MO Rationalization of the Synthesis and Structure of $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl(CO)_2(PMe_3)_2$ Complex

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The sodium amalgam reduction of the compound $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_3(dme)$ in the presence of PMe_3, under CO (2−3 atm), gives the complex $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl(CO)_2(PMe_3)_2$ (**1**). Spectroscopic data for **1** suggest a *trans, trans* configuration of the CO and PMe_3 ligands. Density functional theory (DFT) calculations were carried out in order to verify the proposed structure of **1**. The adoption of the *trans,trans* geometry is preferred on the basis of steric arguments. DFT studies of the last steps in the reduction reaction that yields **1** also support the preferential formation of the *trans,trans* isomer.

Introduction

Research on transition metal complexes containing organoimido ligands has received great impetus in the last few decades due to the importance of these compounds as intermediates and catalysts in a range of reactions.[1,2] In particular, the study of imido vanadium chemistry, which was initiated principally by Preuss and co-workers[3−10] and Maatta and co-workers,[11−14] has attracted considerable attention recently, both from theoretical[15,16] and experimental[17−25] point of views. Although an important amount has been published[3−14,17−30] about the chemistry of d^0 imido vanadium complexes, only a few works have been concerned with d^2 species. The first imido complex of trivalent vanadium, namely $CpV(NC({}^tBu){=}CH{}^tBu)(dmpe)$, was reported some years ago by Teuben and co-workers.[31] More recently, the same authors reported[32] several d^2-imido vanadium derivatives starting from $CpV(NAr)(PMe_3)_2$.

Recently, we have described[33,34] the synthesis and characterization of several d^0-imido vanadium complexes, and as a continuation of these findings, we have explored their reduction reactions toward d^2 compounds. In this paper, we report the preparation and characterization of $V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl(CO)_2(PMe_3)_2$ (**1**), an example of a d^2-imido vanadium complex without the stabilizing aid of the cyclopentadienyl ligand. Density functional theory (DFT) studies were carried out with the aim of corroborating the *trans,trans* geometry of this complex and to account for the ultimate steps in the mechanism of the reduction that shows **1** as the preferred *trans,trans* isomer.

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Experimental Section

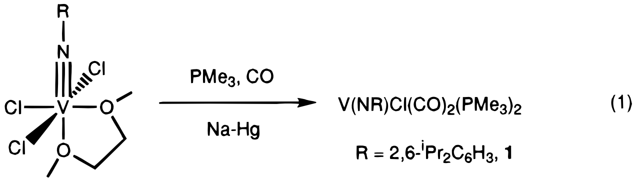
All preparations and other operations were carried out under a dry oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Solvents were scrupulously dried and degassed before use. Microanalyses were carried out by the Microanalytical Service of the IIQ (Sevilla). Infrared spectra were recorded on a Perkin-Elmer model 883 spectrophotometer. ^1H, ^{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. The compound $V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_3(dme)$ was prepared according to the literature.[34]

$V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl(CO)_2(PMe_3)_2$ (1). PMe_3 (3 equiv) was added to a solution of $V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_3(dme)$ (0.5 g, 1.18 mmol) in THF (20 mL), and the resulting mixture was transferred to a pressure vessel containing sodium amalgam (1%, 2 equiv of Na). The vessel was pressurized with 2−3 atm of CO and the reaction stirred for 4−5 h at room temperature. The resulting mixture was centrifuged, and the volatiles were removed under reduced pressure. The residue was extracted with light petroleum. The solvent was partially removed and the resulting reddish-orange solution cooled at −20 °C to give brownish-orange crystals of **1** (0.27 g, 49% yield). Recrystallization of **1** was carried out better under a CO atmosphere. IR (petroleum ether): 2024 w, 1950 s cm^{-1}, $\nu(CO)$. IR (Nujol): 1938 s br cm^{-1}, $\nu(CO)$. ^1H NMR (500 MHz, C_6D_6): δ 6.88 (d, $^3J_{HH} = 7.1$ Hz, 2, C*H* meta), 6.82 (t, $^3J_{HH} = 7.1$ Hz, 1, C*H* para), 3.90 (sept, $^3J_{HH} = 6.6$ Hz, 2, $CH(CH_3)_2$), 1.22 (d, $^3J_{HH} = 6.6$ Hz, 12, $CH(CH_3)_2$), 1.20 (symmetric m, 18, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 0.8 (br plateau, $\Delta\nu = 1660$ Hz). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 144.2 (s, C ortho), 123.4 (s, C para), 122.4 (s, C meta), 27.2 (s, $CH(CH_3)_2$), 23.6 (s, $CH(CH_3)_2$), 17.2 (m, PMe_3). All attempts made to obtain microanalytical data on this compound have proved unsuccessful, the C percentage always being out of the accepted range. The following are the best set of data obtained. Anal. Calcd for $C_{20}H_{35}NClO_2P_2V$: C, 51.1; H, 7.5; N, 3.0. Found: C, 49.0; H, 7.9; N, 3.1.

Computational Details. The electronic structure and geometries were computed within the density functional theory using generalized gradient-corrected functionals. In particular, for the exchange we employ the hybrid Becke[35] three-parameter functional, with the Lee et al.[36] correlation functional. The effective core potential (ECP) approximation of Hay and Wadt was used to describe the inner electrons of V (small core[37]), P, and Cl atoms,[38] while for the valence, a double-ζ basis set was employed.[37,38] For N, C, and H atoms, the standard double-ζ basis set of Dunning was used.[39] The basis set of P, Cl, N, and C was enlarged with a set of d polarization functions. All the calculations were performed using the Gaussian-94 package.[40]

Results and Discussion

Synthesis and Characterization of the Complex $V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl(CO)_2(PMe_3)_2$ (1). The sodium amalgam reduction of the compound $V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_3(dme)$ in the presence of PMe_3, under CO (2−3 atm), produces a red solution from which it is possible to isolate brownish-orange crystals of the complex $V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl(CO)_2(PMe_3)_2$ (**1**) (eq 1). Similar direct reductions were carried out in the presence of other chemicals, such as PMe_3 and ethylene, PMe_3 and isocyanide, PCy_3 and CO, or depe and CO. In these cases, no isolable vanadium complexes were obtained. Complex **1** is unstable in solution under nitrogen, decomposing to an unidentified paramagnetic product through CO dissociation. The process is partially prevented under a CO atmosphere. This decomposition occurs even in the solid state at 0 °C, and this behavior is similar to that observed for the compounds $V(RC{\equiv}CR')X(CO)_2(PMe_3)_2$.[41] The IR spectrum of **1** displays a strong band at 1938 cm^{-1} ($\nu(CO)$, Nujol). This value fits well within the $\nu(CO)$ range (1901−1928 cm^{-1}, pentane) reported for $V(RC{\equiv}CR')X(CO)_2(PMe_3)_2$ compounds, and it is higher than that of $CpV(N\text{-}2,6\text{-}^iPr_2C_6H_3)(CO)(PMe_3)$[32] (1885 cm^{-1}). The shift to high frequency in **1** with respect to the latter complex is ascribed to the presence of two CO ligands sharing the back-donation from the d^2-vanadium center. Although petroleum ether solutions of **1** display a weak additional CO absorption at 2024 cm^{-1}, the presence of only one band in the solid-state IR agrees with a mutually *trans* disposition of the carbonyl groups.



The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a very broad ($\Delta\nu = 1660$ Hz) plateau-form resonance for the phosphorus atoms caused by the unresolved coupling to the vanadium nucleus ($I = 7/2$) and quadrupolar relaxation effects. ^1H and $^{13}C\{^1H\}$ NMR spectra show, besides the typical signals due to the arylimido ligand, symmetric second-order multiplets for the PMe_3 groups. The analysis[42] of these signals gives no decisive information about the disposition of the PMe_3 ligands. Considering that the CO resonances were not observed in the $^{13}C\{^1H\}$ NMR spectrum, on the basis of the NMR data no absolute structural assignment can be conclusively proposed for **1**. Although both *trans,trans* and *cis,cis* structures can be envisaged, spectroscopic data accommodate the *trans,trans* structure better (see Chart 1).

MO Study of the Structure of 1. To assess the structure of compound **1**, a theoretical analysis carried out at the DFT−B3LYP level of theory was performed. In a first stage, and with the aim of speeding calculations, a simple model in which the arylimido, $N\text{-}2,6\text{-}^iPr_2C_6H_3$, and PMe_3 ligands were replaced by NH and PH_3 groups was considered. However, geometry optimization of the *trans,trans* and *cis,cis* isomers (hereafter simply denoted as *trans* and *cis*) led to structures that virtually had the same energy. That is why we designed

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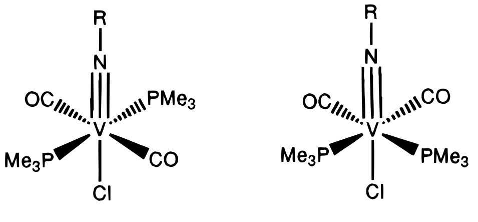
Chart 1



trans,trans-**1** *cis,cis*-**1**

Table 1. Relative Energies (kcal/mol) of *cis* and *trans* $V(NR')Cl(CO)_2(PR_3)_2$ Isomers

R	R′	*cis*	*trans*
H	H	0	−0.1
	Ph	−0.3	0
	$2,6\text{-}Me_2C_6H_3$	0	−0.5
Me	H	0	−3.4
	Ph	0	−3.6
	$2,6\text{-}Me_2C_6H_3$	0	−4.9

a series of models in which the complexity of imido and phosphine ligands was gradually increased. These models may be summarized as $V(NR')Cl(CO)_2(PR_3)_2$, where R = H and Me, and R′ = H, C_6H_5, and $2,6\text{-}Me_2C_6H_3$. The whole set of possible combinations was fully optimized, and their relative energies for *cis* and *trans* isomers are reported in Table 1. Other possible structures, with a CO (π-acceptor) ligand in *trans* position with respect to the imido functionality or with the chloride (formally π-donor) in *cis* position with respect to the imido group, were not considered due to unfavorable electronic reasons.

Inspection of Table 1 shows that when PH_3 ligands are used in the models, *cis* and *trans* isomers are found to be of almost the same energy, whatever the imido substituent is. This result suggests that the relative stability of one of the isomers, if any, has to be originated by the steric interaction arising from a *cis* arrangement of phosphine ligands. In fact, it is sufficient to include the PMe_3 ligands to stabilize one of the isomers, the *trans* one. Notice, on the other hand, how the stabilization remains sensitively the same when the imido group is either NH or NPh, increasing by roughly 1 kcal/mol for $2,6\text{-}Me_2C_6H_3$. The reason for this is the differential increment in the steric repulsion between the methyl groups bound to the apical phenyl group and the equatorial *cis* PMe_3 ligands, as can be observed in Figure 1, where the optimized geometries of some relevant models are reported. In summary, our calculations show that the preferred structure corresponds to a *trans* arrangement of equatorial ligands and that the driving effect is the additional steric interaction between the two PMe_3 ligands. This interaction is expected to be even larger than usual because of the umbrella effect[2,34] commonly observed in imido compounds, as we will see shortly.

An examination of the optimized geometries of Figure 1 shows that the aryl group tends to eclipse the CO ligands in the *trans* isomers, while for the *cis* ones, the more stable geometry is that in which the aromatic plane bisects the P−V−P (or C−V−C) angles. However, it is worth noting that our calculations show that the rotation of the aryl ring is associated with a relatively flat potential surface, in agreement with the almost free rotation experimentally observed in **1** (only one set of signals was observed in the NMR spectra for the two ^{i}Pr groups) and in other imido complexes.[43] Also, when the bulky $N\text{-}2,6\text{-}Me_2C_6H_3$ ligand is considered in the *trans* isomer, the aryl plane appears to be slightly rotated with respect to the C−V−C one, showing that the minimum structure arises from a compromise between the interaction of the apical methyls and CO and PMe_3 ligands.

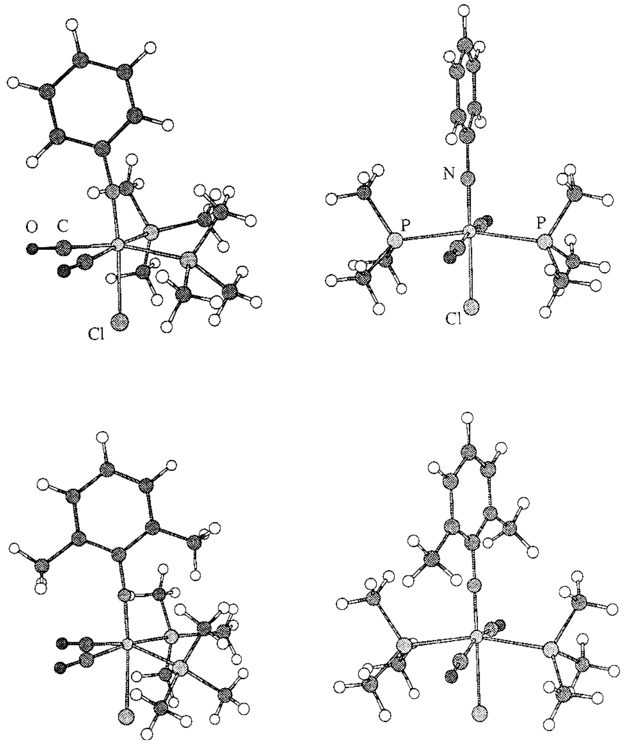


Figure 1. Optimized structures of the *cis* (left) and *trans* (right) $V(NR')Cl(CO)_2(PMe_3)_2$ isomers (R′ = Ph, up, and $2,6\text{-}Me_2C_6H_3$, down).

A more detailed analysis of the molecular structure can be performed from the data collected in Table 2, where some relevant structural parameters for the *trans* series have been reported. The computed V−N bond distance ranges from 1.658 to 1.684 Å, in agreement with experimental data of related imido vanadium derivatives (V−N bond lengths range 1.59−1.78 Å,[44] mean value of 1.652(6) Å). Notice how whatever the PR_3 group is, on going from NH to NPh or $2,6\text{-}Me_2C_6H_3$, it gives rise to a lengthening of this bond distance, reflecting the weakening of the V≡N triple bond due to the delocalization over the aryl ring. In its turn, the V−P bond distance is found to be almost independent of the nature of the N substituent, although it appears to be longer in the PMe_3 series according to the larger steric repulsion. Concomitantly, and because of the lowering of the steric hindrance, the V−C bond distances in that series are computed to be slightly shorter. Finally, the V−Cl distances are found to be noticeably larger than the usually observed value for this bond. This result, together with the fact that the N−V−C and N−V−P

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[43] See for example: Montilla, F., Galindo, A., Carmona, E., Gutiérrez-Puebla, E. and Monge, A. *J. Chem. Soc., Dalton Trans.* **1998**, 1299, and references therein.

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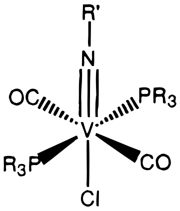
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) Obtained for *trans,trans* V(NR′)Cl(CO)$_2$(PR$_3$)$_2$ Models



	R = H			R = Me		
	R′ = H	R ′= Ph	R′ = Me$_2$C$_6$H$_3$	R′ = H	R′ = Ph	R′ = Me$_2$C$_6$H$_3$
V−N	1.658	1.679	1.680	1.662	1.680	1.684
V−P	2.473	2.474	2.473	2.488	2.489	2.490
V−C	2.002	1.995	1.998	1.992	1.990	1.988
V−Cl	2.462	2.456	2.464	2.496	2.480	2.497
N−V−C	94.9	93.7	96.6	94.3	94.7	97.1
N−V−P	98.6	99.8	98.9	98.2	97.6	98.8

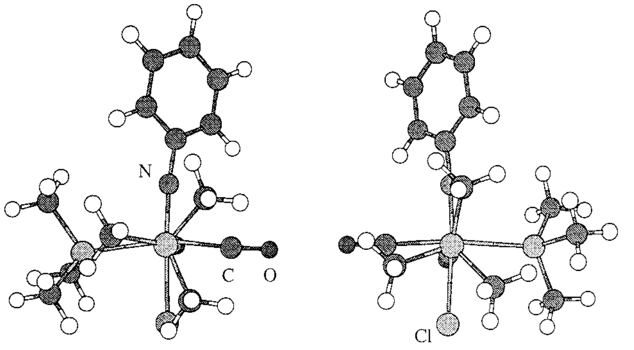
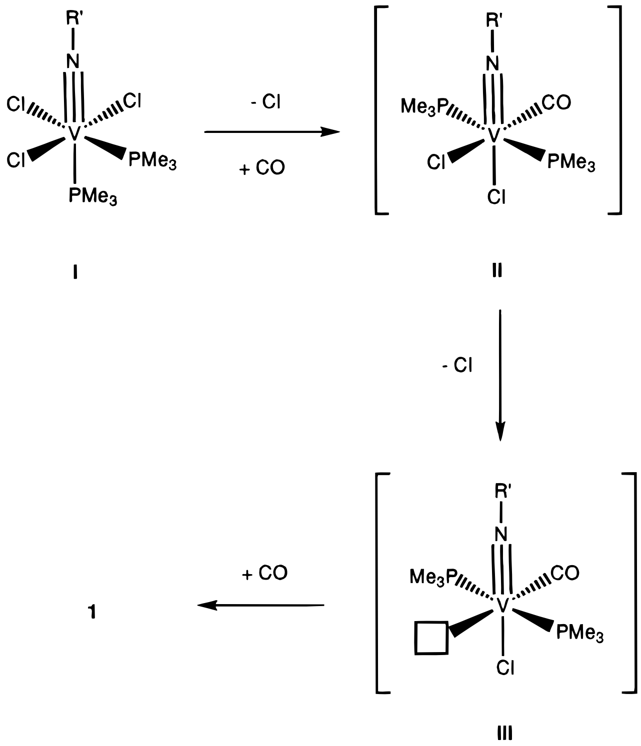


Figure 2. Projections of the optimized *cis* isomer of the model V(NPh)Cl(CO)$_2$(PMe$_3$)$_2$ along the P−V vectors showing the steric interaction between the PMe$_3$ and chloride ligands.

are larger than 90° (umbrella effect), is reflecting the well-known *trans*-influence induced by the imido ligand.[2,34,45,46] It is worth noting, on the other hand, that such a structural influence is observed in both the *cis* and *trans* isomers. Let us now analyze the relative stabilization of these isomers. As shown in Figure 1, the *trans*-favored structure corresponds to a configuration in which there is a P−C bond eclipsing the N−V vector, while the V−Cl bond is alternated with respect to the other P−C bonds. However, in the *cis* isomer, the methyl groups are arranged in a sort of cog formation in such a way that the ideal eclipsed-alternated relationships cannot be maintained. This geometrical arrangement, viewed in the projections for the V(NPh)Cl(CO)$_2$(PMe$_3$)$_2$ model reported in Figure 2, reveals that beyond the expected interaction between the *cis*-phosphines, there is an additional contribution arising from the steric interaction between the methyl groups and the Cl ligand.

MO Study of the Preferential Formation of the *trans,trans* Isomer. Aside from the larger stability of the *trans* isomer discussed above, we have found it interesting to theoretically analyze the last step in the formation of compound **1**. With this purpose in mind we sketched in Scheme 1 a simplified diagram of the plausible mechanism. Starting from the parent V(N-2,6-$^iPr_2C_6H_3$)Cl$_3$(dme) derivative, addition of PMe$_3$ would lead to compound **I**. A similar complex, V(N-2,6-$^iPr_2C_6H_3$)Cl$_3$(depe), was prepared starting from the same dme compound and structurally characterized by us.[34] Successive dechlorination would give a pentacoordinated vanadium intermediate denoted as **III** in the scheme. Further carbonylation of this intermediate would lead to the desired compound **1**. The proposal of **III** as intermediate is in agreement with the easy CO dissociation experimentally observed in complex **1**, which is prevented under CO atmosphere. According to this scheme, the final structure of the product will depend on the ligand arrangement in the intermediate. To find the structure of this intermediate, several possible starting structures were considered. In these computations and according to the previous section, the models used are those corresponding to the V(NH)Cl(CO)(PMe$_3$)$_2$ formula. Our calculations lead to two final

Scheme 1



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structures formally corresponding to highly distorted trigonal bipyramids, which in fact are rather close to the final *cis* and *trans* isomers of **1**, once a CO ligand was removed. The comparison of their energies shows that the *trans* precursor is 5.4 kcal/mol more stable than the *cis* one. Hence, as our calculations make evident, carbonylation of these species to give compound **1** takes place without an energy barrier; the larger stability of the *trans* precursor would also favor formation of the **1** *trans* isomer. On the other hand, and as a further detail, we also considered the internal conversion between *cis* and *trans* precursors. With this aim, we located the transition state connecting these structures and estimated that the energy barrier for the *cis* → *trans* rearrangement is only 0.9 kcal/mol. These results indicate that under ideal equilibrium conditions at room temperature the main product of the carbonylation would be the *trans* isomer of **1**.

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