Synthesis, Structural Characterization, and MO Calculations of Vanadium Imido Complexes Containing Bidentate Phosphine Coligands

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Treatment of complex V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3 with 1,2-dimethoxyethane (dme) gives in quasi-quantitative yield the adduct V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3(dme) (**1**). Interaction of **1** with bidentate phosphines gives V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3(P-P) (P-P = depe, **2a**; dppe, **2b**) compounds. An X-ray analysis (monoclinic, space group $P2_1/c$, a = 14.7387(14) Å, b = 10.6738(10) Å, c = 16.999(3) Å, β = 90.954(2)°, Z = 4, R = 0.0544), carried out on complex **2a**, shows a *mer* arrangement of the chloride ligands and a nonsymmetrical coordination of the diphosphine ligand. One of the phosphorus atoms occupies the trans position with respect to the organoimido ligand. MO calculations on the models V(NR)Cl_3($H_2PCH_2CH_2PH_2$) (R = H, C_6H_5) of complex **2a** were performed. The *mer* isomer, which is more stable than the *fac* isomer, shows good agreement with the experimental data.

Introduction

Low metal electronic configurations are characteristic of organoimido complexes.[1,2] On the other hand, early transition metal species in the highest formal oxidation state containing coordinated phosphine ligands are uncommon.[3] Consequently, the number of characterized d^0 imido−phosphine derivatives is quite scarce.

As a continuation of our work on molybdenum imido complexes,[4,5] we decided to explore the chemical reactivity of d^0 vanadium imido compounds versus tertiary phosphines. In this paper, the preparation of vanadium imido complexes containing bidentate phosphine coligands V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3(P-P) (P-P = depe, **2a**; dppe, **2b**) and the structural characterization of **2a** are reported. As far as we know, this is the first group 5 imido complex containing a phosphine functionality occupying the trans position with respect to the organoimido ligand. Because of the novelty of this compound, a theoretical analysis of its molecular properties based on density functional theory (DFT) calculations is also reported. The *mer* isomer of the models V(NR)Cl_3($H_2PCH_2CH_2PH_2$) (R = H, C_6H_5), which is more stable than the *fac* isomer, shows good agreement with the experimental data.

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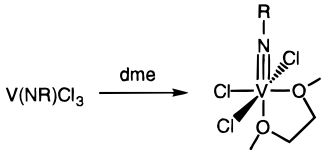
Results and Discussion

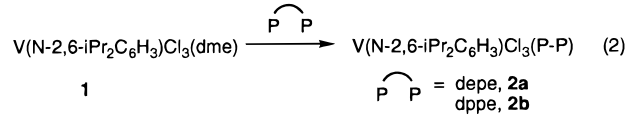
Synthesis and Characterization. Crystal and Molecular Structure of 2a. Addition of 1,2-dimethoxyethane (dme) to petroleum ether solutions of the V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3 compound[6−8] causes precipitation in an almost quantitative yield of V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3(dme) (**1**) as a brown solid (eq 1). NMR



(1)

R = 2,6-$^{i}Pr_2C_6H_3$, **1**

spectra of **1** are in agreement with this structure and compare well with the NMR data of Ta(NR)Cl_3(dme) (R = 2,6-$^{i}Pr_2C_6H_3$,[9] 1-adamantyl[10]) compounds. The structure proposed (eq 1) is similar to that recently reported for the analogous V(N^{t}Bu)Cl_3(dme)[11] and Nb(N^{t}Bu)Cl_3(dme)[10] derivatives. Addition of bidentate phosphines to THF solutions of **1** produces V(N-2,6-$^{i}Pr_2C_6H_3$)Cl_3(P-P) complexes **2a** and **2b** (eq 2).



(2)

A closely related compound V(N-4-MeC_6H_4)Cl_3(PPh_3), containing only one coordinated phosphine, was reported by Maatta.[8] Complex **2b** was obtained in good yields (70%) as an

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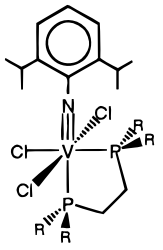
orange solid by precipitation. However, the yields of crystalline **2a** are low. This fact is probably due to a simultaneous reduction−hydrolysis process that occurs during the reaction and the subsequent workup. The isolation of the $VOCl_2$(depe) complex during the crystallization of **2a** confirms this assumption. Similar reduction−hydrolysis processes have been noticed by Cotton and co-workers in the reaction of VCl_4 with phosphines.[12,13] **2a** and **2b** are unstable in the presence of small quantities of air, or prolonged reaction times also decrease the yields.

Both compounds exhibit two broad resonances (caused by unresolved coupling to the vanadium nucleus, $I = {}^7/_2$, and quadrupolar effects) in the $^{31}P\{^1H\}$ NMR spectra, which is characteristic of an AX spin system (for example, δ 14.4 and 48.3, data for **2a**). Their ^1H and $^{13}C\{^1H\}$ NMR spectra are nevertheless quite informative with respect to the structure they exhibit in solution. For example, the C_s symmetry of the molecules of **2a** is manifested by the observation of two different signals for the methyl groups of the depe ligand in either spectrum. The presence of two resonances for the methylene carbon atoms of the phosphine chain in the $^{13}C\{^1H\}$ NMR spectra of both complexes definitively supports structure **I** for compounds **2**.



I

This geometrical disposition is peculiar because a phosphorus atom occupies the trans position with respect to the arylimido ligand. To our knowledge, only five examples of compounds with a coordinated phosphine trans with respect to an organoimido ligand have been structurally characterized for group 6. Four of them are tungsten complexes, namely, W(N-2,6-^{i}-$Pr_2C_6H_3$)Cl_3(dppe),[14] W(NPh)(C≡CPh)$_2$(PhC≡CPh)$(PMe_3)_2$[15] (Nielson and co-workers), and W(NPh)$(R)_2[(Me_3SiN)_2C_6H_4]$-(PMe_3) (R = Cl, Me) (Boncella and co-workers[16]). The other one, recently reported by us,[4] is the somewhat related complex Mo(N-2,4,6-$Me_3C_6H_2$)Cl_3(depe). Therefore, the crystalline depe derivative **2a** was considered a suitable candidate for a solid state structural determination.

The X-ray analysis reveals a pseudooctahedral geometry with a meridional arrangement of the chloride ligands (Figure 1, Table 1).

The main distortion from the octahedral geometry comes from the typical[2] deviations of the N1−V1−P1 angle (95.2(2)°) and the three N1−V1−Cl angles (98.59(13)°, 99.41(13)°, and 99.7-(2)°) from the ideal 90° value. The metal−imido moiety is practically linear (177.0(4)°, V1−N1−C1), and the V1−N1 separation of 1.685(4) Å is in agreement with a vanadium−nitrogen bond order of 3. The bidentate depe ligand is nonsymmetrically coordinated to the metal atom with a normal V1−P1 distance of 2.520(2) Å and an unusually large V1−P2 bond length of 2.642(2) Å. Structurally characterized vanadium−depe complexes display vanadium−phosphorus bond distances in the range 2.50−2.57 Å;[17−19] meanwhile vanadium−phosphorus bond lengths usually cluster around the mean 2.482(5) Å value.[20] Accordingly, the V1−P2 separation of 2.642(2) Å in **2a** can be considered as remarkably large and can be interpreted in terms of the strong trans influence of the imido ligand. Longer V−P bond distances (2.817(3) and 2.826(3) Å) have been reported[21] only in the case of complex {$[(Ph_2P)_2$-$CH]_3V$}$[Li(THF)_4](THF)_2$ and were attributed to crystal packing effects. A similar V−P bond distance is encountered in $VOCl_2$-$(PPh_3)_2$ (2.6217(11) Å),[12] and lower bond lengths were found in two other structurally characterized vanadium(V) imido−phosphine complexes (2.4010(19) Å in CpV(N-2,6-^{i}-$Pr_2C_6H_3$)-(CHPh)(PMe_3)[7] and 2.529(1) Å in V$(NPMe_2Ph)Cl_3(PMe_2$-$Ph)_2$).[22]

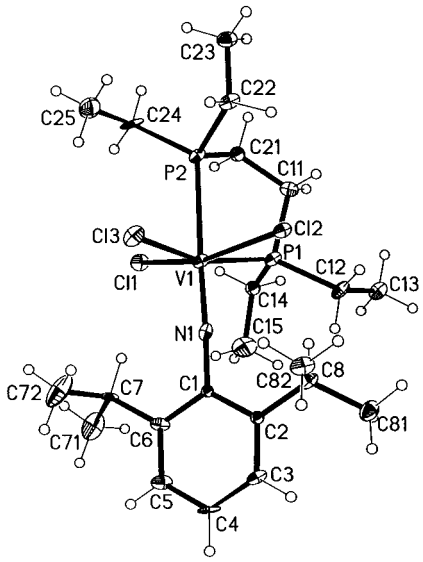


Figure 1. Molecular structure of V(N-2,6-^{i}-$Pr_2C_6H_3$)Cl_3(depe) (**2a**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2a**

V(1)−N(1)	1.685(4)	V(1)−Cl(3)	2.301(2)
V(1)−Cl(1)	2.3204(14)	V(1)−Cl(2)	2.3217(14)
V(1)−P(1)	2.520(2)	V(1)−P(2)	2.642(2)
N(1)−C(1)	1.388(6)		
N(1)−V(1)−Cl(3)	99.7(2)	N(1)−V(1)−Cl(1)	98.59(13)
Cl(3)−V(1)−Cl(1)	97.96(6)	N(1)−V(1)−Cl(2)	99.41(13)
Cl(3)−V(1)−Cl(2)	93.66(6)	Cl(1)−V(1)−Cl(2)	156.57(7)
N(1)−V(1)−P(1)	95.2(2)	Cl(3)−V(1)−P(1)	164.41(7)
Cl(1)−V(1)−P(1)	84.13(5)	Cl(2)−V(1)−P(1)	79.42(5)
N(1)−V(1)−P(2)	173.6(2)	Cl(3)−V(1)−P(2)	86.25(6)
Cl(1)−V(1)−P(2)	78.31(5)	Cl(2)−V(1)−P(2)	82.24(5)
P(1)−V(1)−P(2)	79.02(5)	C(1)−N(1)−V(1)	177.0(4)

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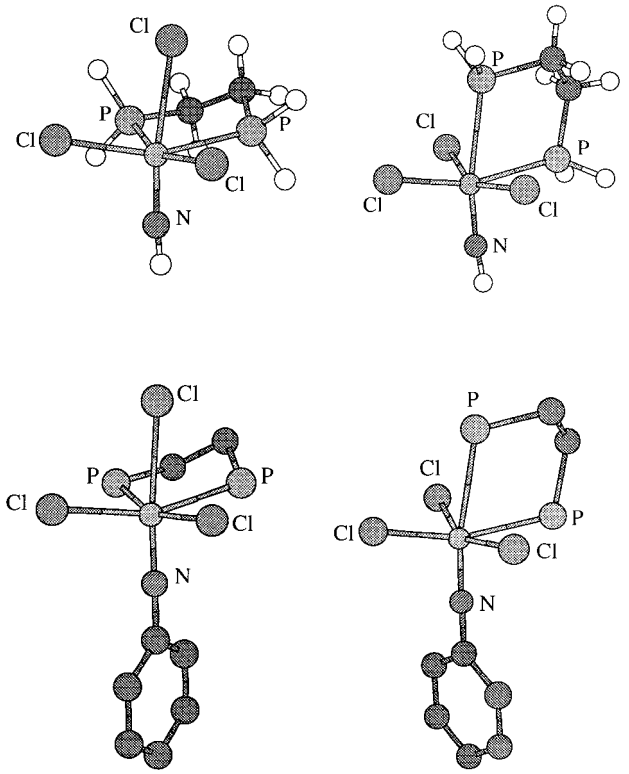


Figure 2. Final optimized geometries of *fac* and *mer* isomers of $V(NR)Cl_3(H_2PCH_2CH_2PH_2)$ (R = H, C_6H_5) models. For R = C_6H_5, hydrogen atoms are not displayed.

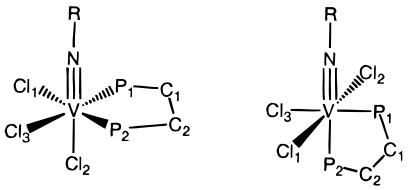
Examples of vanadium complexes containing other triple bonded ligands with a trans phosphine ligand are known for the carbyne functionality (for example, $V(CR)(CO)(dmpe)_2$[23]). However, no example has been reported for an oxo derivative. Efforts are in progress to get new candidates for this geometrical disposition.

Theoretical Calculations on Model Compounds of 2a. To get a deeper insight into the structure of compound **2a** a series of model theoretical calculations were performed. Because of the high number of atoms, and with the aim to speed the calculations, the analysis was undertaken using a model in which the (N-2,6-^{i}Pr$_2$C$_6$H$_3$) ligand was replaced by an NR group, with R = H, C_6H_5. Also, the depe bidentate phosphine was substituted by ($H_2PCH_2CH_2PH_2$).

Two different arrangements were considered for this model compound and correspond to the *fac* and *mer* isomers, respectively, of parent compound **2a**. The final optimized geometries of these isomers are depicted in Figure 2, while selected structural parameters are reported in Table 2. For the sake of comparison, the experimental data are also included in the table. In general, and taking into account that the models are significantly less hindered, one can observe quite a satisfactory agreement between the *mer* and experimental values of geometrical parameters. Bond distances agree within 0.06 Å, while the largest deviation of bond angles appears to be about 6°. The structural data of Table 2 deserve a more careful analysis. Starting with the V−N bond length, it turns out that, whatever the basis set is, this distance is underestimated by 0.04 Å when R = H. This result suggests that such a simple model could not be suitable enough. Actually, when the NH imido ligand is replaced by NC_6H_5, a relaxation of the V−N bond is observed, leading to a better agreement with the experimental value. V−Cl bond distances agree noticeably with the exception of the V−Cl3 one, which is always underestimated by ca. 0.05 Å. Because of this shorter distance, repulsion between the Cl3 atom and imido group increases, leading to larger N−V−Cl3 bond angles. Notice how, disregarding the basis set used in the computations, these angles are found to be about 105° when R = H and, in fact, account for the largest deviations observed in the bond angles. Moreover, it is also worth noting that, for R = C_6H_5, this bond angle lowers according to the drop of the repulsion induced by the lengthening of the V−N bond distance. Concerning the V−P bond lengths, the equatorial V−P1 ones are always found in quite good agreement with the experiment; however, the axial V−P2 distances appear to be systematically overestimated by 0.04−0.07 Å. The best result is obtained with basis II, although the improvement is moderate. A similar trend is observed in the P−C bond distances, on which the use of a better basis set gives rise to a moderately improved agreement. Finally, the C−C distances agree within 0.015 Å. In summary, all of these considerations suggest that the structure of this compound arises from a complex compromise between electronic and steric effects whose modeling slightly depends on the basis set and the nature of the imido group, although the use of NC_6H_5 instead of NH appears preferable.

One of the most outstanding structural aspects of compound **2a** is the large trans influence induced by the imido group. Thus, the V−P2 distance is found to be significantly stressed with respect to a normal V−P bond. In particular, the V−P interatomic distances are 2.520(2) and 2.642(2) Å for cis and trans dispositions, respectively. Such a trans influence is nicely reproduced by the theoretical calculations, which give rise to V−P distances of 2.534 and 2.699 Å. A similar trans influence is observed in the *fac* series, where the V−Cl(trans) bond distance is found to be 0.27−0.28 Å larger that the VCl(cis) one (V−Cl1 = 2.265 Å, V−Cl2 = 2.538 Å, and V−Cl3 =

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) Obtained for *fac* and *mer* $V(NR)Cl_3(H_2PCH_2CH_2PH_2)$ Models



	R = H				R = C_6H_5		
	basis I		basis II		basis I		
	fac	*mer*	*fac*	*mer*	*fac*	*mer*	exptl
V−N	1.654	1.643	1.653	1.642	1.675	1.664	1.685
V−Cl1	2.257	2.344	2.251	2.338	2.265	2.352	2.320
V−Cl2	2.559	2.335	2.545	2.332	2.538	2.337	2.322
V−Cl3	2.251	2.248	2.246	2.242	2.258	2.252	2.301
V−P1	2.494	2.529	2.482	2.511	2.497	2.534	2.520
V−P2	2.492	2.710	2.484	2.689	2.495	2.699	2.642
P1−C1	1.879	1.875	1.869	1.866	1.879	1.876	1.835
P2−C2	1.873	1.883	1.864	1.874	1.873	1.884	1.832
C1−C2	1.554	1.556	1.537	1.538	1.555	1.556	1.541
N−V−Cl1	101.4	98.8	101.4	98.8	98.9	98.0	98.6
N−V−Cl2	161.4	98.4	161.7	98.1	164.7	98.6	99.4
N−V−Cl3	100.9	105.3	101.0	105.8	98.4	103.0	99.7
N−V−P1	91.3	92.6	90.9	91.8	92.1	93.3	95.2
N−V−P2	93.8	168.3	93.3	168.0	96.0	169.5	173.6

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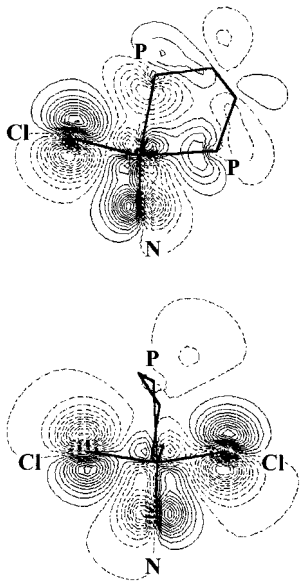

Figure 3. Contour plots for the HOMO (top) and HOMO-1 (bottom) of the model of $V(NH)Cl_3(H_2PCH_2CH_2PH_2)$, showing the two components of the π imido−V bond.

2.258 Å). The origin of the trans influence has been examined in Os nitride[24] and Mo imido[25] complexes and very recently in Ti imido[26] derivatives and has been mainly ascribed to electronic effects. It has been proposed that increasing the bond angles between the imido group and equatorial ligands diminishes the metal−Cl(cis) antibonding interaction, while it favors the π overlap between the metal and imido ligand. Our calculations fully support this interpretation as shown in Figure 3, where the two highest occupied molecular orbitals are depicted. These plots correspond to the orbital contours in the planes N−V−P-P (HOMO, top) and N−V−P−Cl, (HOMO-1, bottom) and show two components of the formally double π N−V bond. It clearly appears that bending away the equatorial ligands allows for some V dp hybridization, increasing the overlap with N orbitals. Concomitantly, the Cl p orbitals lower the antibonding interaction with V d orbitals. However, such a bending increases the Cl−P(trans) antibonding interaction, as clearly observed in the contour plot of the HOMO, where a large contribution of P(trans) is found. This repulsive interaction is again lowered by a lengthening of the V−P(trans) bond distance. Notice on the other hand that such an "umbrella" effect is not exclusive of imido ligands, but it has been observed associated with other transition metal compounds containing multiple bonded ligands,[2] like carbene[27] and analogous derivatives.

Concerning the energetics of the system, the *mer* isomers are always found to be more stable than the *fac* models. The energy differences are computed to be 3.8 (basis I) and 3.7 kcal/mol (basis II) when R = H, while for R = C_6H_5, the stabilization of the *mer* isomer increases up to 5.4 kcal/mol. This result supports the weak dependence on the basis set and is also in agreement with the fact that only the *mer* isomer is isolated. The origin of the larger stability of *mer* isomers can be rationalized analyzing the different way in which formally d^0 metal imido derivatives can bind a phosphine or chloride ligand. For phoshine, the main contribution to the bond is the σ donation toward the metal; however, for chloride, aside from this σ donation, there is an interaction between the filled Cl p orbitals and the metal (π donation). Considering the interaction between a p Cl orbital and d V ones, say $3p_x$ and d_{xz} levels, it turns out that the latter is largely involved in the bond with the imido group, and in fact, the interaction takes place with the V−N π orbital. This consists of a 2-orbital/4-electron interaction which relatively destabilizes the complex. These considerations are illustrated in Figure 4, where the HOMO-3 (bottom) and HOMO-1 (top) orbitals are depicted. As observed, the mix of the 3p Cl orbital and the V−N π orbital leads to *in phase* (mainly V−N π orbital) and *out of phase* (mainly Cl 3p orbital) combinations according to the classical 2-MO/4-electron description.

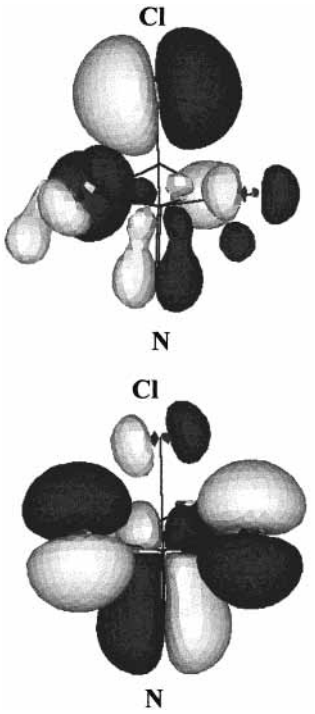

Figure 4. 3D isosurfaces corresponding to the in phase (bottom) and out of phase combinations of the 3p Cl orbital and the N−V π molecular orbital.

Experimental Section

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 were run on Bruker AMX-300 and Bruker AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. The petroleum ether used had bp 40−60 °C.

V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_3$(dme) (1). A solution of the V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_3$ complex (prepared according to the literature procedure[6−8] from $VOCl_3$ (2.19 g, 12.6 mmol) and 2,6-^{i}Pr$_2$C$_6$H$_3$NCO (2.57 g, 12.6 mmol)) in petroleum ether (80 mL) was treated with 1,2-dimethoxyethane (10 mL). The resulting suspension was stirred for a few minutes and filtered. The collected brown solid was washed with petroleum ether and dried under vacuum (90% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 6.87 (d, $^3J_{HH}$ = 7.6 Hz, 2, C*H* meta), 6.63 (t, $^3J_{HH}$ = 7.6 Hz, 1, C*H* para), 5.27 (sept, $^3J_{HH}$ = 6.6 Hz, 2, C*H*(CH$_3$)$_2$), 3.32 (br s, 6, C*H*$_3$O), 3.21 (br s, 4, OC*H*$_2$), 1.41 (d, $^3J_{HH}$ = 6.6 Hz, 12, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 154.9 (s, C ortho), 131.3 (s, C para), 123.3 (s, C meta), 72.1 (br s, CH_3O), 63.0 (br s, OCH_2), 28.1 (s, *C*H-(CH$_3$)$_2$), 25.4 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{16}H_{27}NCl_3O_2V$: C, 45.4; H, 6.4; N, 3.3. Found: C, 44.9; H, 6.2; N, 3.1.

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Synthesis of V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_3$(P-P) (P-P = depe, 2a; dppe, 2b). To a solution of V(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Cl$_3$(dme) (**1**) (0.4 g, 0.95 mmol) in THF (30 mL) was added depe (0.95 mmol, 0.35 M solution in THF). The mixture was stirred at room temperature for 2 h. The volatiles were removed, and the residue was extracted with dme. Cooling to −20 °C gave orange reddish crystals of **2a** (16% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 6.95 (d, $^3J_{HH}$ = 7.6 Hz, 2, C*H* meta), 6.73 (t, $^3J_{HH}$ = 7.6 Hz, 1, C*H* para), 5.15 (sept, $^3J_{HH}$ = 6.7 Hz, 2, C*H*(CH$_3$)$_2$), 1.45 (d, $^3J_{HH}$ = 6.6 Hz, 12, CH(C*H*$_3$)$_2$), 1.09, 0.76 (dt, J_{HP} = 14.7 Hz, $^3J_{HH}$ = 7.5 Hz, 6, PCH$_2$C*H*$_3$), 2.09 (m, 2, C*H*$_2$P), 1.79 (m, 6, C*H*$_2$P), 1.40−1.26 (m, 4, C*H*$_2$P, obscured by Me resonances). ^{31}P{^{1}H} NMR (C_6D_6): AX spin system, δ 48.3 (br), 14.4 (br). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 159.0 (s, C ipso), 154.8 (s, C ortho), 129.4 (s, C para), 122.9 (s, C meta), 28.5 (s, *C*H(CH$_3$)$_2$), 25.2 (s, CH(*C*H$_3$)$_2$), 21.7 (dd, J_{CP} = 23.4 Hz, J_{CP} = 16.1 Hz, P*C*H$_2$CH$_2$P), 19.1 (dd, J_{CP} = 10.3 Hz, J_{CP} = 9.2 Hz, PCH$_2$*C*H$_2$P), 18.3 (d, J_{CP} = 19.4 Hz, P*C*H$_2$CH$_3$), 14.1 (d, J_{CP} = 8.9 Hz, P*C*H$_2$CH$_3$), 7.8, 7.6 (d, J_{CP} = 4.1 Hz, PCH$_2$*C*H$_3$). Anal. Calcd for $C_{22}H_{41}Cl_3NP_2V$: C, 49.0; H, 7.6; N, 2.6. Found: C, 48.8; H, 7.3; N, 2.7.

During the crystallization of **2a** a blue solid precipitated from the mother liquors. Recrystallization from dme gave blue crystals of $VOCl_2$(depe). IR (Nujol): 958 cm^{-1}, ν(V=O). Anal. Calcd for $C_{10}H_{24}Cl_2OP_2V$·dme: C, 45.2; H, 9.1. Found: C, 45.1; H, 9.1.

To a solution of **1** (0.39 g, 0.92 mmol) in THF (15 mL) was added a solution of dppe (0.37 g, 0.92 mmol) in THF (15 mL). The mixture was stirred at room temperature for 2 min, and the volatiles were removed. The residue was washed several times with Et$_2$O and dried under vacuum. Crude **2b** was obtained in 70% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 8.05, 7.49, 6.95 (s, Ph, dppe), 6.77 (t, $^3J_{HH}$ = 7 Hz, 1, C*H* para), 5.02 (sept, $^3J_{HH}$ = 6.3 Hz, 2, C*H*(CH$_3$)$_2$), 2.62 (br s, 4, C*H*$_2$P), 1.30 (d, $^3J_{HH}$ = 6.3 Hz, 12, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): AX spin system, δ 31.9 (br), −1.5 (br). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 161.05 (s, C ipso, N-2,6-^{i}Pr$_2$C$_6$H$_3$), 156.2 (s, C ortho, N-2,6-^{i}Pr$_2$C$_6$H$_3$), 142.1−124.1 (several s, Ph, dppe), 129.4 (s, C para, N-2,6-^{i}Pr$_2$C$_6$H$_3$), 122.85 (s, C meta, N-2,6-^{i}Pr$_2$C$_6$H$_3$), 28.75 (s, *C*H(CH$_3$)$_2$), 24.8 (s, CH(*C*H$_3$)$_2$), 20.2 (br, P*C*H$_2$CH$_2$P). Anal. Calcd for $C_{38}H_{43}NCl_3P_2V$: C, 62.2; H, 5.9; N, 1.9. Found: C, 60.7; H, 5.6; N, 1.6. No satisfactory analytical data (C percentage) were obtained for this compound.

Computational Details. The electronic structure and geometries of these models were computed within the density functional theory using gradient corrected functionals. In particular, we employed the Becke exchange[28] with the Perdew−Wang correlation functional.[29] The effective core potential (ECP) approximation of Stevens et al. was used.[30,31] For V atom, the electrons described by the ECP were those of 1s, 2s, and 2p shells, while for 3s, 3p, and valence electrons a basis set of sp type was used with the contraction (8s8p6d)/[4s4p3d]. For P, Cl, N, and C two different approaches were used. In the first, inner electrons were also described through an ECP, and valence electrons were accounted for using a (4s4p)/[2s2p] basis set enlarged with d polarization functions (basis I). In a second series of calculations intended to test the stability of the results against the basis set, these atoms were treated using the all-electron 6-311G(d) basis set (basis II). For H atoms, the standard (4s)/[2s] DZ basis set was used. All of the calculations were performed using the Gaussian-94 package.[32]

Table 3. Crystallographic Data for **2a**

formula	$C_{22}H_{41}Cl_3NP_2V$
fw	716.14
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	14.7387(14)
b (Å)	10.6738(10)
c (Å)	16.999(3)
β (deg)	90.954(2)
V (Å^3)	2673.8(6)
Z	4
D_{calc} (g cm^{-3})	1.338
μ (mm^{-1})	0.801
T, K	153(2)
λ (Å)	0.710 73
Θ range (deg)	2.65−22.99
R^a	0.0544
R_w^{b}	0.1046

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

X-ray Diffraction Study of Complex 2a. A summary of the fundamental crystal data is given in Table 3. A red crystal showing well-defined faces was mounted on a Brucker-Siemens Smart CCD diffractometer equipped with a low-temperature device and normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation) operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of two exposure sets. Each exposure of 10 s covered 0.3° in ω. The unit cell dimensions were determined by a least squares refinement using 121 reflections with $I > 20\sigma$ and $6° < 2\theta < 46°$. The crystal to detector distance was 6.05 cm. Coverage of the unique set was over 92% complete to at least 23° in θ. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for V, Cl, and P were taken from the *International Tables for X-Ray Crystallography*.[33] The structure was solved by Multan and Fourier methods. Full matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. H atoms were included in their calculated positions. Refinement was on F^2 for all reflections. Weighted R factors (R_w) and all goodness of fit S are based on F^2, and conventional R factors (R) are based on F. Most of the calculations were carried out with SMART[34] software for data collection and for data reduction, and SHELXTL[34] for structure solution and refinements.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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