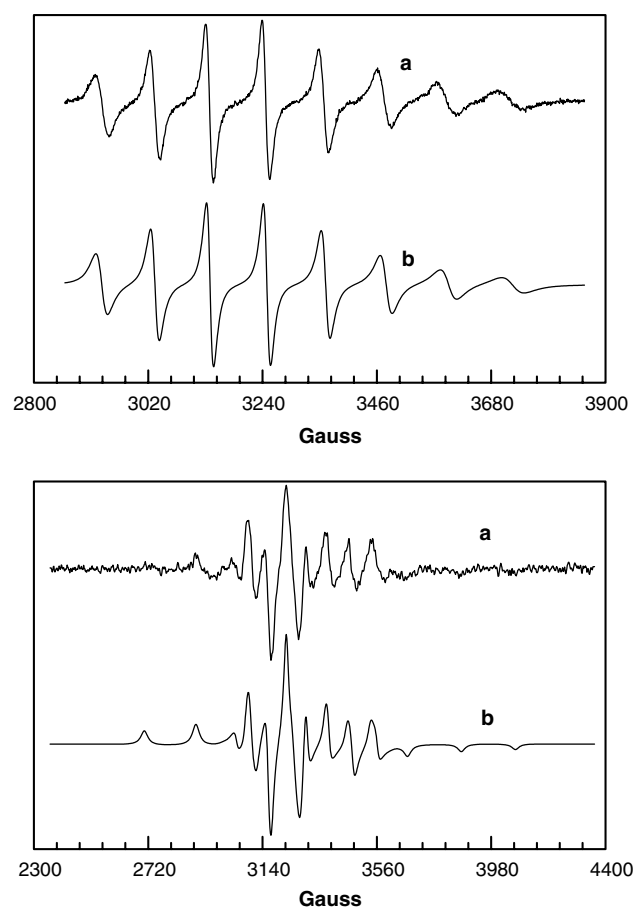Fig. 1. Experimental (a) and simulated (b) EPR spectra of vanadyl impurities in a MeCN solution of V(pcmcp)$_3$ at 298 K (top) and 140 K (bottom).

amounts of oxygen react with V(II) and V(III) species in the course of the preparation giving vanadyl complexes of general formula VO(pcmcp)$_2$.

As expected, further treatment of VO(pcmcp)$_2$ with dioxygen in THF results in the formation of a mixture

Table 2
EPR spectral parameters of VO(pcmcp)$_2$ and of the vanadyl impurities present in vanadium(II) and vanadium(III) complexes

	g_{iso}	g_x	g_y	g_z	A_{iso}	A_x	A_y	A_z
VO(pcmcp)$_2$[a,b]	1.984	1.9990	1.9986	1.9542	112	74.6	70.3	191.2
V(pcmcp)$_2$(THF)$_2$[b,c]	1.984	1.9992	1.9989	1.9539	112	74.8	70.0	191.4
V(pcmcp)$_2$[b,c]	1.984				113			
V(pcmcp)$_2$[c,d]		2.0014	1.9976	1.9480		76.7	71.0	191.3
V(pcmcp)$_3$[c,e]	1.981	1.9964	1.9953	1.9513	108	72.7	65.6	187.9
V(dbcp)$_2$[c,d]		2.0014	2.0002	1.9533		71.3	73.3	187.9

[a] Pure compound.
[b] THF solution.
[c] Spectral parameters refer to vanadyl impurities.
[d] Solid state.
[e] CH$_3$CN solution.

of compounds whose nature was not further investigated.

Due to the fact that vanadium(II) derivatives are formed even in the presence of an excess of pcmcpH, it appeared that other synthetic routes should be explored to obtain vanadium(III) derivatives. As a matter of fact, V(pcmcp)$_3$ has been prepared by reaction of VCl$_3$ with three equivalents of K[pcmcp], see the following equation:

$$VCl_3 + 3\ K[pcmcp] \rightarrow V(pcmcp)_3 + 3\ KCl \qquad (4)$$

The reaction is slow at room temperature, so heating to reflux temperature of the mixture is required in order to complete it. The IR spectrum of V(pcmcp)$_3$ (Table 1) shows several strong absorption bands due to the stretching of the coordinated (1729 and 1712 cm^{-1}) and uncoordinated (1585 cm^{-1}) C=O bonds and of the C–OMe bonds (ca. 1200 cm^{-1}).

The compound crystallizes from cold THF as well-shaped octahedra in the trigonal R$\bar{3}$ space group with six molecules per unit cell and the V atom occupying a crystallographic threefold axis. The metal atom is coordinated to six carbonyl oxygen atoms of three [pcmcp]$^-$ ligands, see Fig. 2, and the resulting idealized coordination geometry is an octahedron. Table 3 reports a selection of bond distances and angles.

The average length of the V–O [1.958(3) Å] and C–O [1.236(4) Å] bonds involved in coordination are similar to those observed for the chromium(III) derivative Cr(pcmcp)$_3$ [1.93(3) and 1.24(3) Å, respectively]. The C$_5$ ring is planar within experimental error [max. deviation from planarity 0.010(5) Å] and the two coordinated COOMe groups are rotated by 19.0(3) and 20.0(4)° with respect to it. The equatorial plane of the octahedron and that defined by the C$_5$ ring form angles of 134.4(3) (C1–O1–V1) and 137.0(3)° (C5–O3–V1). As far as the uncoordinated COOMe groups are concerned, one of them (defined by C11, C12, O7, and O8) is almost coplanar with the central ring [19.0(4)°], whereas the other carbomethoxy groups, attached to C7 and C13, are almost perpendicular to the C$_5$ ring with torsion angles of 84.9(4) and 76.5(4)°, respectively.
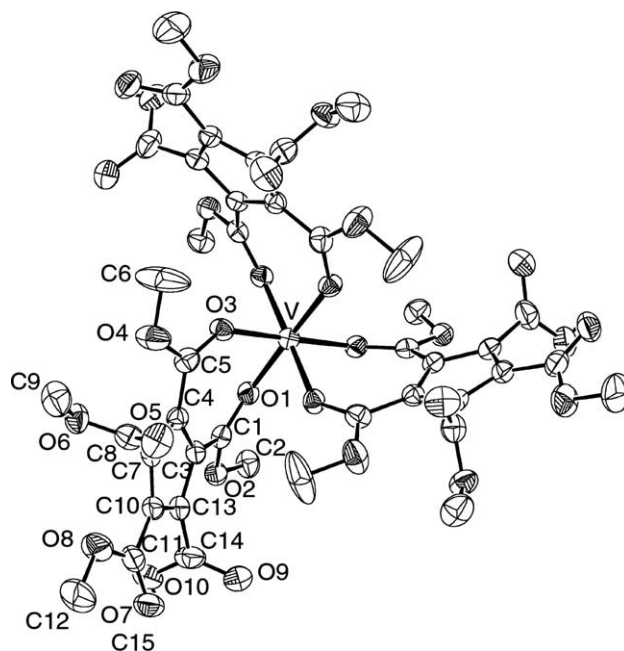

Fig. 2. View of the molecular structure of V(pcmcp)$_3$. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms and the alternative minority conformation of a disordered methoxy group associated with C14/O9/O10/C15 have been omitted.

The two ester functionalities, being forced to be coplanar due to the metal chelation, introduce some strain in the ligand itself, which is reflected in the opening of the C$_{carbonyl}$–C$_{ring}$–C$_{ring}$ angles on going from the chelated [123.6(4)°, av.] to the uncoordinated ester groups [125.8(4)°, av.] and in the lengthening of the C–C bond bearing the two carbonyl groups [1.435(6) Å versus 1.398(6) Å, av.]. Similar distortions are also observed in other structurally characterized derivatives of the [pcmcp]$^-$ anion [6] and in the sodium salt [Na(18-crown-6)][1,2-(COOEt)$_2$C$_5$H$_3$] [17].

Structurally characterized vanadium(III) complexes with three symmetrical O,O′-bidentate ligands are not common in the literature, the only examples being V(acac)$_3$ [18], V(CF$_3$COCHCOCH$_3$)$_3$ [19], and V(CF$_3$COCHCOCF$_3$)$_3$ [20]. It must be noticed that all

Table 3
Bond distances (Å) and angles (°) in V(pcmcp)$_3$

V1–O1	1.958(3)
V1–O3	1.958(3)
O1–C1	1.237(5)
O2–C1	1.304(5)
O2–C2	1.429(5)
O3–C5	1.234(5)
O4–C5	1.326(5)
O5–C8	1.211(6)
O6–C8	1.317(6)
O7–C11	1.199(6)
O8–C11	1.316(6)
O9–C14	1.243(6)
O10–C14	1.288(6)
C1–C3	1.420(6)
C3–C13	1.409(6)
C3–C4	1.435(6)
C4–C7	1.390(6)
C4–C5	1.417(6)
C7–C10	1.389(6)
C10–C13	1.403(6)
C10–C11	1.466(7)
O1#1–V1–O1	91.30(12)
O1#1–V1–O3	88.23(12)
O1–V1–O3	89.68(12)
O1#2–V1–O3	178.93(12)
O3–V1–O3#1	90.80(13)
C1–O1–V1	134.4(3)
C1–O2–C2	116.3(3)
C5–O3–V1	137.0(3)
C5–O4–C6	117.1(4)
C11–O8–C12	114.4(5)
O1–C1–O2	118.4(4)
O1–C1–C3	127.5(4)
O2–C1–C3	114.1(4)
C13–C3–C1	123.2(4)
C13–C3–C4	106.6(4)
C1–C3–C4	130.1(4)
C7–C4–C5	124.1(4)
C7–C4–C3	108.2(4)
C5–C4–C3	127.6(4)
O3–C5–O4	118.0(4)
O3–C5–C4	128.7(4)
O4–C5–C4	113.3(4)
C10–C7–C4	108.3(4)
C10–C7–C8	124.7(4)
C7–C10–C13	108.9(4)
C7–C10–C11	126.9(5)
C13–C10–C11	124.2(5)
O7–C11–O8	124.4(5)
O7–C11–C10	123.5(6)
O8–C11–C10	112.1(5)
C10–C13–C3	108.0(4)

Numbers in parentheses refer to the least significant digits.
Symmetry transformations used to generate equivalent atoms: #1: $-x+y, -x+1, z$; #2: $-y+1, x-y+1, z$.

of them show a V–O distance comparable to that observed for V(pcmcp)$_3$ [1.977 av. versus 1.958(3) Å]. Longer V–O distances [2.010 Å, av.] are observed for the vanadium(III) complexes [(ML)$_3$V(L′)$_3$], ML = Li(DME), L′ = phenolate [21a]; ML = Li(OEt$_2$),

L′ = 2,2′-biphenolate [21b] ML = Na(OEt$_2$), L′ = 2,2′-binaphtholate, [21c]. This difference is probably to be ascribed to the interaction of vanadium with the [ML]$^+$ cations.

In attempts to crystallize V(pcmcp)$_3$ a compound of the formula K(THF)(pcmcp) was also obtained. It crystallizes in the triclinic $P\bar{1}$ space group with two molecules per unit cell. The compound is polynuclear with all of oxygen atoms of the five ester C=O groups involved in the coordination to the potassium, the environment of the alkali cation being comprised of two oxygen atoms of one bidentate [pcmcp]$^-$ anion (O1 and O9), three oxygen atoms of three different anions (O7A, O3A, O5A) behaving as monodentate ligands, and one oxygen atom (O11) of THF. The methanol derivative K(MeOH)(pcmcp) [3] has a structure similar to the THF solvate, the main difference consisting in the fact that two [pcmcp]$^-$ anions behave as bidentate ligands in the former compound. The coordination of potassium is distorted octahedral with K–O$_{pcmcp}$ distances ranging from 2.671(5) to 2.784(5) Å and the K–O11 distance which amounts to 2.823(6) Å. These values are similar to those observed in [K(THF)$_6$]$^+$ cations [2.70 Å (average)][22], K(18-crown-6)(ethylacetoacetate) [2.651(5)–2.972(5) Å][23], dipotassium tetrafluorophthalate [2.75(2)–2.94(2) Å][24], and K(acac)·0.5H$_2$O [2.65(1)–3.05(1) Å] [25] (see Fig. 3, Table 4).

A different behavior is observed in the reaction of Nb(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ or Ti(η^6-MeC$_6$H$_5$)$_2$ with a threefold amount of pcmcpH; in fact, oxidation to +III species is quickly brought about for both metals with formation of M(pcmcp)$_3$, Eq. (5). Moreover, when the reaction is performed with a pcmcpH/M molar ratio lower than 3, M(pcmcp)$_3$ is obtained in a correspondingly lower yield and the excess starting arene derivative can be recovered from the reaction mixture:
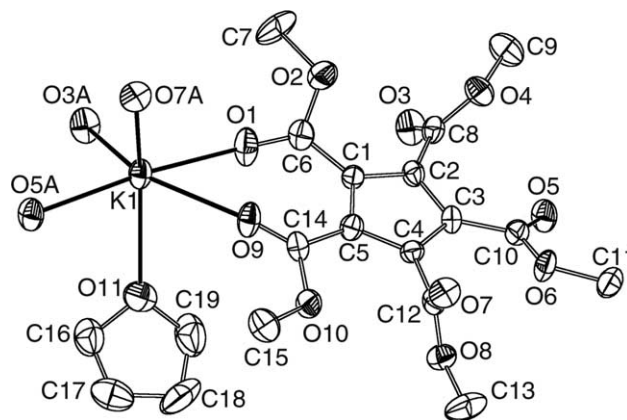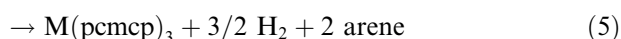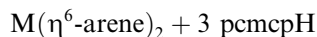

Fig. 3. View of the molecular structure of [K(THF)pcmcp]$_n$, showing coordination at potassium. Displacement ellipsoids are drawn at 30% probability level.

Table 4
Bond distances (Å) and angles (°) in [K(THF)pcmcp]$_n$

|	
K1–O1	2.671(5)
K1–O9	2.730(5)
K1–O5#1	2.744(5)
K1–O3#2	2.763(5)
K1–O7#3	2.784(5)
K1–O11	2.823(6)
O1–C6	1.201(7)
O2–C6	1.354(8)
O3–C8	1.221(6)
O4–C8	1.340(7)
O5–C10	1.214(7)
O6–C10	1.346(7)
O7–C12	1.207(7)
O8–C12	1.338(7)
O9–C14	1.200(7)
O10–C14	1.355(7)
C1–C2	1.393(7)
C1–C5	1.435(7)
C1–C6	1.458(8)
C2–C3	1.417(8)
C2–C8	1.473(8)
C3–C4	1.427(7)
C3–C10	1.458(8)
C4–C5	1.391(7)
C5–C14	1.471(8)
O1–K1–O9	63.36(14)
O1–K1–O5#1	173.18(16)
O9–K1–O5#1	116.20(14)
O1–K1–O3#2	82.86(14)
O9–K1–O3#2	144.76(13)
O5#1–K1–O3#2	96.10(13)
O1–K1–O7#3	107.01(16)
O9–K1–O7#3	85.51(14)
O5#1–K1–O7#3	79.54(14)
O3#2–K1–O7#3	115.51(15)
O1–K1–O11	90.90(18)
O9–K1–O11	79.54(17)
O5#1–K1–O11	82.39(17)
O3#2–K1–O11	91.90(17)
O7#3–K1–O11	148.44(16)
C2–C1–C5	107.8(5)
C2–C1–C6	125.7(5)
C5–C1 C6	126.4(5)
C1–C2–C3	109.1(5)
C1–C2–C8	124.7(5)
C3–C2–C8	126.2(5)
C2–C3–C4	106.6(5)
C2–C3–C10	125.4(5)
C4–C3–C10	127.9(6)
C5–C4–C3	109.0(5)
C5–C4–C12	126.1(5)
C3–C4–C12	124.8(5)
C4–C5–C1	107.5(5)
C4–C5–C14	125.8(6)
C1–C5–C14	126.5(5)
O1–C6–O2	120.9(7)
O1–C6–C1	128.7(7)
O9–C14–O10	121.2(6)
O9–C14–C5	128.7(6)

Numbers in parentheses refer to the least significant digits.
Symmetry transformations used to generate equivalent atoms: #1: $x, y, z - 1$; #2: $-x + 2, -y + 1, -z$; #3: $-x + 2, -y + 2, -z$.

$$M(\eta^6\text{-arene})_2 + 3 \text{ pcmcpH}$$
$$\rightarrow M(\text{pcmcp})_3 + 3/2 \text{ H}_2 + 2 \text{ arene} \qquad (5)$$

M = Ti, arene = MeC$_6$H$_5$; M = Nb, arene = 1,3,5-Me$_3$-C$_6$H$_3$.

The IR spectra of Ti(pcmcp)$_3$ and Nb(pcmcp)$_3$ are very similar to those of the analogous vanadium(III) and chromium(III) complexes (see Table 1), suggesting that all these compounds possess a similar structure, characterized by an octahedral coordination at the metal by three *O,O'*-chelate [pcmcp]$^-$ anions.

As in the case of vanadium, Nb(pcmcp)$_3$ can be obtained via a metathesis reaction between NbCl$_3$-(DME)$_{1.4}$ and three equivalents of K[pcmcp] in THF, see the following equation:

$$NbCl_3(DME)_{1.4} + 3 \text{ K[pcmcp]}$$
$$\rightarrow Nb(\text{pcmcp})_3 + 3 \text{ KCl} + 1.4 \text{ DME} \qquad (6)$$
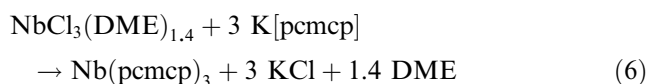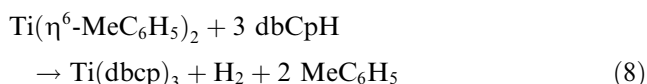
2.1.2. 1-Benzoyl-6-hydroxy-6-phenyl fulvene (dbcpH)

On the basis of the results obtained with pcmcpH and considering the lower acidity of dbcpH with respect to pcmcpH, we set up the reaction between V(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$and dbcpH using a ligand to metal molar ratio of 2, see the following equation:

$$V(\eta^6\text{-}1,3,5\text{-Me}_3C_6H_3)_2 + 2 \text{ dbCpH}$$
$$\rightarrow V(\text{dbcp})_2 + H_2 + 2 \text{ }1,3,5\text{-Me}_3C_6H_3 \qquad (7)$$
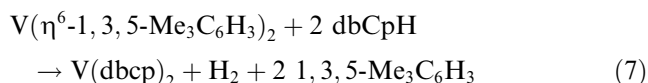
The dark red microcrystalline compound isolated from the reaction mixture after a prolonged reflux indeed corresponds to the formula V(dbcp)$_2$ and has a rather limited solubility in common solvents, CH$_3$CN being the only medium that can dissolve it to a reasonable extent. At variance to the reaction performed with pcmcpH in THF, solvent molecules are not retained by V(dbcp)$_2$. In view of the generally observed hexacoordination of vanadium(II) [26] we suppose that this rather insoluble material might be a oligomeric derivative resulting from the stacking of V(pcmcp)$_2$ units. To support this hypothesis, we can observe that the electron-withdrawing power of the two benzoyl groups on the fulvene ring of [dbcp]$^-$ is not strong enough to deplete the vanadium centre of its electron density, thus favouring vanadium$\cdots$vanadium interactions with respect to vanadium$\cdots$oxygen ones. On the other hand, strong electron withdrawing power can be attributed to the [pcmcp]$^-$ ligand, which bears as many as five carbomethoxy groups; coordination of these ligands could promote metal acidity enhancement and subsequent interactions of vanadium with THF oxygens.

The reactions of both titanium and niobium bis(arene) derivatives with dbcpH are not as clean as in the case of vanadium: Nb(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ fails to give any recognizable product, and Ti(η^6-MeC$_6$H$_5$)$_2$ reacts

with dbcpH giving the off-green Ti(III) derivative Ti(dbcp)$_3$, Eq. (8), in low yields (27%):

$$\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2 + 3 \text{ dbCpH}$$
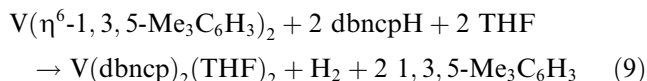$$\rightarrow \text{Ti}(\text{dbcp})_3 + \text{H}_2 + 2 \text{ MeC}_6\text{H}_5 \quad (8)$$

The IR spectrum of Ti(dbcp)$_3$ does not show the absorption at 1697 cm^{-1} attributed to the C=O stretching vibration of the parent ligand, suggesting that the carbonyl groups are involved in coordination to the metal center. Mass spectrum supports this formulation, showing a parent peak (M$^+$) at $m/z = 867$, with successive fragmentation peaks (due to the loss of dbcp groups) at $m/z = 594$ and 321.

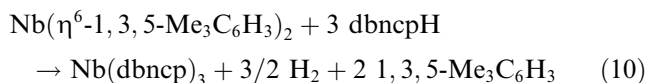### 2.1.3. 1-Benzoyl-3-nitro-6-hydroxy-6-phenyl fulvene (dbncpH)

Although the experimental procedure for preparing dbncpH [4] is quite tricky (reaction times just slightly longer than those required for a yellow precipitate to appear lead to fast decomposition of the product with formation of a black tar), yield as high as 40% could be secured.

When V(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ is added to the yellow suspension of dbncpH in THF, a reaction immediately occurs affording a dark red microcrystalline solid which analyzes correctly for V(dbncp)$_2$(THF)$_2$, see the following equation:

$$\text{V}(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2 + 2 \text{ dbncpH} + 2 \text{ THF}$$
$$\rightarrow \text{V}(\text{dbncp})_2(\text{THF})_2 + \text{H}_2 + 2 \text{ } 1,3,5\text{-Me}_3\text{C}_6\text{H}_3 \quad (9)$$

The O,O'-chelate coordination of [dbncp]$^-$ is confirmed by the presence of an absorption at 1582 cm^{-1} attributed to the stretching vibration of the benzoyl group (the C=O stretching vibration of the benzoyl fragment of dbcpH is observed at 1641 cm^{-1}). The possibility of coordination of [dbncp]$^-$ through the oxygen atoms of the nitro group is ruled out as the positions of –NO$_2$ stretching bands are practically unaffected by complexation: the asymmetric and the symmetric NO$_2$ stretching vibrations, occurring at 1518–1294 cm^{-1} in dbncpH, are observed at 1531–1281 cm^{-1} in the coordinated anion, the slight shift being probably due to negative charge delocalization on the whole ligand.

As in the case of pcmcpH, the hexacoordinate Nb(III) compound, Nb(dbncp)$_3$, is formed by reaction of Nb(η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$ with dbncpH, see Eq. (10).

$$\text{Nb}(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2 + 3 \text{ dbncpH}$$
$$\rightarrow \text{Nb}(\text{dbncp})_3 + 3/2 \text{ H}_2 + 2 \text{ } 1,3,5\text{-Me}_3\text{C}_6\text{H}_3 \quad (10)$$

The IR spectrum of Nb(dbncp)$_3$ shows that coordination to the metal centre is attained by means of carbonyl groups oxygens of [dbncp]$^-$; the C=O stretching absorptions are shifted to lower wavenumbers with respect to those of dbncpH, whereas a small shift to 1530/1280 cm^{-1} is observed for the NO$_2$ bands.

3. Conclusions

The results reported in this paper show that the reaction of bis(arene) derivatives of titanium(0), vanadium(0), and niobium(0) with the fulvene precursors reported in Chart 2 proceeds with oxidation of the metal and loss of the aromatic ligand to give O,O'-coordinated compounds of vanadium(II) or titanium(III) and niobium(III). This reactivity has to be compared with that of the bis(toluene) derivatives of chromium(0) and molybdenum(0) which under the same experimental conditions afford salts of general formula [M(η^6-toluene)$_2$][Anion] (M = Cr, Anion = [pcmcp]$^-$, [dbcp]$^-$, [dbncp]$^-$; M = Mo, Anion = [pcmcp]$^-$), as shown in Scheme 1. This behavior is related to the much higher aptitude to oxidation with consequent loss of the π-acid arene ligands of the elements of Groups 4 and 5 with respect to those of Group 6.

Moreover, the isolation of compounds in a different oxidation state for vanadium with respect to titanium and niobium (+II instead of +III), while operating under the same experimental conditions, confirms the general rule [27] stating that the stability of the higher oxidation states decreases from left to right within a period and increases on descending a vertical sequence of transition elements.

4. Experimental

4.1. General procedures

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.
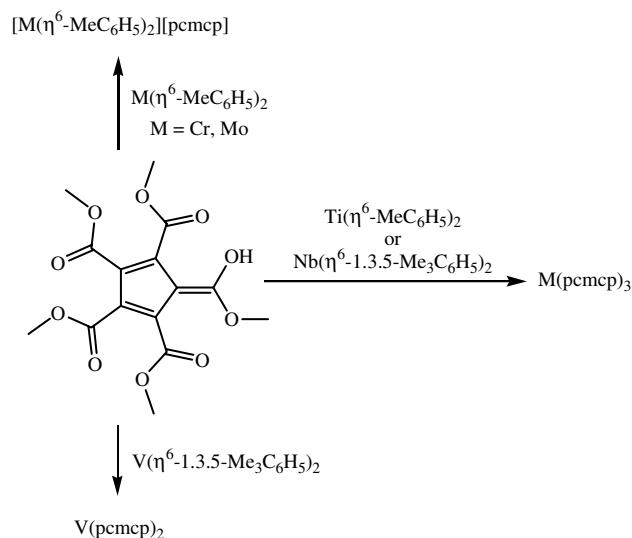
Scheme 1.

IR spectra were recorded with a FT-1725X instrument on nujol mull prepared under rigorous exclusion of moisture and air. EPR spectra were recorded using a Varian (Palo Alto, CA, USA) E112 spectrometer operating at X band, equipped with a Varian E257 temperature control unit and interfaced to an IPC 610/P566C industrial grade Advantech computer by means of an acquisition board [28] and a software package especially designed for EPR experiments [29]. Solution experiments were run by placing the sample (typically 15–20 μl) into quartz tubes fitted with a quartz-Pyrex joint and a Bibby Quickfit Rotaflo PTFE tap (DISA, Milan). Powder samples were enclosed into sealed quartz tubes under argon atmosphere. EPR spectra were simulated using the WinSim 32 program [30]. The following compounds were prepared as reported in the literature: $Ti(\eta^6-MeC_6H_5)_2$ [31], $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ [32], $Nb(\eta^6-1,3,5-Me_3C_6H_3)_2$ [33], $NbCl_3(DME)_{1.4}$ [34], "pentacarbomethoxycyclopentadiene" [35], K[pcmcp] [3], 1-benzoyl-6-hydroxy-6-phenyl fulvene [4a], and 1-benzoyl-3-nitro-6-hydroxy-6-phenyl fulvene [4b].

4.2. Reaction of $Ti(\eta^6-MeC_6H_5)_2$ with pcmcpH

Crude $Ti(\eta^6-MeC_6H_5)_2$ (0.137 g, 0.59 mmol), obtained from a MVS experiment, was dissolved in 20 ml of THF; the resulting red-violet suspension (some metal residues were present) was filtered in a dropping funnel and added dropwise to a solution of pcmcpH (0.63 g, 1.8 mmol) in THF (20 ml). A rapid reaction took place with formation of a green solution which, after 12 h stirring, was concentrated to about 2 ml; then heptane (20 ml) was added obtaining an oil. The liquid phase was evaporated and fresh heptane was added. By vigorous stirring the oil solidified and green $Ti(pcmcp)_3$ (0.285 g, 43% yield) was recovered by filtration and vacuum-dried. Anal. Calc. for $C_{45}H_{45}O_{30}Ti$: C, 48.5; H, 4.1. Found: C, 49.0; H, 4.8%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1712 vs, 1583 vs, 1462 m, 1342 s, 1212 s,br, 1091 m, 1070 m, 1004 s, 941 w, 816 w, 793 w, 751 w.

4.3. Reaction of $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ with pcmcpH in THF

$V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.402 g, 1.3 mmol) was added to the pale yellow solution formed by dissolving pcmcpH (1.00 g, 2.7 mmol) in THF (100 ml). After 15 min stirring, the blood red solution became cloudy and a dark solid precipitated within 1 h. This solid was recovered by filtration, washed with heptane (10 ml), dried in vacuo and identified as $V(pcmcp)_2(THF)_2$ (0.951 g, 74.5% yield, dark red microcrystalline solid. Anal. Calc. for $C_{38}H_{46}O_{22}V$: C, 50.4; H, 5.1. Found: C, 50.6; H, 5.5%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1742 s, 1721 vs, 1694 s, 1645 vs, 1406 w, 1328 s, 1267 w, 1218 vs, 1166 m, 1087 w, 1065 w, 1045 w, 1006 s, 903 m, 791 m.

4.4. Reaction of $V(pcmcp)_2(THF)_2$ with dioxygen. Synthesis of $VO(pcmcp)_2$

$V(pcmcp)_2(THF)_2$ (0.455 g, 0.502 mmol) was suspended in 100 ml THF and dry dioxygen (0.25 mmol) was slowly added at room temperature with a syringe through a rubber stopper. Upon stirring of the suspension, a slow gas absorption was noticed and the initial red suspension turned into a dark violet solution after 15 h. (*Important notice*: the O_2/V molar ratio must be rigorously controlled and the addition of dioxygen should be performed as slowly as possible, otherwise an intractable mixture is obtained, see below). The volume of the solution was reduced to 10 ml and heptane (20 ml) was added causing the separation of $VO(pcmcp)_2$ as a red-violet microcrystalline solid (0.356 g, 91% yield). Anal. Calc. for $C_{30}H_{30}O_{21}V$: C, 46.3; H, 3.9. Found: C, 45.9; H, 4.2%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1735 vs, 1708 s, 1647 vs, 1334 vs, 1259 m, 1206 s, 1168 m, 1087 w, 1067 w, 1004 s, 984 m-s ($\tilde{v}_{V=O}$), 868 w, 793 m.

A gasvolumetric control of the reaction, performed by exposing a THF solution of $V(pcmcp)_2(THF)_2$ to pure dioxygen, showed that the gas absorption is initially fast (the O_2/V molar ratio reaches 2.5 in 1 h) turning slow within some hours. The reaction was stopped after 15 h (O_2/V molar ratio = 7.8) when the gas absorption was very slow but not finished yet. The solution was dried in vacuo a room temperature affording a black-green tar: no attempt was made to identify the reaction products.

4.5. Reaction of $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ with pcmcpH in toluene

$V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.323 g, 1.1 mmol) was dissolved in toluene (100 ml) and pcmcpH (0.794 g, 2.2 mmol) was added to the resulting blood red solution: gas evolution and formation of a precipitate were observed. The suspension was stirred for 3 h and, then, filtered; the obtained solid was washed with toluene (2×5 ml), dried in vacuo and identified as $V(pcmcp)_2$ (0.601 g, 69% yield). Anal. Calc. for $C_{30}H_{30}O_{20}V$: C, 47.3; H, 4.0. Found: C, 47.5; H, 4.2%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1733 vs, 1705 s, 1637 vs, 1314 vs, 1217 vs, 1166 m, 1089 w, 1070 w, 1008 s, 796 m.

4.6. Reaction of VCl_3 with K(pcmcp)

To a solution of K(pcmcp) (2.10 g, 5.33 mmol) in THF (120 ml), solid VCl_3 (0.272 g, 1.73 mmol) was added. The red brown mixture was stirred at room temperature for 12 h and refluxed for 4 h obtaining a dark red suspension. After filtration, the volume was reduced to 40 ml and the solution was cooled at ca. 4°C. Well formed dark red crystals of $V(pcmcp)_3$, in admixture with small pale yellow platelets, formed within 3 days

which were recovered by filtration. The pale yellow crystals [ca. 40 mg, identified as K(THF)pcmcp (Anal. Calc. for $C_{19}H_{23}KO_{11}$: C, 48.9; H, 5.0. Found: C, 49.3; H, 5.2%)] were separated under the microscope from the dark red ones (0.324 g). The solution was added of toluene (100 ml) and the solid which formed was collected by filtration and dried in vacuo affording further V(pcmcp)$_3$ (0.989 g, 51% total yield). Anal. Calc. for $C_{45}H_{45}O_{30}V$: C, 48.4; H, 4.0. Found: C, 47.7; H, 4.4%. IR (Nujol) $\tilde{v}$/cm^{-1} 1729 vs, 1712 vs, 1585 vs, 1412 m-w, 1338 s, 1228 vs, 1170 m, 1089 m, 1070 m,1004 m, 944 w, 872 w, 837 w, 792 m, 761 m-w.

4.7. Crystal structures of V(pcmcp)$_3$ and [K(THF)pcmcp]$_n$: solution and refinement

Deep red crystals of V(pcmcp)$_3$ were grown by slow cooling a THF solution at ca. 4°C. Diffraction data, see Table 5, were collected at 193 K with Mo Kα ($\lambda = 0.71073$ Å) radiation on a CCD area detector diffractometer equipped with a graphite monochromator on a crystal of approximate dimensions $0.48 \times 0.48 \times 0.48$ mm. 11 395 reflections were collected with the ω-scan method in the range $1.54 \leqslant \theta \leqslant 26.15°$. An empirical

absorption correction was applied with SADABS [36]. After merging, 3939 independent reflections remained for structure solution by direct methods [37]. The structure model was completed by Fourier difference syntheses and refined with Full-matrix least-squares on F^2 [38]. The unit cell contains three significant voids centered around Wyckoff positions 3a (site symmetry $\bar{3}$). Each of this solvate regions corresponds to a volume of more than 600 Å^3. As no reasonable model at atomic resolution could be derived for the disordered solvent, the BYPASS procedure [39] as implemented in PLATON [40] was used to include its contribution to the overall structure factors. The electron density in each void amounted to ca. 280 electrons. This electron count as well as the volume are in agreement with the presence of approximately 6–7 molecules of THF per void. The methoxy group associated with atoms C14/O9/O10/C15 shows disorder: an alternative minority conformation was refined. Convergence was reached for 3939 reflections and 235 variables at agreement factors of $wR_2 = 0.1833$ (all data), $R_1 = 0.0741$ [observations with $I > 2\sigma(I)$].

Crystals of [K(THF)pcmcp]$_n$ were obtained from the mother liquors of the V(pcmcp)$_3$ crystallization after several days at 4 °C. Diffraction data, see Table 5, were

Table 5
Crystal data and parameters of the structure solution of V(pcmcp)$_3$ and [K(THF)pcmcp]$_n$.

	[K(THF)pcmcp]$_n$	V(pcmcp)$_3$
Empirical formula	$C_{19}H_{23}KO_{11}$	$C_{45}H_{45}O_{30}V$
Formula weight	466.47	1116.75
Temperature (K)	193(2)	
Wavelength (Å)	0.71073	
Crystal size (mm)	$0.20 \times 0.10 \times 0.10$	$0.48 \times 0.48 \times 0.48$
Crystal system	Triclinic	Trigonal
Space group	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)
Unit cell dimensions		
a (Å)	9.882(7)	16.273(5)
b (Å)	10.931(8)	–
c (Å)	11.409(8)	39.099(18)
α (°)	96.49(1)	–
β (°)	92.27(1)	–
γ (°)	115.13(1)	–
V (Å^3)	1103.3(14)	8967(6)
Z	2	6
D_{calc} (Mg m^{-3})	1.404	1.241
Absorption coefficient (mm^{-1})	0.297	0.249
$F(000)$	488	3468
θ-Range for data collection (°)	2.08–26.06	1.54–26.15
Index ranges	$-12 \leqslant h \leqslant 12$,	$-20 \leqslant h \leqslant 19$,
	$-13 \leqslant k \leqslant 13$,	$-20 \leqslant k \leqslant 16$,
	$-14 \leqslant l \leqslant 14$	$-47 \leqslant l \leqslant 39$
Reflections collected	12 880	11 395
Independent reflections [R_{int}]	4337 [0.1857]	3939 [0.0642]
Absorption correction		Empirical
Refinement method		Full-matrix least-squares on F^2
Data/ restraints/ parameters	4337/0/285	3939/1/235
Goodness-of-fit on F^2	1.000	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0808$, $wR_2 = 0.1517$	$R_1 = 0.0741$, $wR_2 = 0.1686$
R indices (all data)	$R_1 = 0.2383$, $wR_2 = 0.2126$	$R_1 = 0.1418$, $wR_2 = 0.1833$
Largest diff. peak and hole (e Å^{-3})	0.270 and −0.299	0.416 and −0.467

collected at 193 K with Mo Kα ($\lambda = 0.71073$ Å) radiation on a CCD area detector diffractometer equipped with a graphite monochromator on a crystal of approximate dimensions $0.20 \times 0.10 \times 0.10$ mm. 12 880 reflections were collected with the ω-scan method in the range $2.08 \leqslant \theta \leqslant 26.06°$. A empirical absorption correction (min. trans. 0.943, max. trans. 0.971) was applied before averaging symmetry equivalent data ($R_{int} = 0.1857$). After merging, 4337 independent reflections remained for structure solution by direct methods [37]. The structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on F^2 [38]. Convergence was reached for 4337 reflections and 285 variables at agrement factors of $wR_2 = 0.2126$ (all data), $R_1 = 0.0808$ [observations with $I > 2\sigma(I)$].

4.8. Reaction of $Nb(\eta^6-1,3,5-Me_3C_6H_3)_2$ with pcmcpH

PcmcpH (0.917 g, 2.6 mmol) was dissolved in THF (120 ml) and $Nb(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.286 g, 0.86 mmol) was added to the clear solution. Gas evolution was noticed and the reaction mixture turned brown. After stirring for 24 h, the solution was concentrated and heptane was added (50 ml). The resulting yellow brown precipitate was recovered by filtration, washed with heptane (2×10 ml) and dried in vacuo to afford 0.723 g of $Nb(pcmcp)_3$ (73% yield). Anal. Calc. for $C_{45}H_{45}NbO_{30}$: C, 46.6; H, 3.9. Found: C, 46.6; H, 4.5%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1736 vs, 1712 s, 1615 s, 1376 m, 1358 s, 1337 s, 1219 vs, 1091 w, 1070 w, 1005 w, 809 w, 794 w.

4.9. Reaction of $NbCl_3(DME)_{1.4}$ with K(pcmcp)

K(pcmcp) (1.464 g, 3.7 mmol) was dissolved in THF (100 ml) and $NbCl_3(DME)_{1.4}$ (0.42 g, 1.3 mmol) was added to the yellow solution. The brown suspension quickly turned to a green solution containing colorless KCl. After 8 h at the reflux temperature, the resulting golden brown solution was allowed to cool and filtered. After concentration in vacuo heptane (50 ml) was added. The brown precipitate was collected, washed with heptane and dried in vacuo affording brown $Nb(pcmcp)_3$ (0.553 g, 37% yield), whose IR spectral features were superimposable to those of the compound described in Section 4.8.

4.10. Reaction of $Ti(\eta^6-MeC_6H_5)_2$ with dbcpH

A freshly prepared THF solution of $Ti(\eta^6-MeC_6H_5)_2$ (0.335 g, 1.4 mmol, in 25 mL) was added dropwise to a solution of dbcpH (1.19 g, 4.3 mmol) in THF (50 ml). On mixing a slow but steady gas evolution was noted. After stirring overnight, most of the solvent was removed in vacuo and heptane (50 ml) was added; after filtration, washing and vacuum-drying, $Ti(dbcp)_3$ (0.332 g,

27% yield) was recovered as a greenish polycrystalline solid. Anal. Calc. for $C_{57}H_{39}O_6Ti$: C, 78.9; H, 4.5. Found: C, 79.3; H, 4.5%. IR (Nujol) $\tilde{v}/cm^{-1}$ 3054 w, 1582 s, 1541 vs, 1488 m, 1422 m, 1305 w, 1129 m, 1048 m, 1026 m, 847 vs, 789 m, 701 m. MS (assignment): 867 (M^+), 594 ($M - dbcp^+$), 321 ($M - 2dbcp^+$).

4.11. Reaction of $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ with dbcpH

Solid $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.388 g, 1.2 mmol) was added to the solution obtained by dissolving dbcpH (0.635 g, 2.3 mmol) in THF (100 ml), and the mixture was refluxed for 8 h. After cooling to room temperature, the resultant red-brown solution was partially evaporated and heptane (50 ml) was added. The precipitated solid was filtered, washed and dried in vacuo, recovering $V(dbcp)_2$ (0.225 g, 38% yield) as a red-brown solid. Anal. Calc. for $C_{38}H_{26}O_4V$: C, 76.4; H, 4.4%. Found: C, 76.9; H, 4.9%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1581 w, 1563 w, 1536 s, 1480 s, 1421 m, 1317 w, 1131 m, 1076 w, 1046 m, 846 vs, 791 w, 756 w, 707 vs.

4.12. Reaction of $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ with dbncpH

$V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.322 g, 1.1 mmol) was added to a well-stirred yellow suspension of dbncpH (0.706 g, 2.2 mmol) in THF (125 ml); gas (identified as H_2 by GC) evolution was observed and the color of the reaction mixture turned rapidly to brick-red. After 24 h stirring, most of the solvent was removed in vacuo and heptane (70 ml) was added. $V(dbncp)_2(THF)_2$ was collected by filtration, washed with heptane (2×5 ml) and dried in vacuo (0.526 g, 57% yield). Anal. Calc. for $C_{46}H_{40}N_2O_{10}V$: C, 66.4; H, 4.8; N, 3.4%. Found: C, 66.3; H, 4.3; N, 3.6%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1582 m, 1531 s, 1415 m, 1365 s, 1281 s, 1096 w, 866 m, 714 m.

4.13. Reaction of $Nb(\eta^6-1,3,5-Me_3C_6H_3)_2$ with dbncpH

$Nb(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.248 g, 0.74 mmol) was added to a yellow suspension of dbncpH (0.712 g, 2.2 mmol) in 125 ml of THF. Immediate gas evolution took place with formation of a brick-red solution. After 12 h stirring, the solution was concentrated to 5 ml and added of heptane (50 ml). $Nb(dbncp)_3$ was collected by filtration, washed with heptane (2×5 ml) and dried in vacuo (0.619 g, 79% yield). Anal. Calc. for $C_{57}H_{36}N_3NbO_{12}$: C, 65.3; H, 3.5; N, 4.0%. Found: C, 65.2; H, 3.9; N, 3.7%. IR (Nujol) $\tilde{v}/cm^{-1}$ 1583 m, 1530 s, 1519 s, 1418 m, 1280 s, 1167 w, 1136 w, 1095 s, 868 m, 712 s.

Appendix A. Supplementary data

Crystallographic data for V(pcmcp)$_3$ and [K(THF)(pcmcp)]$_n$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC 263464 and CCDC 274552, respectively. Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.093.

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