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FULL PAPER

Synthesis and characterization of d^0 imido complexes of vanadium. Crystal structure of $[V(2,6\text{-}^iPr_2C_6H_3N)(S_2CNC_4H_4)_3]$

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Interaction of $[V(NR)Cl_3]$ compounds with 1,2-dimethoxyethane (dme) afforded $[V(NR)Cl_3(dme)]$ (R = 2,6-$^iPr_2C_6H_3$ **1a** or 1-adamantyl **1b**) complexes in a nearly quantitative yield. Compounds **1** are suitable sources for the synthesis of other d^0 imidovanadium complexes. Metathesis reactions of **1** with the sodium salt of the Kläui's ligand, NaL_{OEt} (L_{OEt} = $(\eta\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$), yielded complexes $[V(NR)Cl_2(L_{OEt})]$ (R = 2,6-$^iPr_2C_6H_3$ **2a** or 1-adamantyl **2b**). Treatment of **1** with several bidentate monoanionic dithio-ligands, $^-S_2CR'$, gave the corresponding imido complexes of general formulation $[V(NR)(S_2CR')_3]$ (for R = 2,6-$^iPr_2C_6H_3$; R′ = NC_4H_4 **3a**, N^iPr_2 **4**, O^{i}Pr **5a** or S^{i}Pr **6a**; for R = 1-adamantyl; R′ = NC_4H_4 **3b**, O^{i}Pr **5b** or S^{i}Pr **6b**). The molecular structure of $[V(2,6\text{-}^iPr_2C_6H_3N)(S_2CNC_4H_4)_3]$ **3a** has been determined by an X-ray study. Finally, the reaction of **1a** with Na(acac), in a 1 : 2 molar ratio, produces complex $[V(2,6\text{-}^iPr_2C_6H_3N)Cl(acac)_2]$ **7**.

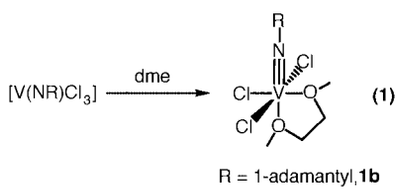
Imido ligands are widely used as stabilizing groups in high-oxidation-state transition metal complexes.[1] Their chemistry has experienced a remarkable growth in the last years due to the role they play in many important reactions. In particular, several imido derivatives of vanadium have been reported as active species in significant processes, such as C–H activation,[2] polymerization of olefins[3] and others.[4] The use of imido ligands in vanadium chemistry was initiated mainly by Preuss and co-workers[5] and Maatta and co-workers.[6] More recently, a number of studies[7] have been concerned with the properties of d^0 imidovanadium complexes.

Following our research in this area, we have extended our results on imido complexes of molybdenum[8] to vanadium compounds. Very recently, we have employed the complex $[V(2,6\text{-}^iPr_2C_6H_3N)Cl_3(dme)]$ **1a** to prepare $[V(2,6\text{-}^iPr_2C_6H_3N)Cl_3(P\text{–}P)]$ derivatives.[9] The dme was used as a good stabilizing coligand in $[V(NR)Cl_3]$ compounds; its lability in solution leads to complexes $[V(NR)Cl_3(dme)]$ (R = 2,6-$^iPr_2C_6H_3$ **1a** or 1-adamantyl **1b**) in advantageous starting materials. Here, we report the synthesis and characterization of d^0 2,6-diisopropylphenyl- and 1-adamantyl-imido vanadium complexes containing monoanionic tridentate ligands, such as Kläui's ligand,[10] and monoanionic bidentate dithio-ligands, $^-S_2CR'$. While our work was in progress, Maatta and co-workers[11] reported the synthesis of related tolylimidovanadium dithiocarbamate $[V(NC_6H_4Me)(S_2CNR'_2)_3]$ complexes.

Results and discussion

The synthesis of complex $[V(2,6\text{-}^iPr_2C_6H_3N)Cl_3(dme)]$ **1a**, by addition of 1,2-dimethoxyethane (dme) to light petroleum solutions of $[V(2,6\text{-}^iPr_2C_6H_3N)Cl_3]$,[12] has recently been reported by us.[9] Following a similar procedure, we have prepared the analogous $[V(NC_{10}H_{15})Cl_3(dme)]$ **1b** ($C_{10}H_{15}$ = 1-adamantyl) as a brown greenish solid, eqn. (1). The NMR spectra of **1b** are in agreement with this formulation and compare well with the data of **1a** and $[Ta(NC_{10}H_{15})Cl_3(dme)]$.[13] The structure proposed is similar to that reported for complex $[V(N^tBu)Cl_3(dme)]$.[14]

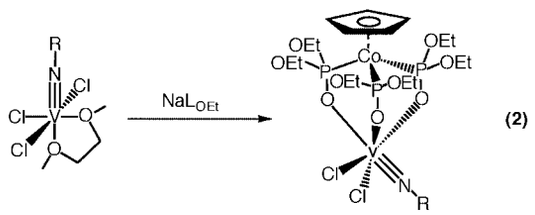
The presence of the dme ligand enhances the stability of complexes **1** making their manipulation easier than that for the parent $[V(NR)Cl_3]$ compounds. Additionally, the lability of dme (single broad resonances arise for the OCH_3 and OCH_2 groups in the ^{1}H NMR spectra for this ligand) makes **1** suitable starting materials for the synthesis of several d^0 imido complexes of vanadium.



(1)

R = 1-adamantyl, **1b**

Interaction of compounds **1** with the sodium salt of the monoanionic tridentate L_{OEt} ligand $[(\eta\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3]$, in a 1 : 1 molar ratio, affords the expected $[V(NR)Cl_2(L_{OEt})]$ (R = 2,6-$^iPr_2C_6H_3$ **2a** or 1-adamantyl **2b**) compounds in good yields, eqn. (2). Compounds **2** are orange yellowish crystalline materials, readily soluble in common organic solvents, that exhibit moderate stability to air. A C_s structure may readily be inferred from their NMR data. For example, three separate triplet signals (1 : 1 : 1 intensity ratio) are observed in the ^{1}H NMR spectrum of **2a** for the methyl groups, $POCH_2CH_3$, of the L_{OEt} ligand. Similarly, an AX_2 spin system appears in the ^{31}P-{^{1}H} NMR spectrum of **2** (δ_A = 105.3, δ_X = 121.9, J_{AX} = 158 Hz, for **2a**). Free rotation around the N–C bond of the organoimido ligand takes place in solution since, for example for **2a**, only one CH resonance of the ^{i}Pr groups is observed (^{1}H

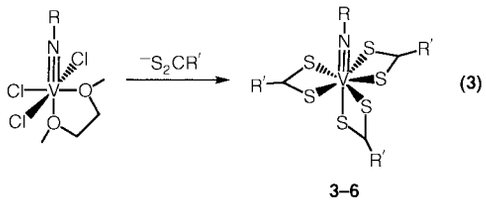


(2)

R = 2,6-$^iPr_2C_6H_3$, **2a**
1-adamantyl, **2b**

and ^{13}C-{^1H} NMR spectra). Related imidovanadium complexes containing hydrotris(pyrazolyl)borato ligands, namely [V(NR)Cl_2Tp′], are known.[3c,15]

The interaction of compounds **1** with several dithio-ligands of general formulation $^-S_2CR'$ gives the corresponding [V(NR)-(S_2CR')$_3$] (for R = 2,6-^{i}Pr$_2$C$_6$H$_3$; R′ = NC_4H_4 **3a**, N^{i}Pr$_2$ **4**, O^{i}Pr **5a** or S^{i}Pr **6a**; for R = 1-adamantyl; R′ = NC_4H_4 **3b**, O^{i}Pr **5b** or S^{i}Pr **6b**) eqn. (3). Complexes **3**–**6** are orange crystalline



(3)

3–6

materials, soluble in Et_2O and other more polar solvents, and moderately stable to air in the solid state.

The overall spectroscopic data for [V(NR)(S_2CR')$_3$] complexes are consistent with a pentagonal bipyramidal geometry. This assumption has been confirmed with the structural characterization of **3a**. Seven-co-ordinate pentagonal bipyramidal structures have been established by X-ray crystallography for related [V(O)(S_2CNEt_2)$_3$][16] and [Nb(NC_6H_4Me-*p*)(S_2CNEt_2)$_3$] complexes.[17] The ^1H NMR spectra indicate that these complexes are fluxional at room temperature. Besides the characteristic sharp resonances due to the organoimido ligand, broad signals are observed for the R′ groups of the S_2CR' dithioligands. For example, all the methyl groups of the three dithiocarbamate $S_2CN^iPr_2$ ligands of **4** produce a single pattern at room temperature (very broad signal covering the δ 1.52–0.97 range). Similar fluxional processes have been observed for compounds [M(NR′)(S_2CNR_2)$_3$] (M = Ta or Nb).[17]

Variable-temperature ^1H NMR studies (300 MHz) have been carried out for complexes **4** and **5a**. For **5a** the spectrum obtained at 293 K reveals two broad resonances (pseudotriplet and doublet, 2:1 ratio) for the methyl groups of the S_2CO^iPr ligands. In the fast interchange limit, 343 K, a single doublet resonance is observed for the same groups. The exchange process responsible for the magnetic equivalence of the Me groups, observed at 343 K, is the interconversion of the axial and equatorial co-ordination positions of the pentagonal bipyramidal arrangement. For both complexes the slow-exchange limit was not reached at 243 K. Similar dynamic behaviour has recently been recognized in [Nb(R′C≡CR″)-(S_2CNR_2)$_3$] complexes[18] containing a 4e-alkyne ligand, suggested to be similar to the imido functionality.[19]

The molecular structure of [V(2,6-^{i}Pr$_2$C$_6$H$_3$N)($S_2CNC_4H_4$)$_3$] **3a** has been determined by an X-ray study, Fig. 1. Selected bond distances and angles are collected in Table 1. The structure can be described as distorted pentagonal bipyramidal. The imido functionality, that occupies an axial position, is linear (175.0(7)°) and the V(1)–N(1) separation of 1.689(8) Å is in agreement with a vanadium–nitrogen bond order of three. Two dithiocarbamate ligands and the S(6) atom fit the equatorial plane and the S(5) atom occupies the second axial site, *trans* to the imide (N(1)–V(1)–S(5) bond angle of 168.2(3)°). The vanadium–equatorial sulfur bond distances span the 2.494(3)–2.504(3) Å range, whereas the V(1)–S(5) length (2.564(3) Å) shows the expected *trans* influence of the imido ligand. The Δ(V–S) between the V–S_{eq} and V–S_{ax} is *ca.* 0.06 Å and compares well with the corresponding Δ(Nb–S) in [Nb(PhC≡CMe)-(S_2CNMe_2)$_3$][18] (*ca.* 0.06 Å). Larger Δ(M–S) differences and consequently stronger *trans* influences can be found in compounds [M(O)(S_2CNEt_2)$_3$] (Δ(V–S) ≈ 0.13 and Δ(Nb–S) ≈ 0.16 Å),[16] [V(O)(S_2COEt)$_3$] (Δ(V–S) ≈ 0.15 Å),[20] [Ta(S)(S_2CNEt_2)$_3$] (Δ(Ta–S) ≈ 0.14 Å),[21] [Nb(S)(S_2CNEt_2)$_3$] (Δ(Nb–S) ≈ 0.14 Å)[22] and [Nb(NC_6H_4Me-*p*)(S_2CNEt_2)$_3$] (Δ(Nb–S) ≈ 0.10 Å).[17] All these complexes that can be regarded as [M(E)(S_2CNR_2)$_3$] derivatives, where M is a Group 5 metal and E a multiple bonded ligand, display high structural similarities.

Table 1 Selected bond lengths (Å) and angles (°) for [V(2,6-^{i}Pr$_2$-C_6H_3N)($S_2CNC_4H_4$)$_3$] **3a**

V(1)–N(1)	1.689(8)	V(1)–S(1)	2.494(3)
V(1)–S(3)	2.497(3)	V(1)–S(4)	2.500(3)
V(1)–S(6)	2.500(3)	V(1)–S(2)	2.504(3)
V(1)–S(5)	2.564(3)	S(4)–C(7)	1.676(11)
S(1)–C(1)	1.708(10)	S(6)–C(13)	1.704(11)
S(5)–C(13)	1.658(12)	S(2)–C(1)	1.675(12)
S(3)–C(7)	1.680(10)	N(1)–C(19)	1.374(12)
N(1)–V(1)–S(1)	98.1(3)	N(1)–V(1)–S(3)	92.5(3)
S(1)–V(1)–S(3)	140.37(11)	N(1)–V(1)–S(4)	100.6(3)
S(1)–V(1)–S(4)	72.07(10)	S(3)–V(1)–S(4)	68.46(9)
N(1)–V(1)–S(6)	98.8(3)	S(1)–V(1)–S(6)	139.88(11)
S(3)–V(1)–S(6)	74.63(10)	S(4)–V(1)–S(6)	138.69(10)
N(1)–V(1)–S(2)	92.7(3)	S(1)–V(1)–S(2)	68.54(10)
S(3)–V(1)–S(2)	149.16(11)	S(4)–V(1)–S(2)	139.76(13)
S(6)–V(1)–S(2)	74.54(10)	N(1)–V(1)–S(5)	168.2(3)
S(1)–V(1)–S(5)	90.82(11)	S(3)–V(1)–S(5)	85.42(10)
S(4)–V(1)–S(5)	89.41(10)	S(6)–V(1)–S(5)	69.46(10)
S(2)–V(1)–S(5)	83.35(10)		

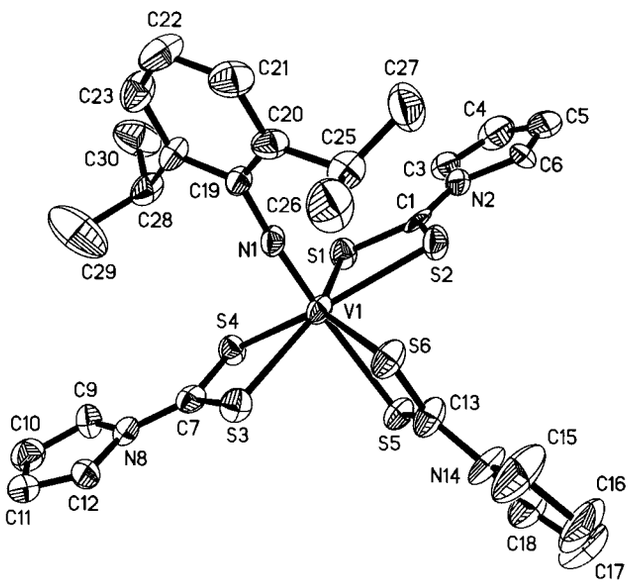
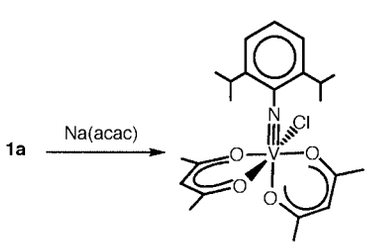


Fig. 1 Molecular structure of [V(2,6-^{i}Pr$_2$C$_6$H$_3$N)($S_2CNC_4H_4$)$_3$].

Metathesis reaction of complex **1a** with Na(acac), in a 1:2 molar ratio, gives, after appropriate work-up, [V(2,6-^{i}Pr$_2$C$_6$-H_3N)Cl(acac)$_2$] **7**, eqn. (4), as a brown solid. An alternative



(4)

7

procedure for the synthesis of **7** is the direct interaction of **1a** with Hacac in CH_2Cl_2 at reflux (see Experimental section). The structure proposed can easily be deduced from the NMR data. For example, four carbonyl and four methyl resonances are detected in the ^{13}C-{^1H} NMR spectrum, in agreement with the presence of two inequivalent acac ligands.

Experimental

All preparations and other operations were carried out under

a dry oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Solvents were dried and degassed before use. Microanalyses were carried out by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer, ^{1}H, ^{13}C and ^{31}P NMR spectra on Bruker AMX-300 and AMX-500 spectrometers. The ^{31}P shifts were measured with respect to external 85% H_3PO_4, ^{13}C using the resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. The light petroleum used had bp 40–60 °C. Complex **1a** was prepared according to the literature.[9]

Syntheses

[V(NC$_{10}$H$_{15}$)Cl$_3$(dme)] 1b. A 100 ml round-bottom flask was loaded with $VOCl_3$ (1.6 g, 9 mmol), $C_{10}H_{15}NCO$ (9 mmol) and octane (35 ml) and the mixture warmed at reflux. After heating for 5 h, volatiles were removed under reduced pressure. Light petroleum (20 ml) and dme (1 ml) were added and **1b** was collected by filtration as a brown greenish solid (2.6 g, 78%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.90 (br s, 4, OCH_2), 3.72 (br s, 6, OCH_3), 2.30 (br s, 6, CH_2), 2.16 (br s, 3, CH) and 1.63 (br s, 6, CH_2). ^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 73.0 (br s, OCH_2), 64.0 (br s, OCH_3), 41.7 (s, CH_2), 35.6 (s, CH_2) and 29.4 (s, CH). Found: C, 41.3; H, 5.9; N, 3.6. $C_{10}H_{15}Cl_3NV\cdot\frac{2}{3}$dme requires C, 41.5; H, 5.9; N, 3.8%.

[V(2,6-^{i}Pr$_2$C$_6$H$_3$N)Cl$_2$(L$_{OEt}$)] 2a. A reaction flask was charged with complex **1a** (0.40 g, 0.95 mmol) and NaL_{OEt} (0.53 g, 0.95 mmol), THF (30 ml) was added and the resulting solution stirred at ambient temperature for 7 h. Volatiles were then removed, the residue was extracted with Et_2O (20 ml) and filtered to separate NaCl. Concentration of the solution and cooling to −20 °C afforded orange crystals of compound **2a** (75%). ^{31}P-{^{1}H} NMR (C_6D_6): AX_2 spin system, δ 121.9 (d, J_{AX} = 158 Hz), 105.3 (t). ^{1}H NMR (500 MHz, C_6D_6): δ 6.95 (d, $^3J_{HH}$ = 7.5, 2, *m*-CH), 6.63 (t, $^3J_{HH}$ = 7.5, 1, *p*-CH), 5.46 (h, $^3J_{HH}$ = 6.7, 2, C*H*(CH_3)$_2$), 4.83 (s, 5, CH, Cp), 4.53–3.98 (m, 12, CH_2), 1.53 (d, $^3J_{HH}$ = 6.7, 12, CH(CH_3)$_2$), 1.30, 1.19, 0.97 (t, $^3J_{HH}$ = 7 Hz, 6, CH_3). ^{13}C-{^{1}H} NMR (125 MHz, C_6D_6): δ 159.4 (C *ipso*), 154.2 (*o*-C), 129.1 (*p*-C), 122.1 (*m*-C), 88.9 (Cp), 62.9–60.9 (CH_2), 27.6 (*C*H(CH_3)$_2$), 25.6 (CH(*C*H$_3$)$_2$) and 16.6–16.1 (CH_3). Found: C, 42.0; H, 6.4; N, 1.7. $C_{29}H_{52}Cl_2CoNO_9P_3V$ requires C, 41.8; H, 6.3; N, 1.7%.

Following a similar synthetic procedure, starting from complex **1b** (0.21 g, 0.5 mmol) and NaL_{OEt} (0.5 mmol), was prepared [V(NC$_{10}$H$_{15}$)Cl$_2$(L$_{OEt}$)] **2b** (65% yield). ^{31}P-{^{1}H} NMR (C_6D_6): AX_2 spin system, δ 122.9 (d, J_{AX} = 152 Hz), 104.2 (t). ^{1}H NMR (300 MHz, C_6D_6): δ 4.86 (s, 5, CH, Cp), 4.31–4.17 (br m, 12, CH_2, L_{OEt}), 2.42 (br s, 6, CH_2, $C_{10}H_{15}N$), 1.83 (br s, 3, CH, $C_{10}H_{15}N$), 1.36 (br s, 3, CH_2, $C_{10}H_{15}N$), 1.29 (br s, 3, CH_2, $C_{10}H_{15}N$) and 1.2 (br m, 18, CH_3, L_{OEt}). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6): δ 88.9 (Cp), 84.4 (C, $C_{10}H_{15}N$), 62.7 (2 CH_2, L_{OEt}), 61.8 (CH_2, L_{OEt}), 61.7 (CH_2, L_{OEt}), 60.8 (2 CH_2, L_{OEt}), 41.8 (3 CH_2, $C_{10}H_{15}N$), 35.6 (3 CH_2, $C_{10}H_{15}N$), 28.9 (3 CH, $C_{10}H_{15}N$) and 16.5 (6 CH_3, L_{OEt}). Found: C, 41.3; H, 6.5; N, 1.7. $C_{27}H_{50}Cl_2CoNO_9P_3V\cdot0.5Et_2O$ requires C, 41.3; H, 6.5; N, 1.7%.

[V(2,6-^{i}Pr$_2$C$_6$H$_3$N)(S$_2$CNC$_4$H$_4$)$_3$] 3a. To a solution of complex **1a** (0.21 g, 0.5 mmol) in THF (20 ml), $KS_2CNC_4H_4$ (0.23 g, 1.4 mmol) in THF (10 ml) was added. The orange mixture was stirred at room temperature overnight. Volatiles were removed and the residue was extracted with 1:1 light petroleum–Et_2O. After cooling at −20 °C, orange crystals of **3a** were obtained (46%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.59 (pseudo t, $^3J_{HH}$ = 2.3, 2, pyrrole), 7.44 (pseudo t, $^3J_{HH}$ = 2.3, 4, pyrrole), 6.83 (m, 3, *m*- and *p*-CH), 5.93 (pseudo t, $^3J_{HH}$ = 2.3, 2, pyrrole), 5.89 (pseudo t, $^3J_{HH}$ = 2.3, 4, pyrrole), 4.58 (h, $^3J_{HH}$ = 6.7, 2, C*H*(CH_3)$_2$) and 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 12, CH(CH_3)$_2$). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6): δ 214.5 (S_2C ax), 214.2 (S_2C eq), 159.2 (C *ipso*), 152.4 (*o*-C), 127.9 (*p*-C), 122.9 (*m*-C), 118.6, 117.3, 115.1, 114.6 (CH, pyrrole), 29.1 (*C*H(CH_3)$_2$) and 24.5 (CH(*C*H$_3$)$_2$). Found: C, 49.6; H, 4.5; N, 8.7. $C_{27}H_{29}N_4S_6V$ requires C, 49.7; H, 4.5; N, 8.6%.

Complex [V(NC$_{10}$H$_{15}$)(S$_2$CNC$_4$H$_4$)$_3$] **3b** was prepared as for **3a**, but using **1b** (0.33 g, 0.8 mmol) and $KS_2CNC_4H_4$ (0.46 g, 2.5 mmol) in THF (25 ml), as yellow crystals in 35% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (br, 4, pyrrole), 7.56 (br, 2, pyrrole), 6.40 (br, 4, pyrrole), 6.27 (br, 2, pyrrole), 2.01 (br, 6, CH_2, $C_{10}H_{15}N$), 1.67 (br, 3, CH, $C_{10}H_{15}N$) and 1.50 (br, 6, CH_2, $C_{10}H_{15}N$). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$): δ 214.4 (S_2C), 118.6, 117.5, 115.0, 114.2 (CH, pyrrole), 42.0 (CH_2, $C_{10}H_{15}N$), 35.6 (CH_2, $C_{10}H_{15}N$) and 28.8 (CH, $C_{10}H_{15}N$).

[V(2,6-^{i}Pr$_2$C$_6$H$_3$N)(S$_2$CN^{i}Pr$_2$)$_3$] 4. To a mixture of complex **1a** (0.34 g, 0.80 mmol) and $KS_2CN^iPr_2$ (0.57 g, 2.6 mmol) was added THF (20 ml). The resulting suspension was stirred at room temperature overnight. The volatiles were removed under reduced pressure, the residue extracted with a light petroleum–Et_2O mixture and filtered to remove KCl. The filtrate was concentrated and orange crystals of **4** were obtained on standing the solution at room temperature (58%). ^{1}H NMR (300 MHz, toluene-d$_8$): δ 7.08 (d, $^3J_{HH}$ = 7.5, 2, *m*-CH), 6.91 (t, $^3J_{HH}$ = 7.5, 1, *p*-CH), 4.98 (h, $^3J_{HH}$ = 6.7, 2, C*H*(CH_3)$_2$, Ph), 4.14 (br, 3, C*H*(CH_3)$_2$, dtc), 1.63 (d, $^3J_{HH}$ = 6.7 Hz, 12, CH(CH_3)$_2$, Ph) and 1.52–0.97 (br, 18, CH(CH_3)$_2$, dtc). ^{13}C-{^{1}H} NMR (75 MHz, toluene-d$_8$): δ 207.6 (S_2C ax), 205.4 (S_2C eq), 158.3 (C *ipso*), 151.1 (*o*-C), 125.4 (*p*-C), 122.5 (*m*-C), 50.3 (*C*H(CH_3)$_2$ ax, dtc), 49.7 (*C*H(CH_3)$_2$ eq, dtc), 28.9 (*CH*(CH_3)$_2$, Ph), 25.4 (CH(*C*H$_3$)$_2$, Ph) and 19.9–19.7 (CH(*C*H$_3$)$_2$, dtc). Found: C, 52.1; H, 7.8; N, 7.5; S, 25.9. $C_{33}H_{59}N_4S_6V$ requires C, 52.5; H, 7.8; N, 7.4; S, 25.5%.

[V(2,6-^{i}Pr$_2$C$_6$H$_3$N)(S$_2$CO^{i}Pr)$_3$] 5a. Prepared as for complex **4**, using **1a** (0.34 g, 0.80 mmol) and KS_2CO^iPr (0.57 g, 2.6 mmol) in THF (20 ml), as orange crystals in 67% yield. ^{1}H NMR (300 MHz, toluene-d$_8$, 298 K): δ 6.86–6.74 (m, 3, *m*- and *p*-CH), 5.32–5.21 (m, 3, C*H*(CH_3)$_2$, carbonate), 4.56 (h, $^3J_{HH}$ = 6.8, 2, C*H*(CH_3)$_2$, Ph), 1.35 (d, $^3J_{HH}$ = 6.8, 12, CH(CH_3)$_2$, Ph), 1.00 (d, $^3J_{HH}$ = 6.2 Hz, 6, CH(CH_3)$_2$ ax, carbonate) and 0.93 (m, 12, CH(CH_3)$_2$ eq, carbonate). ^{1}H NMR (300 MHz, toluene-d$_8$, 343 K): δ 5.31 (h, $^3J_{HH}$ = 6.2, 3, C*H*(CH_3)$_2$, carbonate), 0.92 (s, $^3J_{HH}$ = 7.2 Hz, C*H*(CH_3)$_2$, carbonate). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 228.3 (S_2C ax), 227.5 (S_2C eq), 159.5 (C *ipso*), 152.6 (*o*-C), 123.4 (*m*-C), 77.2 (*C*H(CH_3)$_2$ ax, carbonate), 76.8 (*C*H(CH_3)$_2$ eq, carbonate), 29.7 (*C*H(CH_3)$_2$ Ph), 25.4 (CH(*C*H$_3$)$_2$ Ph) and 21.4–20.1 (CH(*C*H$_3$)$_2$, carbonate). Found: C, 45.7; H, 5.9; N, 2.3. $C_{24}H_{38}NO_3S_6V$ requires C, 45.6; H, 6.0; N, 2.2%.

[V(NC$_{10}$H$_{15}$)(S$_2$CO^{i}Pr)$_3$] 5b. Prepared as for complex **4**, using **1b** (0.24 g, 0.6 mmol) and KS_2CO^iPr (0.31 g, 1.8 mmol) in THF (30 ml), as orange crystals in 60% yield. ^{1}H NMR (300 MHz, toluene-d$_8$, 298 K): δ 5.38 (h, $^3J_{HH}$ = 6.1, 2, C*H*(CH_3)$_2$), 5.27 (h, $^3J_{HH}$ = 6.1 Hz, 1, C*H*(CH_3)$_2$), 2.08 (br, 6, CH_2, $C_{10}H_{15}N$), 1.72 (br, 3, CH, $C_{10}H_{15}N$), 1.29 (br, 6, CH_2, $C_{10}H_{15}N$) and 1.02 (br, 18, CH(CH_3)$_2$). ^{13}C-{^{1}H} NMR (75 MHz, toluene-d$_8$, 298 K): δ 227.7 (S_2C), 227.1 (S_2C), 81.0 (C, $C_{10}H_{15}N$), 76.6 (*C*H(CH_3)$_2$), 76.0 (*C*H(CH_3)$_2$), 42.4 (CH_2, $C_{10}H_{15}N$), 36.0 (CH_2, $C_{10}H_{15}N$), 29.4 (CH, $C_{10}H_{15}N$) and 21.5 (CH(*C*H$_3$)$_2$). Found: C, 45.1; H, 5.9; N, 2.3. $C_{22}H_{36}NO_3S_6V$ requires C, 43.6; H, 5.9; N, 2.3%.

[V(2,6-^{i}Pr$_2$C$_6$H$_3$N)(S$_2$CS^{i}Pr)$_3$] 6a. Prepared as for complex **4**, using **1a** (0.34 g, 0.80 mmol) and NaS_2CS^iPr (0.57 g, 2.6 mmol) in THF (25 ml), as orange crystals in 45% yield. ^{1}H NMR (500 MHz, toluene-d$_8$): δ 6.83 (d, $^3J_{HH}$ = 8, 2, *m*-CH), 6.76 (t, $^3J_{HH}$ = 8, 1, *p*-CH), 4.49 (h, $^3J_{HH}$ = 7, 2, C*H*(CH_3)$_2$, Ph), 3.83 (h, $^3J_{HH}$ = 7, 3, C*H*(CH_3)$_2$, carbonate), 1.35 (d, $^3J_{HH}$ = 7, 12, CH(CH_3)$_2$, Ph), 1.04 (d, $^3J_{HH}$ = 7, 6, CH(CH_3)$_2$ ax, carbonate) and 0.95 (d, $^3J_{HH}$ = 7 Hz, 12, CH(CH_3)$_2$ eq, carbonate). ^{13}C-{^{1}H}

Table 2 Crystallographic data for complex **3a**

Formula	$C_{27}H_{29}N_4S_6V$
M	652.84
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	25.913(3)
b/Å	10.0434(12)
c/Å	27.989(3)
β/°	106.690(2)
U/Å^3	6977(2)
Z	8
D_c/g cm^{-3}	1.243
μ(Mo-Kα)/cm^{-1}	0.665
T/K	148(2)
λ(Mo-Kα)/Å	0.71073
Unique reflections, $I \geq 2\sigma(I)$	4005
R	0.0782
R'	0.2087

NMR (75 MHz, toluene-d_8): δ 244.4 (S_2C eq), 241.4 (S_2C ax), 159.4 (C *ipso*), 152.6 (*o*-C), 122.9 (*m*-C), 41.4 ($CH(CH_3)_2$ ax, carbonate), 39.7 ($CH(CH_3)_2$ eq, carbonate), 29.6 ($CH(CH_3)_2$, Ph), 24.8 ($CH(CH_3)_2$, Ph), 22.1 ($CH(CH_3)_2$ ax, carbonate) and 21.9 ($CH(CH_3)_2$ eq, carbonate). Found: C, 42.3; H, 5.9; N, 2.0. $C_{24}H_{38}NS_9V$ requires C, 42.4; H, 5.6; N, 2.1%.

[V(NC$_{10}$H$_{15}$)(S$_2$CS^{i}Pr)$_3$] 6b. Prepared as for complex **4**, using **1b** (0.21 g, 0.50 mmol) and NaS_2CS^iPr (0.26 g, 1.5 mmol) in THF (40 ml), as orange crystals in 30% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 3.93 (br, 3, $CH(CH_3)_2$), 2.15 (br, 6, CH_2, $C_{10}H_{15}N$), 1.70 (br, 3, CH, $C_{10}H_{15}N$), 1.28 (br, 6, CH_2, $C_{10}H_{15}N$) and 1.02 (br, 18, $CH(CH_3)_2$). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6): δ 244.3 (S_2C), 241.4 (S_2C), 81.0 (C, $C_{10}H_{15}N$), 42.2 (CH_2, $C_{10}H_{15}N$), 41.4 ($CH(CH_3)_2$), 39.4 ($CH(CH_3)_2$), 35.5 (CH_2, $C_{10}H_{15}N$), 29.0 (CH, $C_{10}H_{15}N$), 22.3 ($CH(CH_3)_2$) and 21.6 ($CH(CH_3)_2$). Found: C, 40.8; H, 5.6; N, 2.2. $C_{22}H_{36}NS_9V$ requires C, 40.4; H, 5.5; N, 2.1%.

[V(2,6-^{i}Pr$_2$C$_6$H$_3$N)Cl(acac)$_2$] 7. To a mixture of complex **1a** (0.24 g, 0.57 mmol) and Na(acac) (0.14 g, 1.15 mmol) was added THF (25 ml). The resulting suspension was stirred at room temperature overnight. The volatiles were removed under reduced pressure and the red residue extracted with light petroleum and filtered to remove NaCl. The filtrate was concentrated and cooled to −20 °C. Crystals of **7** were obtained in 54% yield.

Alternatively, to a solution of complex **1a** (0.35 g, 0.83 mmol) in CH_2Cl_2 (25 ml) was added an excess of Hacac (0.3 ml) and the mixture stirred overnight at reflux. The resulting solution was taken to dryness and worked up as stated before. ^{1}H NMR (300 MHz, Cl_3CD): δ 6.98 (d, $^3J_{HH}$ = 7.6, 2, *m*-CH), 6.84 (t, $^3J_{HH}$ = 7.6, 1, *p*-CH), 5.63, 5.52 (s, 1, CH, acac), 4.38 (h, $^3J_{HH}$ = 6.6, 2, $CH(CH_3)_2$), 2.24, 2.12, 2.10, 1.93 (s, 3, CH_3, acac), 1.27, 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6, $CH(CH_3)_2$). ^{13}C-{^{1}H} NMR (75 MHz, Cl_3CD): δ 194.6, 190.1, 189.9, 181.4 (CO, acac), 160.1 (C *ipso*), 153.3 (*o*-C), 129.7 (*p*-C), 122.1 (*m*-C), 102.1, 100.4 (CH, acac), 28.0 (CH_3, acac), 27.6 ($CH(CH_3)_2$), 26.1, 25.6, 24.65 (CH_3, acac), 24.6, 24.2 ($CH(CH_3)_2$). Found: C, 58.3; H, 6.9; N, 3.4. $C_{22}H_{31}ClNO_4V$ requires C, 57.5; H, 6.8; N, 3.1%.

Crystallography

A summary of the fundamental crystal and refinement data is given in Table 2. A crystal was mounted on a Brucker-Siemens Smart CCD detector diffractometer equipped with a low temperature device. Full matrix least-squares refinement was carried out on F^2 for all reflections. Weighted R factor (R') based on F^2, conventional R on F. Most of the calculations were carried out with SMART[23] software for data collection and reduction and SHELXTL[23] for structure solution and refinements.

CCDC reference number 186/1515.

See http://www.rsc.org/suppdata/dt/1999/2893/ for crystallographic files in .cif format.

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