FULL PAPER

Dalton
www.rsc.org/dalton

Vanadium complexes incorporating the β-diketiminato ligand L. Syntheses and structures of $LV(OSO_2CF_3)_2$ and $LVPPh_2$

Dante Neculai,[a] Ana Mirela Neculai,[a] Herbert W. Roesky,*[a] Regine Herbst-Irmer,[a] Bernhard Walfort[b] and Dietmar Stalke[b]

[a] *Institut für Anorganische Chemie der Universität Göttingen, Tammannstr. 4, D-37077, Göttingen, Germany. E-mail: hroesky@gwdg.de; Fax: +49-551-393373; Tel: +49-551-393001*

[b] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074, Würzburg, Germany*

Received 20th March 2003, Accepted 4th June 2003
First published as an Advance Article on the web 23rd June 2003

The reaction of LLi (where L = *N*,*N′*-bis(2-diethylaminoethyl)-2,4-pentanediimine-ate(-1)) with $VCl_3 \cdot 3THF$ yielded $LVCl_2$, which was characterized by EI-MS and elemental analysis. Subsequent reactions of $LVCl_2$ with $AgOSO_2CF_3$ and $KPPh_2$ afforded two new complexes, $LV(OSO_2CF_3)_2$ and $LVPPh_2$ which were characterized by ^{19}F, ^{31}P NMR spectroscopy, EI-MS, elemental analysis, and single crystal X-ray structural analysis.

Introduction

Recently, the groups of Theopold, Gibson, and Budzelaar have exploited the multifariousness of the β-diketiminato ligands to prepare various complexes of Cr(III),[1] V(III),[2,1b] and Ti(III).[1b,2,3] Also, it has been shown that such systems might act as paramagnetic homogeneous catalysts for the polymerization of small olefins (ethylene, propene *etc.*).[1,2] In spite of all these efforts the β-diketiminato chemistry of such metals is not adequately developed. Previously we have reported the synthesis and structural characterization of new derivatives of titanium $LTiX_2$ (L = *N*,*N′*-bis(2-diethylaminoethyl)-2,4-pentanediimineate(1−), X = Cl, $F \cdot SnMe_3Cl$), belonging to a novel class of metal complexes containing a β-diketiminato-based ligand which possesses two dangling arms.[4] Herein we report the synthesis of $LVCl_2$ and subsequent reactions with different nucleophiles, other than alkyls, that were carried out. The structure of $LV(OSO_2CF_3)_2$, which represents the first vanadium(III) triflate derivative structurally characterized, and the structure of $LVPPh_2$ which represents the first neutral heteroleptic terminal diorganophosphido complex of vanadium(II), are also described.

Experimental

General methods

All manipulations were performed on a dual-manifold line or in a glove box under a purified N_2 atmosphere, using Schlenk techniques with rigorous exclusion of moisture and air. The samples for spectral measurements were prepared inside a MBraun MB 150-GI glove-box where the O_2 and H_2O levels were normally maintained below 1 ppm. Commercial grade solvents were purified and freshly distilled following usual procedures prior to their use.[5] Melting points of all new compounds were measured in sealed capillaries and are reported uncorrected. ^{19}F and ^{31}P NMR spectra (C_6D_6) were recorded on a Bruker MSL-400 instrument. The chemical shifts are reported in ppm with reference to external standards, more explicitly: $C_6F_6/CFCl_3$ for ^{19}F nuclei and 85% H_3PO_4 for ^{31}P nuclei. The heteroatom NMR spectra were measured in the ^1H-decoupled mode. The downfield shifts from the reference are quoted positive and the upfield shifts are reported as negative values. The C_6D_6 for NMR measurements was dried over K or CaH_2 and trap-to-trap distilled prior to use. Mass spectra were obtained on a Finnigan MAT 8230 instrument by EI technique. Elemental analyses were performed at the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. The conjugated acid of the ligand L, (2-diethylaminoethyl)[3-(2-diethylaminoethylimino)-1-methylbut-1-enyl]amine, and its lithium salt were prepared according to the literature protocols.[6] The following substances were purchased from Aldrich and used as received: $VCl_3 \cdot 3THF$, $AgOSO_2CF_3$, and 0.5 M THF solution of $KPPh_2$.

$LVCl_2$

A solution of LLi (2.23 g, 7.37 mmol), freshly prepared, in toluene (40 mL) was allowed to react with a toluene (30 mL) suspension of $VCl_3 \cdot 3THF$ (2.75 g, 7.37 mmol) at room temperature overnight. After the solvent removal and extraction in CH_2Cl_2, followed by subsequent CH_2Cl_2 removal and washing the remaining green substance with cold hexane, 1.80 g of $LVCl_2$ (58%) were obtained. Melting point: 156 °C. Anal. Calc. for $C_{17}H_{35}Cl_2N_4V$ (%): C, 48.93; H, 8.45; N, 13.42. Found: C, 48.74; H, 8.45; N, 13.55. EI-MS: *m*/*z* (rel. int.%): 416 [M^+, 5], 381 [$M^+ - Cl$, 2], 86 [$C_5H_{12}N$, 100].

$LV(OSO_2CF_3)_2$

A mixture of 0.80 g (1.91 mmol) **1** and 0.985 g (3.83 mmol) of $AgOSO_2CF_3$ in a 100 mL Schlenk flask in toluene (40 mL) was stirred for two days. The suspension was filtered. The resulting clear green solution was concentrated under reduced pressure to obtain yellow crystals of $LV(OSO_2CF_3)_2$, which were collected by filtration, and washed with pentane (10 mL). Yield 0.98 g (81%). Melting point: 195 °C. Anal. Calc. for $C_{19}H_{35}F_6N_4O_6S_2V$ (%): C, 35.40; H, 5.47; N, 8.69. Found: C, 35.60; H, 5.91; N, 7.81. ^{19}F NMR (188.28 MHz, C_6D_6): δ −136 (s, CF_3). EI-MS: *m*/*z* (rel. int.%): 644 [M^+, 79], 495 [$M^+ - SO_3CF_3$, 100], 558 [$M^+ - C_5H_{12}N$, 5].

$LVP(C_6H_5)_2$

30 mL of dry THF were added to 0.46 g (1.1 mmol) of **1** in a 100 mL Schlenk flask. The mixture was cooled to −78 °C and a solution of 4.41 mL (0.5 M, 2.2 mmol) $KPPh_2$ in THF was added dropwise. The mixture was stirred for 2 h at −78 °C, and then stirred overnight at room temperature. After the solvent removal and extraction in toluene (25 mL), the resulting solution was concentrated to 15 mL and cooled at −26 °C. The formed dark red crystals were filtered off. Yield 0.24 g (41%). Melting point: 160–163 °C. Anal. Calc. for $C_{29}H_{45}N_4PV$ (%): C, 65.52; H, 8.53; N, 10.54. Found: C, 65.14; H, 8.31; N, 9.70. ^{31}P NMR (200.13 MHz, C_6D_6): δ −40.27 (s, $VP(C_6H_5)$). EI-MS: *m*/*z* (rel. int.%): 641 [$M^+ + C_6H_5PH$, 30], 460 [$M^+ - C_5H_{12}N$, 2], 371 [$(C_6H_5)_4P_2$, 100].

DOI: 10.1039/b303196a

Table 1 Crystal data and summary of X-ray data collection for $LV(OSO_2CF_3)_2{\cdot}2C_7H_8$ and $LVP(C_6H_5)_2$

Empirical formula	$C_{33}H_{51}F_6N_4O_6S_2V$	$C_{29}H_{45}N_4PV$
M_r	828.84	531.60
T/K	173(2)	100(2)
λ/Å	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
Unit cell dimensions		
a/Å	15.329(2)	12.740(3)
b/Å	13.388(2)	14.466(3)
c/Å	19.652(3)	15.247(3)
β/°	97.77(3)	93.55(3)
V/Å^3, Z	3995.8(11), 4	2804.6(10), 4
D_c/g cm^{-3}	1.378	1.259
μ/mm^{-1}	0.426	3.667
F(000)	1736	1140
Crystal size/mm	0.4 × 0.3 × 0.1	0.2 × 0.2 × 0.1
θ Range for data collection/°	1.34–28.22	3.48–59.67
Index ranges, hkl	−20 to 19, 0 to 17, 0 to 24	−13 to 14, −16 to 16, −15 to 16
Reflections collected	30036	17902
Independent reflections (R_{int})	9058 (0.0315)	7400 (0.0197)
Completeness to $\theta = \theta_{max}$ (%)	91.8	95.0
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	9058/0/477	7400/1/645
Goodness-of-fit on F^2	1.032	1.153
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.1273$	$R_1 = 0.0264$, $wR_2 = 0.0647$
R indices (all data)	$R_1 = 0.0723$, $wR_2 = 0.1392$	$R_1 = 0.0264$, $wR_2 = 0.0648$
Largest diff. peak, hole/e Å^{-3}	0.613, −0.428	0.351, −0.360

General aspects of X-ray data collection, structure determination, and refinement for complexes $LV(OSO_2CF_3)_2$ and $LVP(C_6H_5)_2$

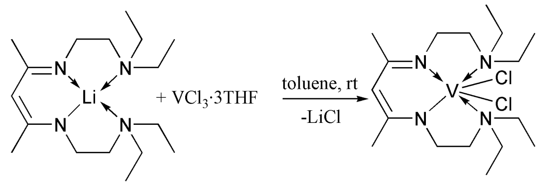
Suitable crystals were mounted on glass fibers in rapidly cooled perfluoropolyether.[7] Data for the crystal structure of $LV(OSO_2CF_3)_2$ was collected on a Bruker Smart Apex CCD diffractometer and for $LVP(C_6H_5)_2$ was collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. The data for both compounds were collected at low temperature (the temperatures for individual compounds are mentioned in Table 1) using graphite Mo-Kα or Cu-Kα radiation. Crystal data collection details, and the solution and refinement procedures are summarized in Table 1. All structures were solved by direct methods, SHELXS-97,[8] and refined against F^2 using SHELXL-97.[9] Heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms. The structure of $LVP(C_6H_5)_2$ was refined as a racemic twin (the fractional contribution of the second domain 0.503(3)). There is a pseudo-inversion center on 0.262, 0.369, 0.255. Refinement on $P2_1/n$ leads to a disordered model with high R-values ($R_1 \approx 0.15$).

CCDC reference numbers 206412 and 206413.

See http://www.rsc.org/suppdata/dt/b3/b303196a/ for crystallographic data in CIF or other electronic format.

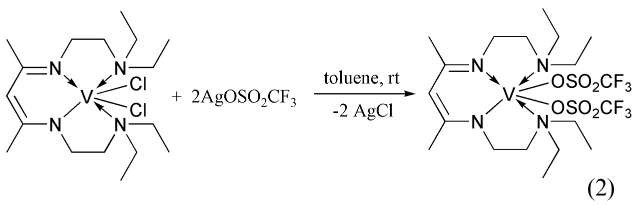
Results and discussion

Treatment of LLi with an equivalent amount of $VCl_3{\cdot}3THF$ in toluene at room temperature afforded $LVCl_2$ in good yield (eqn. (1)). $VCl_3{\cdot}3THF$ constitutes the usual common entry for many vanadium complexes in different oxidation states due to the straightforward accessibility and hence relatively low cost.[10] $LVCl_2$ is well soluble in toluene, dichloromethane and THF, respectively. It is thermally very stable, but moisture- and air-sensitive, and represents facile entry into the vanadium(III) chemistry of the β-diketiminato ligand L. Mass spectrometry and elemental analysis showed that $LVCl_2$ is monomeric and contains neither coordinated lithium salt nor coordinated THF. It may be compared with $[Sc\{(N(CH_2CH_2NEt_2)C(Me))_2CH\}Cl_2]$ which is a similar compound of a highly electrophile metal.[11] The ^1H NMR spectrum could not be interpreted because it exhibits a broad NMR resonance due to the paramagnetic nature of the vanadium nucleus. The ^{51}V NMR spectrum could not be recorded. Unfortunately the poor quality of the crystals of $LVCl_2$ precluded an X-ray diffraction experiment. Further proofs showing the readiness of $LVCl_2$ to participate in substitution reactions have been given by the following experiments.



(1)

$LVCl_2$ reacted with $AgSO_3CF_3$ to yield the expected product $LV(OSO_2CF_3)_2$ due to the oxophilic nature of vanadium and the thermodynamically favored formation of AgCl (eqn. (2)). $LV(OSO_2CF_3)_2$ is a green solid which is very soluble in aromatic solvents and THF, and it has been characterized by ^{19}F NMR, EI-MS, elemental analysis and single crystal X-ray diffraction. The ^{19}F NMR spectrum shows, as expected, only one sharp resonance due to the equivalency of the CF_3 groups. $LV(OSO_2CF_3)_2$ constitutes the first vanadium(III) triflate derivative to be structurally characterized (two triflate containing complexes of vanadium(II) were structurally characterized, namely $V(py)_4(OSO_2CF_3)_2$[12] and $V(H_2O)_6(OSO_2CF_3)_2$).[13] $LV(OSO_2CF_3)_2$ is expected to be a superior starting material than $LVCl_2$ for further substitution reactions owing to the weak nucleophilicity of the CF_3SO_3 anion, which is a better leaving group compared to the Cl anion.[12]



(2)

Suitable single crystals of $LV(OSO_2CF_3)_2$ for an X-ray structural analysis were obtained from toluene at −26 °C within several hours. $LV(OSO_2CF_3)_2$ crystallizes in the monoclinic

Table 2 Selected bond lengths (Å) and angles (°) of $LV(OSO_2CF_3)_2$

V(1)–N(3)	2.0080(18)	N(3)–V(1)–N(1)	89.13(8)
V(1)–N(1)	2.0090(18)	N(3)–V(1)–N(4)	82.09(7)
V(1)–N(2)	2.3223(18)	N(1)–V(1)–N(2)	81.39(7)
V(1)–N(4)	2.3379(19)	N(2)–V(1)–N(4)	107.40(7)
C(2)–N(1)	1.327(3)	O(1)–V(1)–O(4)	167.89(6)
C(2)–C(3)	1.401(4)	S(2)–O(4)–V(1)	130.27(10)
C(3)–C(4)	1.408(4)	S(1)–O(1)–V(1)	132.67(10)
C(4)–N(3)	1.327(3)	C(2)–N(1)–V(1)	128.80(16)
V(1)–O(1)	2.0606(16)	C(4)–N(2)–V(1)	128.66(16)
V(1)–O(4)	2.0637(16)	N(3)–C(4)–C(3)	122.7(2)
O(1)–S(1)	1.4733(16)	C(2)–C(3)–C(4)	127.3(2)
O(4)–S(2)	1.4788(16)	N(1)–C(2)–C(3)	122.7(2)

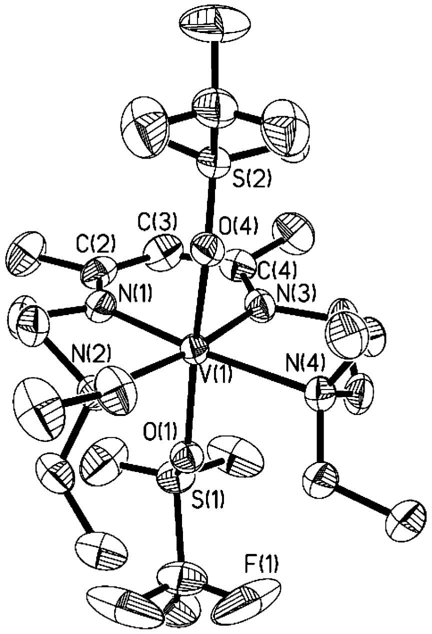


Fig. 1 Molecular structure of $LV(OSO_2CF_3)_2$ showing 50% probability ellipsoids (the hydrogen atoms are omitted for clarity).

space group $P2_1/c$ together with two molecules of toluene (the toluene molecules are omitted in Fig. 1 for clarity).

The crystal structure reveals that the vanadium atom in $LV(OSO_2CF_3)_2$ is hexacoordinated (ligand is tetradentate) with a pseudo-octahedral geometry and the triflate anions are arranged in the apical positions (O(4)–V–O(1) 167.89(6)°) (Table 2). This distortion might be attributable to the existence of the C–H–X (X = O, F) hydrogen bond like interaction between the discrete molecules (F ··· H 2.48 Å, O ··· H 2.57 Å). From sterical and electronical reasons the triflate groups are not coordinated to vanadium in a chelate fashion, they bind rather as monodentate through an oxygen atom. The V–O distances (av. 2.06 Å) in $LV(OSO_2CF_3)_2$ are slightly shorter than those reported for $V(py)_4(OSO_2CF_3)_2$ (2.127(6) Å)[12] or for $V(H_2O)_6(OSO_2CF_3)_2$ (2.129(6) Å)[13] as a consequence of a smaller radius of vanadium(III) compared to that of vanadium(II). The NC_3N atoms of the β-diketiminato backbone as well as the nitrogen atoms of the ligand arms are almost coplanar. The deviation of the vanadium atom from the NC_3N plane (0.09 Å) clearly indicates a σ-bond interaction (η^2) between vanadium and the β-diketiminato ligand. The V–N (belonging to the ligand core) bond lengths are comparable to those found in literature[2,14] (*e.g.* 1.963(2) and 1.940(2) Å for $[V\{(N(C_6H_3{i}Pr_2\text{-}2,6)C(Me))_2CH\}Cl_2]$).[2b]

Table 3 Selected bond lengths (Å) and angles (°) for $LVP(C_6H_5)_2$

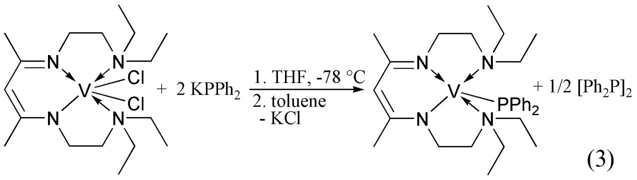
Molecule a

V(1)–N(2)	2.3253(18)	N(2)–V(1)–N(1)	77.89(6)
V(1)–N(1)	2.0446(17)	N(1)–V(1)–N(3)	89.73(7)
V(1)–N(3)	2.0499(17)	N(3)–V(1)–N(4)	78.21(7)
V(1)–N(4)	2.3078(17)	N(2)–V(1)–N(4)	108.19(6)
V(1)–P(1)	2.5752(9)	N(1)–C(2)–C(3)	123.26(19)
N(1)–C(2)	1.337(3)	N(3)–C(4)–C(3)	123.57(18)
C(2)–C(3)	1.398(3)	C(4)–C(3)–C(2)	128.87(17)
C(3)–C(4)	1.399(3)	C(2)–N(1)–V(1)	127.29(14)
N(3)–C(4)	1.332(2)	C(4)–N(3)–V(1)	127.09(14)

Molecule b

V(2)–N(5)	2.0392(17)	N(5)–V(2)–N(6)	89.58(7)
V(2)–N(6)	2.0511(17)	N(6)–V(2)–N(8)	79.50(6)
V(2)–N(8)	2.2781(18)	N(5)–V(2)–N(7)	79.01(6)
V(2)–N(7)	2.2882(18)	N(8)–V(2)–N(7)	103.80(6)
V(2)–P(2)	2.5600(9)	N(6)–C(33)–C(32)	123.07(18)
N(5)–C(31)	1.333(3)	N(5)–C(31)–C(32)	122.79(18)
N(6)–C(33)	1.337(3)	C(33)–C(32)–C(31)	129.30(18)
C(33)–C(32)	1.395(3)	C(31)–N(5)–V(2)	127.88(14)
C(31)–C(32)	1.402(3)	C(33)–N(6)–V(2)	127.27(14)

Surprisingly, the reaction of $LVCl_2$ with 2 equivalents of $KPPh_2$ in THF yielded, after removal of the THF and extraction in toluene, complex $LVP(C_6H_5)_2$ as an unexpected product which represents the first neutral heteroleptic terminal diorganophosphido-complex of vanadium(II) (eqn. (3)). Even though the synthesis of some diorganophosphido complexes of vanadium in different oxidation states (${t}BuN{=}V(N{i}Pr_2)[P(SiMe_3)_2]_2$,[15] ${t}BuN{=}V[P(SiMe_3)_2]_3$,[16] $[Li(DME)V(P(C_6H_{11})_2)_4]$[17]) have been previously published, none has been structurally characterized.



(3)

$LVP(C_6H_5)_2$ has been characterized by ^{31}P NMR, EI-MS, elemental analysis, and single crystal X-ray diffraction. Support for the reaction pathway has been given by confirmation of $[Ph_2P]_2$ by multinuclear NMR spectroscopy. This type of reduction is not unusual when diorganophosphides are involved. Previously, a similar reaction has been reported for $LnI_3{\cdot}3THF$ (Ln = Sm, Yb) giving as the major product $Ln[P(C_6H_5)_2]_2{\cdot}4THF$.[18] In the precedent not so numerous examples, ligands of composition PR_2 mainly act as bridging units ($\mu\text{-}PR_2$).[19] There are only a few complexes of transition metals structurally characterized where the bonding pattern is terminal.[20] Interestingly, a terminal diorganophosphido-platinum(II) complex has found application as a catalyst in the asymmetric hydrophosphination of acrylonitrile.[20c]

Single crystals of $LVP(C_6H_5)_2$ have been obtained from toluene at −26 °C and crystallize in the monoclinic $P2_1$ space group (Fig. 2) with two crystallographically independent but chemically equivalent molecules in the unit cell (Tables 1 and 3). The crystal structure analysis reveals that, unlike for $LV(OSO_2CF_3)_2$, the vanadium atom in $LVP(C_6H_5)_2$ is pentacoordinated (four coordination positions being occupied by the tetradentate ligand) with a square-pyramidal geometry. The vanadium atom lies on the NC_3N β-diketiminato backbone plane (the mean deviation from the plane is 0.09 and 0.05 Å for the two molecules). However the vanadium atom is placed about 0.38 Å (av.) above the plane formed by the four nitrogen atoms of the ligand. Similarly to $LV(OSO_2CF_3)_2$, the V–N (belonging to the ligand core) bond lengths are comparable to those found in literature,[2,14] although they are slightly longer due to the larger vanadium(II) radius. As expected the delocalization of the π-electrons is reflected by the C–C and C–N bond lengths of the backbone. The phosphido ligands are substantially pyramidalyzed with large V–P bond lengths

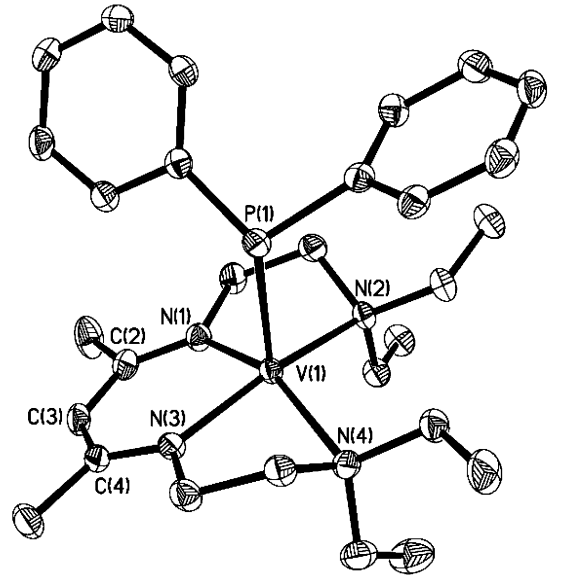


Fig. 2 Molecular structure of one $LVP(C_6H_5)_2$ molecule showing 50% probability ellipsoids (the hydrogen atoms are omitted for clarity).

(2.5752(9) and 2.5600(9) Å). These V–P distances are notably longer than those reported for a diphosphene vanadium(II) complex, *trans*-$[\{V(\eta^5\text{-}C_5H_5)(CO)_3\}_2(PMes)_2]$[21] (2.397(1) Å) or a phospinidene vanadium complex, $[V_2(CO)_4(\eta^5\text{-}C_5H_5)_2\text{-}\{\mu\text{-}P(2,4,6\text{-}(tBu)_3C_3H_2)\}]$[22] (2.268(1) and 2.243(1) Å). Intriguingly, they are also longer than the V–P distances found in some complexes that contain coordinated phosphine, such as $V(N\text{-}2,6\text{-}iPr_2C_6H_3)Cl_3(depe)$ (2.520(2) Å) (depe = $Et_2PCH_2CH_2PEt_2$).[23] This can be attributed to the larger radius of vanadium(II) compared to vanadium(III), and to a greater extent of the ionic character of the V–P bond in $LVP(C_6H_5)_2$.

Conclusions

In this study it has been shown that the ligand L functions as an ancillary system for vanadium, thereby providing an easy access to a novel class of β-diketiminato vanadium complexes. Not only does the β-diketiminato ligand L provide a suitable coordination environment for vanadium(II) or vanadium(III) cations but its built-in amine donor allows the isolation of base- and salt-free complexes. While the substitution reaction of $LVCl_2$ with $AgOSO_2CF_3$ follows a well established pattern, the reaction of $LVCl_2$ with $KPPh_2$ is interesting due to its product formation, which constitutes the first structurally characterized terminal vanadium phosphido complex that features a remarkably long V–P bond length.

Acknowledgements

Dedicated to Professor Friedrich Hensel on the occasion of his 70th birthday. We are thankful to the Deutsche Forschungsgemeinschaft for financial support.

References

1 (*a*) D. S. Richeson, J. F. Mitchell and K. H. Theopold, *Organometallics*, 1989, **8**, 2570–2577; (*b*) K. H. Theopold, W.-K. Kim, J. M. Power, J. M. Mora and A. P. Masino, *Int. Pat. Appl., WO 01/12637, 2001;* (*c*) V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Eur. J. Inorg. Chem.*, 2001, 1895–1903; (*d*) V. C. Gibson, C. Newton, C. Redshaw, G. Solan, A. J. P. White, P. J. Maddox and D. J. Williams, *Chem. Commun.*, 1998, 1651–1652.

2 (*a*) W.-K. Kim, M. J. Fevola, L. M. Liable-Sands, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1998, **17**, 4541–4543; (*b*) P. H. M. Budzelaar, A. B. V. Oort and A. G. Orpen, *Eur. J. Inorg. Chem.*, 1998, 1485–1494.

3 L. Kakaliou, W. J. Scanlon, B. Qian, S. W. Baek, M. R. Smith and D. H. Motry, *Inorg. Chem.*, 1999, **38**, 5964–5977.

4 G. B. Nikiforov, H. W. Roesky, J. Magull, M. Noltemeyer, H.-G. Schmidt, E. G. Ilyin, Y. B. Kokunov and A. Demsar, *Eur. J. Inorg. Chem.*, 2003, 437–441.

5 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, London, 3rd edn., 1988.

6 D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, H.-G. Schmidt and M. Noltemeyer, *J. Organomet. Chem.*, 2002, **643**, 47–52.

7 T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615–619.

8 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467–473.

9 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Germany, 1997.

10 J. S. Overby, K. C. Jayaratne, N. J. Schoell and T. P. Hanusa, *Organometallics*, 1999, **18**, 1663–1668.

11 A. M. Neculai, H. W. Roesky, D. Neculai and J. Magull, *Organometallics*, 2001, **20**, 5501–5503.

12 P. Ghosh, H. Taube, T. Hasegawa and R. Kuroda, *Inorg. Chem.*, 1995, **34**, 5761–5775.

13 D. G. L. Holt, L. F. Larkworthy, D. C. Povey, G. W. Smith and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1990, 3229–3233.

14 (*a*) G. Aharonian, K. Feghali, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2001, **20**, 2616–2622; (*b*) E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 1998, **17**, 4090–4095.

15 F. Preuss, M. Steidel, M. Vogel, G. Overhoff, G. Hornung, W. Towae, W. Frank, G. Reiss and S. Müller-Becker, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1220–1228.

16 F. Preuss and F. Tabellion, *Z. Naturforsch., Teil B*, 2000, **55**, 735–737.

17 R. T. Baker, P. J. Krusic, T. H. Tulip, J. C. Calabrese and S. S. Wreford, *J. Am. Chem. Soc.*, 1983, **105**, 6763–6765.

18 G. W. Rabe, G. P. A. Yap and A. L. Rheingold, *Inorg. Chem.*, 1995, **34**, 4521–4522.

19 (*a*) C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 2451–2460; (*b*) F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Inorg. Chem.*, 1998, **37**, 6035–6043; (*c*) G. Boni, P. Sauvageot, E. Marpeaux and C. Moise, *Organometallics*, 1995, **14**, 5652–5656; (*d*) L. R. Falvello, J. Fornies, C. Fortuno, F. Duran and A. Martin, *Organometallics*, 2002, **21**, 2226–2234.

20 (*a*) R. Melenkivitz, D. J. Mindiola and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2002, **124**, 3846–3847; (*b*) M. A. Zhuravel, D. S. Zakharov, N. Lev and A. L. Rheingold, *Organometallics*, 2002, **21**, 3208–3214; (*c*) D. K. Wicht, I. Kovacik, D. S. Glueck, L. M. Liable-Sands, C. D. Incarvito and A. L. Rheingold, *Organometallics*, 1999, **18**, 5141–5151.

21 R. A. Bartlett, H. V. R. Dias and P. P. Power, *J. Organomet. Chem.*, 1989, **362**, 87–94.

22 A. M. Arif, A. H. Cowley, N. C. Norman, A. G. Orpen and M. Pakulski, *Organometallics*, 1988, **7**, 309–318.

23 F. Montilla, A. Monge, E. Gutiérrez-Puebla, A. Pastor, D. del Rio, N. C. Hernandez, Y. F. Sanz and A. Galindo, *Inorg. Chem.*, 1999, **38**, 4462–4466.