MO Rationalization of the Synthesis and Structure of V(η2,N-CR2C6H3)Cl(CO)2(PMe3)2 Complex

Francisco Montilla,† Norge Cruz Hernández,‡ Diego del Río,† Javier Fernández Sanz,*§ Antonio Pastor,† and Agustín Galindo*,†

Departamento de Química Inorgánica, Universidad de Sevilla, Apto 553, 41071 Sevilla, Spain, and Departamento de Química Física, Universidad de Sevilla, 41071 Spain

Received July 1, 1999

The sodium amalgam reduction of the compound V(η2,N-CR2C6H3)Cl(dme) in the presence of PMe3, under CO (2–3 atm), gives the complex V(η2,N-CR2C6H3)Cl(CO)2(PMe3)2 (1). Spectroscopic data for 1 suggest a trans, trans configuration of the CO and PMe3 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-workers3–10 and Maatta and co-workers11–14 has attracted considerable attention recently, both from theoretical15,16 and experimental17–25 point of views.

Although an important amount has been published3–14,17–30 about the chemistry of d0 imido vanadium complexes, only a few works have been concerned with d2 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 reported32 several d2-imido vanadium derivatives starting from CpV(NAr)2(PMe3)2.

Recently, we have described33,34 the synthesis and characterization of several d2-imido vanadium complexes, and as a continuation of these findings, we have explored their reduction reactions toward d2 compounds. In this paper, we report the preparation and characterization of V(η2,N-CR2C6H3)Cl(CO)2(PMe3)2 (1), an example of a d2-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.

Note: The full reference list is not included here. However, the reference numbers correspond to the authors' contributions to the field, as indicated in the text.
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 IQ (Sevilla). Infrared spectra were recorded on a Perkin-Elmer model 883 spectrophotometer. ¹H, ¹³C, and ³¹P NMR spectra were run on Bruker AMX-300 and Bruker AMX-500 spectrometers. ³¹P shifts were measured with respect to external 85% H₃PO₄. ¹³C NMR spectra were referenced using the ¹³C resonance of the solvent as an internal standard but are reported with respect to SiMe₄. The petroleum ether used had bp 40–60 °C. The compound V(N-2,6-iPr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1) was prepared according to the literature.³⁴

(V-2,6-Pr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1), PMe₃ (3 equiv) was added to a solution of (V-2,6-Pr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (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 under a CO atmosphere. IR (petroleum ether): 2024 w, 1950 s cm⁻¹. V(R=C₃H₃) (41) Gailus, H.; Maelger, H.; Rehder, D. Inorg. Chem. 1994, 33, 3074.¹H, ¹³C, and ³¹P NMR spectra were recorded on a Perkin-Elmer model 883 spectrophotometer. ¹H, ¹³C, and ³¹P NMR spectra were referenced using the ¹³C resonance of the solvent as an internal standard but are reported with respect to SiMe₄. The petroleum ether used had bp 40–60 °C. The compound V(N-2,6-iPr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1) was prepared according to the literature.³⁴

Results and Discussion

Synthesis and Characterization of the Complex V(N-2,6-Pr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1). The sodium amalgam reduction of the compound V(N-2,6-Pr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1) was 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 IQ (Sevilla). Infrared spectra were recorded on a Perkin-Elmer model 883 spectrophotometer. ¹H, ¹³C, and ³¹P NMR spectra were run on Bruker AMX-300 and Bruker AMX-500 spectrometers. ³¹P shifts were measured with respect to external 85% H₃PO₄. ¹³C NMR spectra were referenced using the ¹³C resonance of the solvent as an internal standard but are reported with respect to SiMe₄. The petroleum ether used had bp 40–60 °C. The compound V(N-2,6-iPr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1) was prepared according to the literature.³⁴

(V-2,6-Pr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (1), PMe₃ (3 equiv) was added to a solution of (V-2,6-Pr₂C₆H₃)Cl(CO)₂(PMe₃)₂ (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 under a CO atmosphere. IR (petroleum ether): 2024 w, 1950 s cm⁻¹. V(R=C₃H₃) (41) Gailus, H.; Maelger, H.; Rehder, D. Inorg. Chem. 1994, 33, 3074.

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 ligand, N-2,6-Pr₂C₆H₃, and PMe₃ ligands were replaced by NH and PH₃ groups was considered. However, geometry optimization of the trans, trans, 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 ligand, N-2,6-Pr₂C₆H₃, and PMe₃ ligands were replaced by NH and PH₃ groups was considered. However, geometry optimization of the trans, trans, cis, cis isomers (hereafter simply denoted as trans and cis) led to structures that virtually had the same energy. That is why we designed

References:

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-Me$_2$C$_6$H$_3$. 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.

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

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>0</td>
<td>-0.1</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>-0.3</td>
<td>0</td>
</tr>
<tr>
<td>2,6-Me$_2$C$_6$H$_3$</td>
<td>H</td>
<td>0</td>
<td>-0.5</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>0</td>
<td>-3.4</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>0</td>
<td>-3.6</td>
</tr>
<tr>
<td>2,6-Me$_2$C$_6$H$_3$</td>
<td>0</td>
<td>-4.9</td>
<td></td>
</tr>
</tbody>
</table>

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-Me$_2$C$_6$H$_3$. 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 PR$_3$ groups) and in other imido complexes.$^{43}$ Also, when the bulky N-2,6-Me$_2$C$_6$H$_3$ 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.

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 however the PR$_3$ group, which is on going from NH to NPh or 2,6-Me$_2$C$_6$H$_3$, it gives rise to a shortening of this bond distance, reflecting the weakening of the V≡N bond as the result of 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


are larger than 90° (umbrella effect), is reflecting the well-known trans-influence induced by the imido ligand.\(^\text{2,34,45,46}\) 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-\(\text{Pr}_2\text{C}_6\text{H}_3\))Cl(CO)\(_2\)(dme) derivative, addition of PMe\(_3\) would lead to compound 1. A similar complex, V(N-2,6-i-\(\text{Pr}_2\text{C}_6\text{H}_3\))Cl(dpe), was prepared starting from the same dme compound and structurally characterized by us.\(^\text{34}\) 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

<table>
<thead>
<tr>
<th>(R = \text{H})</th>
<th>(R' = \text{H})</th>
<th>(R' = \text{Ph})</th>
<th>(R' = \text{Me}_2\text{C}_6\text{H}_3)</th>
<th>(R = \text{Me})</th>
<th>(R' = \text{H})</th>
<th>(R' = \text{Ph})</th>
<th>(R' = \text{Me}_2\text{C}_6\text{H}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V—N</td>
<td>1.658</td>
<td>1.679</td>
<td>1.680</td>
<td>1.662</td>
<td>1.680</td>
<td>1.684</td>
<td></td>
</tr>
<tr>
<td>V—P</td>
<td>2.473</td>
<td>2.474</td>
<td>2.473</td>
<td>2.488</td>
<td>2.489</td>
<td>2.490</td>
<td></td>
</tr>
<tr>
<td>V—C</td>
<td>2.002</td>
<td>1.995</td>
<td>1.998</td>
<td>1.992</td>
<td>1.990</td>
<td>1.988</td>
<td></td>
</tr>
<tr>
<td>V—Cl</td>
<td>2.462</td>
<td>2.456</td>
<td>2.464</td>
<td>2.496</td>
<td>2.480</td>
<td>2.497</td>
<td></td>
</tr>
<tr>
<td>N—V—C</td>
<td>94.9</td>
<td>93.7</td>
<td>96.6</td>
<td>94.3</td>
<td>94.7</td>
<td>97.1</td>
<td></td>
</tr>
<tr>
<td>N—V—P</td>
<td>98.6</td>
<td>99.8</td>
<td>98.9</td>
<td>98.2</td>
<td>97.6</td>
<td>98.8</td>
<td></td>
</tr>
</tbody>
</table>

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

**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.
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 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.

Acknowledgment. This work was supported by the DGES (PB97-740 and PB98-1125) and Junta de Andalucía.

OM9905052