J. Braz. Chem. Soc., Vol. 11, No. 2, 112-120, 2000.
Printed in Brazil

©2000 Soc. Bras. Química
0103 - 5053 $6.00+0.00

Article

On the Cis → Trans Isomerization of the Square-Planar $[Pt(Cl)(SnCl_3)(PH_3)_2]$ Compound: *Ab Initio* Gas Phase Reaction Mechanism and Solvent Effects Using Continuum Models

Willian R. Rocha[a] ***and Wagner B. de Almeida***[a,b,*]

[a]*Departamento de Química, ICEx, Universidade Federal de Minas Gerais,*
31270-901, Belo Horizonte, MG, Brazil

[b]*Departamento de Química, ICE, Universidade Federal de Juiz de Fora,*
Campus Universitário, Martelos, 36.036-330, Juiz de Fora, MG, Brazil

A isomerização cis → trans do composto quadrático plano d^8 $[Pt(Cl)(SnCl_3)(PH_3)_2]$ foi investigada utilizando-se o nível *ab initio* de cálculo MP4(SDQ)//MP2. As estruturas otimizadas, localizadas na superfície de energia potencial em fase gasosa, indicam que esta reação se processa através de um estado de transição quase-tetraédrico. A influência dos efeitos eletrônicos dos ligantes no mecanismo da reação foi investigada utilizando-se o método de Análise de Decomposição de Carga (CDA), o qual forneceu suporte para a compreensão do forte efeito trans do ligante $SnCl_3$. O efeito devido ao solvente na energia de reação em fase gasosa foi avaliado utilizando-se os modelos contínuos SCRF e IPCM. Em ambos os casos um aumento na barreira de energia para o processo foi observado, sendo que a estabilidade termodinâmica dos isômeros cis e trans foi alterada pela solvatação.

The cis → trans isomerization of the d^8 square planar $[Pt(Cl)(SnCl_3)(PH_3)_2]$ compound was investigated at the MP4(SDQ)//MP2 level of theory. The optimized structures located on the gas-phase potential energy surface indicate that this reaction proceeds through a quasi-tetrahedral transition state. The influence of electronic effects of the ligands on the reaction mechanism was investigated with the Charge Decomposition Analysis (CDA) method, which gave support to understand the strong trans effect of the $SnCl_3$ ligand. The solvent effect on the gas phase energy reaction was evaluated using the SCRF and IPCM continuum models. In both cases, an increase on the energy barrier for the process was observed and, the thermodynamical stability of the cis and trans isomers was changed upon solvation.

Keywords: isomerization, square-planar $[Pt(Cl)(SnCl_3)(PH_3)_2]$, *ab initio*, solvent effects

Introduction

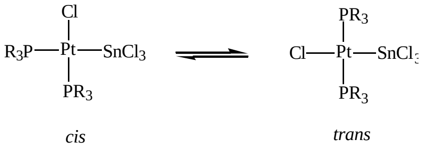
The square planar geometry is quite common amongst compounds of transition elements having d^8 configuration, for example Rh(I), Ir(I), Pd(II), Pt(II) and Au(III). These 16-electron complexes can act as precursors, intermediates or products in several catalytic processes, where they can participate in associative elementary steps (in which they are readily converted into a 18-electrons compound) or in associative reactions, in which they can act as a 14-electrons species[1-3]. The existence of cis → trans isomerism in square planar d^8 complexes is well known. The isomerization mechanism of compounds involving platinum group metals is of particular interest due to their catalytic properties and to the fact that some isomers of this group show antitumor activity[4]. For example the cis isomer of cisplatin, $[Pt(Cl)_2(NH_3)_2]$, is a very active antitumor agent but, the trans isomer is inactive[4a]. On the other hand, the Pd analog of cisplatin, $[Pd(Cl)_2(NH_3)_2]$, is inactive[4b]. Some questions become apparent such as (i) how does the geometric arrangements affect the reactivity? (ii) what is the influence of the ligands and solvent on the relative stability of these isomers and on the isomerization mechanism?

Since the early 50's several studies have appeared, trying to rationalize the factors which affect the relative stability of the isomers, as well as the reaction mechanism, for compounds of the MX_2L_2 type (where M=Pd(II), Pt(II); X=halide ion and L is a phosphine ligand). Indeed several interesting general rules about the solvent effects, electronic

---

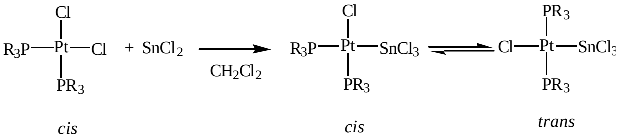
[*] e-mail:wagner@netuno.qui.ufmg.br

effects of the phosphine and the electronegativity of the halides were obtained[5-7]. Most of these studies were carried out for compounds where the Pt-X bond is of the same nature. The situation becomes more challenging in compounds of the $M(PR_3)_2XY$ type where the Pt-X and Pt-Y bonds are dissimilar, as in the process exemplified in Scheme 1. Compounds with the general formulation $[Pt(Cl)(SnCl_3)(PR_3)_2]$, possessing the Pt-Sn bond, have been shown to be highly active and selective in hydroformylation of olefins[8]. These compounds are formed *in situ* when $SnCl_2$ reacts with *cis*-$[Pt(Cl)_2(PR_3)_2]$ through an insertion mechanism.



Scheme 1

The ^{31}P and ^{195}Pt Nuclear Magnetic Resonance (NMR) characterization of the complexes that are formed in solution when $SnCl_2$ reacts with *cis*-$[Pt(Cl)_2(PR_3)_2]$ was studied by Pregosin and Sze[9]. The reaction scheme proposed by these authors is shown in Scheme 2. These authors found that the insertion of $SnCl_2$ into the Pt-Cl bond in *cis*-$[Pt(Cl)_2(PR_3)_2]$ is followed by rapid isomerization.



Scheme 2

The electronic effects of the phosphine and $SnCl_3^-$ ligands on the thermodynamic stability of the isomers in the gas phase, as well as the insertion mechanism, were recently investigated theoretically by our group[10]. The application of this Pt-Sn catalytic system on the first step of the hydroformylation reaction was also investigated theoretically[11].

There is a consensus that three mechanisms can explain the cis→trans isomerism: the consecutive displacement mechanism[3], the Berry pseudorotation mechanism[12,13] and the dissociative pathway[14]. The operating mechanism will depend on the nature of the solvent, electronic effects of the ligands and temperature. The aim of this work is to investigate the reaction mechanism for the cis→trans isomerization showed in Scheme 1, using PH_3 as a model phosphine. The work can be divided in two parts: the first one will focus on the electronic and structural effects of the ligands on the thermodynamic stability of the stationary points located on the Potential Energy Surface (PES) for the gas phase cis→trans isomerization reaction of the $[Pt(Cl)(SnCl_3)(PH_3)_2]$ heterobimetallic compound, as well as to study the nature of the Pt-ligand bonds. The second goal of this work is to evaluate the solvent effects on the gas phase PES for this reaction.

Recently much theoretical effort has been directed to the development of new methodologies to better understand reactive processes in solution. These methods can be classified according to the form they treat explicitly the solute-solvent interactions, such as Molecular Mechanics force fields (MM)[15], Empirical Valence Bond method (EVB)[16] and the whole variation of hybrid Quantum Mechanics/ Molecular Mechanics potentials (QM/MM)[17]. The other models are based on an implicit approach, which treats the solvent as a dielectric continuum medium in which the solute molecule is surrounded by a cavity, such as the Self Consistent Reaction Field method (SCRF)[18], the Polarizable Continuum Model (PCM)[19], the Isodensity Polarizable Continuum Model (IPCM)[20] and the Generalized Conductor-like Screening Model (GCOSMO)[21]. The implicit and explicit approaches to treat the solute-solvent interactions have been successfully applied to understand the role of the solvent in some relevant organic reactions[22]. Despite some progress, the study of solvent effects on reactions involving transition metal compounds remains a challenge. Since many of these compounds are active catalytic species in homogeneous catalysis, which occurs in solution, these methodologies have to be extended to this kind of reactions. The explicit treatment of the solute-solvent interaction when the solute molecule is an organometallic compound is a hard task because of the intermolecular potential parametrization. To the best of our knowledge, the only study reported so far for such kind of reactions is due to Morokuma and co-workers[23], who used the Honda-Kitaura potential[24] to investigate the ligand substitution reaction $[Pt(NH_3)_3(H_2O)]^{2+} + Cl^- \rightarrow [Pt(NH_3)_3Cl]^+ + H_2O$ in solution. Based on the arguments presented in this section, this work can be viewed as an attempt to extend the continuum solvent approaches to study organometallic reactions in solution, as well as to test the applicability of these models to such reactions.

Method of Calculation

Full geometry optimizations were performed at the second-order Møller-Plesset perturbation (MP2) level of theory, without any symmetry constraint, using the LANL2DZ effective core potential (ECP) and valence double-x basis set of Hay and Wadt[25] for the Pt and Sn atoms. For the P and Cl atoms, the split-valence basis set 6-31G(d)[26], which includes a set of five d polarization functions, was used. For the spectator hydrogen atoms, we used a smaller split-valence 3-21G[26] basis set. The valence basis set for the tin atom was augmented with a set of five d polarization functions, with an exponential coefficient of 0.180[27]. All the stationary points located on the gas phase potential energy surface for the *cis*-$[Pt(Cl)(SnCl_3)(PH_3)_2] \rightarrow$ *trans*-$[Pt(Cl)(SnCl_3)(PH_3)_2]$ isomerization reaction (see Figure 1) were characterized as minima or transition state through harmonic vibrational frequency calculations. The calculated harmonic frequencies were also used to compute the entropy contribution to the energy variation. To obtain better energetic results, we carried out single-point calculations at the fourth-order Møller-Plesset perturbation level of theory (MP4) with single, double and quadruple excitations MP4(SDQ) on the MP2 optimized geometries, denominated MP4(SDQ)//MP2, using the same basis set.

The nature of the Metal-Ligand (M-L) bonds was investigated through the Charge Decomposition Analysis (CDA) of Frenking and co-workers[28], in which a Linear Combination of Fragment Orbitals (LCFO) is performed and the charge donation, charge backdonation and repulsive polarization between the molecular fragments are obtained. The CDA method has been shown to be a very suitable method to investigate the nature of M-L interactions[29].

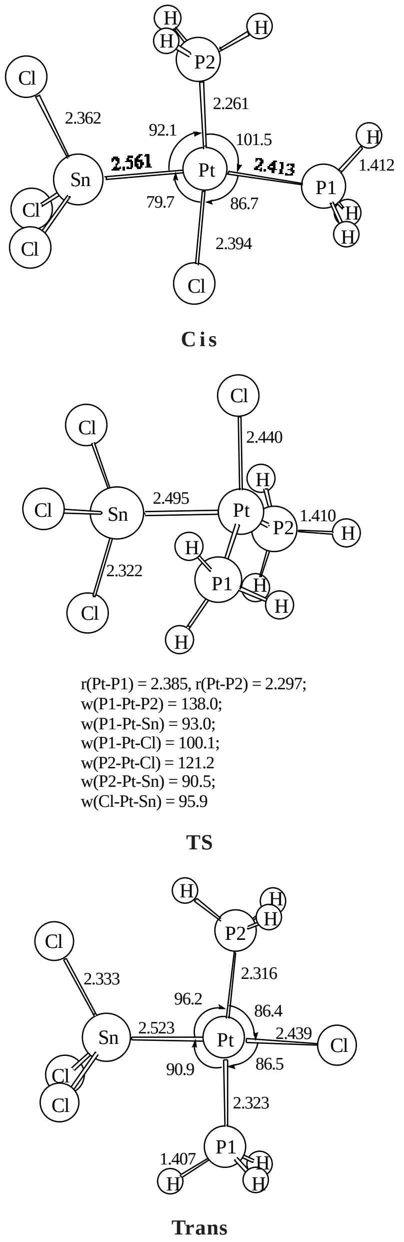
The solvent effects on the reaction energetics were evaluated using the thermodynamic cycle shown in Scheme 3, where the indices g, sol and solv stand for gas phase, solution and solvation, respectively.

$$\begin{tikzcd}
\mathbf{Cis}_{(g)} \arrow[r, "\Delta G^0_{(g)}(\mathbf{Cis\text{-}TS})"] \arrow[d, "\Delta G^0_{solv}(\mathbf{Cis})"] & \mathbf{TS}_{(g)} \arrow[r, "\Delta G^0_{(g)}(\mathbf{TS\text{-}Trans})"] \arrow[d, "\Delta G^0_{solv}(\mathbf{TS})"] & \mathbf{Trans}_{(g)} \arrow[d, "\Delta G^0_{solv}(\mathbf{Trans})"] \\
\mathbf{Cis}_{(sol)} \arrow[r, "\Delta G^0_{sol}(\mathbf{Cis\text{-}TS})"'] & \mathbf{TS}_{(sol)} \arrow[r, "\Delta G^0_{sol}(\mathbf{TS\text{-}Trans})"'] & \mathbf{Trans}_{(sol)}
\end{tikzcd}$$

Scheme 3

What Scheme 3 tells us is that, in order to follow the reaction path in solution, we need to perform vibrational frequency calculations at every point on the gas phase PES necessary for the calculation of the free energy of solvation of each species, that is, of course, a difficult task. What we did was to assume that the gas phase PES has the same profile of the PES in solution so, Scheme 3 can be written as follows:

$$\Delta G^0_{sol}(\text{Cis} \rightarrow \text{Trans}) = \Delta G^0_{sol}(\text{Cis} \rightarrow \text{Trans}) + \left[\Delta E^0_{solv}(\text{TS}) - \Delta E^0_{solv}(\text{Cis})\right] \quad (1)$$



r(Pt-P1) = 2.385, r(Pt-P2) = 2.297;
w(P1-Pt-P2) = 138.0;
w(P1-Pt-Sn) = 93.0;
w(P1-Pt-Cl) = 100.1;
w(P2-Pt-Cl) = 121.2
w(P2-Pt-Sn) = 90.5;
w(Cl-Pt-Sn) = 95.9

Figure 1. MP2 Optimized structural parameters for the *cis*-$[Pt(Cl)(SnCl_3)(PH_3)_2]$ (Cis) isomer, Transition State (TS) and the *trans*-$[Pt(Cl)(SnCl_3)(PH_3)_2]$ (Trans) isomer. Bond lengths are in angstroms and bond angles in degrees.

$$\Delta G^0_{sol}(\text{TS} \rightarrow \text{Trans}) = \Delta G^0_{sol}(\text{TS} \rightarrow \text{Trans}) + \left[\Delta E^0_{solv}(\text{Trans}) - \Delta E^0_{solv}(\text{TS})\right] \quad (2)$$

$$\Delta G^0_{sol}(\text{Cis} \rightarrow \text{Trans}) = \Delta G^0_{sol}(\text{Cis} \rightarrow \text{Trans}) + \left[\Delta E^0_{solv}(\text{Trans}) - \Delta E^0_{solv}(\text{Cis})\right] \quad (3)$$

where DE$^0_{solv}$(N) is the solvation energy of the species N, obtained by the difference between the energy of the species N in gas phase and in solution. As formulated, we only add the difference in solvation energy of the involved species to the gas phase free energy. We can use even classical expressions to estimate the solvation energy of the species involved[30].

Two continuum methods were used to evaluate the solvation energy of the Cis, TS and Trans species [ΔE^0_{solv}(Cis), ΔE^0_{solv}(TS) and ΔE^0_{solv}(Trans)]. These methods have in common the fact that the solute molecule is treated as a charge distribution embedded in a polarizable and continuum dielectric (solvent), characterized by a dielectric constant e. The solvation energy is described as a function of the interaction between the solute charge distribution (ρ) and the induced charges on the dielectric (solvent) (σ) (eq. 4). The solute-solvent interaction is reduced to the determination of the electric potential (Φ_σ) generated by the charge distribution s, which is a consequence of the solvent polarization by the solute (eq. 4).

$$V^{int} = \int_\tau \rho \Phi_\sigma d\tau \qquad (4)$$

The two continuum models used in this work differ in the way that the electrostatic potential Fs is obtained.

The first method used was the SCRF (Self Consistent Reaction Field)[18], in which a homogeneous solute charge distribution is assumed and so, the cavity defined for the solute is symmetric (spherical in this case). In this situation, the electric potential inside this cavity can be expressed as a multipolar expansion (eq. 5) and the solvation energy is given by $E_{solv}=V^{int}/2$.

$$\Phi_{(r)} = \sum_{k=1}^{M} \frac{e_k}{|r-r_k|} + \sum_{k=1}^{M} \left(\frac{e_k}{a}\right) \sum_{1=0}^{\infty} \left[\frac{(l+1)(l-\varepsilon)}{\varepsilon(l+1)+1}\right] \left(\frac{rr_k}{a^2}\right)^l P_l(\cos\theta_k) \qquad (5)$$

The first term on this multipolar expansion(l = 0) leads to the Born equation[18e]:

$$E^{int}_{l=0} = -\frac{1}{2}\left(\frac{q^2}{a}\right)\left(1-\frac{1}{\varepsilon}\right) \qquad (6)$$

in which q is the solute net charge. If neutral molecules are considered, as in the present study, the next term which contributes to the solute-solvent interaction energy is l = 1, which gives the Onsager equation[18f]:

$$E^{int}_{l=1} = -\frac{1}{2}\left[\frac{2(\varepsilon-1)}{2\varepsilon+1}\right]\left(\frac{\mu^2}{\alpha^3}\right) \qquad (7)$$

where ε is the solvent dielectric constant, μ is the solute dipole moment and a is the cavity radius which is occupied by the solute molecule. So, the solute charge distribution is represented by a single-center multipolar expansion, truncated at the dipolar term. As can be seen from equations 5-7, the SCRF model is strongly dependent on the cavity radius assumed for the solute molecule. In this study, the spherical cavity radius for the solute was obtained taking half the maximum distance between non-bonded atoms and adding half the van der Waals radii of the atoms which form this maximum distance. Using this approach, we obtained a cavity radius a_0 of 4.472 Å for the Cis isomer, 4.099 Å for the Trans isomer and 4.196 Å for TS.

The other method used to study the solvent effects was the IPCM (Isodensity Polarizable Continuum Model)[20], which uses a more realistic molecular-shape cavity, derived from the solute electron density. This method overcomes two main deficiencies of the SCRF approach: the assumption of a uniform charge distribution and the symmetric shape of the cavity. In the IPCM method, s is given by eq. 8.

$$\sigma = \frac{\varepsilon-1}{4\pi\varepsilon}\frac{\partial\left(\Phi_\rho^- + \Phi_\sigma^-\right)}{\partial n} \qquad (8)$$

where Φ_ρ^- designates the contribution from the solute charge distribution to the potential and Φ_σ^- is the contribution due to the induced charge distribution on the dielectric. The determination of the electrostatic potential Φ_σ (eq. 9) is carried out self-consistently.

$$\Phi_\sigma(r) = \int\sum\frac{\sigma(s)}{|r-s|}d^2s \qquad (9)$$

In all IPCM calculations an isodensity value of 0.001 electrons Å^{-3} was used. The SCRF and IPCM calculations were carried out in CH_2Cl_2 (e = 9.080) at the MP2 level of theory. The reason to choose this solvent is that the *cis*-[Pt(Cl)($SnCl_3$)(PH_3)$_2$], *trans*-[Pt(Cl)($SnCl_3$)(PH_3)$_2$] isomerization was experimentally observed in dichloromethane[9], so some comparisons can be made. As CH_2Cl_2 is a non-coordinating solvent, consequently no specific solute-solvent interaction can be expected. The system investigated here seems to be good to test the adequacy of continuum solvent approaches to organometallic reactions. All the calculations reported here were performed using the GAUSSIAN-94 package[31].

Results and Discussion

Equilibrium structures, vibrational spectra, electronic effects of the ligands and relative energies in gas phase

Geometries

The MP2 optimized structural parameters obtained for the reactants *cis*-[Pt(Cl)($SnCl_3$)(PH_3)$_2$], (Cis), Transition State (TS), and the product *trans*-[Pt(Cl)($SnCl_3$)(PH_3)$_2$], (Trans) are shown in Figure 1. The main structural parameters obtained are in good agreement with experimental findings. For example, the optimized angles around the platinum metal, for the Cis and Trans isomers are a little distorted from the expected optimal value of 90° for a d^8 square planar compound. The calculated Pt-P bond distances are in agreement with the experimentally observed values of 2.284 Å and 2.303 Å in $[Pt(CH_3)_2(PCH_3Ph_2)_2]$[32] and *trans*-$[Pt(H)(SnCl_3)(PPh_3)_2]$[8e], respectively. The Pt-Sn bond lengths of 2.561 Å in Cis and 2.523 Å in Trans are also in good accordance with the experimental Pt-Sn lengths of 2.634 Å in *trans*-$[Pt(SnCl_3)(COPh)(PEt_3)_2]$[33], 2.601 Å in *trans*-$[Pt(H)(SnCl_3)(PPh_3)_2]$[8e] and 2.600 Å in *trans*-$[Pt(H)(SnCl_3)(PCy_3)_2]$[34]. The Sn-Cl bond distances of 2.362 and 2.333 Å in compounds Cis and Trans agree with the experimental values of 2.283-2.367 Å found in the *trans*-$[Pt(H)(SnCl_3)(PPh_3)_2]$[8e] complex. The structural parameters obtained for the transition state, TS, indicate that it is a quasi-tetrahedral species, arising from an intramolecular rearrangement, which can be viewed as a pseudorotation of the Cl-Pt-P1 angle in Cis, in which the Cl atom stays trans to the $SnCl_3$ group and the phosphines trans to each other. The Pt-P1 bond length of 2.385 Å is shortened from its original value of 2.413 Å in the Cis isomer, and the Pt-Cl bond a little stretched.

In organometallic chemistry the structural parameters are a very rich source of information, from where some electronic effects of the ligands can be qualitatively analyzed, such as the ability of some ligands to labilyze the bond trans to it, the so called trans influence. For example, the Pt-P bond distance trans to the $SnCl_3$ group in the Cis isomer (2.413 Å) is greater than the Pt-P bond in the Trans isomer (2.320 Å), indicating that the $SnCl_3$ group weakens the Pt-P bond trans to it. The Pt-Cl bond in Cis (2.394 Å) trans to the PH_3 ligand is shorter than is the Pt-Cl bond length in Trans (2.439 Å) , also indicating the trans influence of the $SnCl_3$ group. The Pt-Sn bond length of 2.495 Å in TS is shorter than the values found for the Cis (2.561 Å) and Trans (2.523 Å) isomers. This can be qualitatively explained by the fact that in TS the $SnCl_3$ group does not have any ligand directly bonded trans to it and so, it can make a more effective interaction with the platinum atom. What these structural parameters tell us is that the $SnCl_3^-$ ligand is a stronger trans director than the PH_3 ligand and this explains qualitatively why the isomerization takes place. These facts will be discussed quantitatively later.

Vibrational spectra

The calculated vibrational frequencies for the Pt-Cl, Pt-Sn, Pt-P and Sn-Cl bonds are shown in Table 1. The values quoted in Table 1 are in good agreement with experimental values obtained for similar compounds[35]. As can be seen from Table 1, the trans effect of the $SnCl_3$ group is reflected in the vibrational spectra for the Cis and Trans isomers. The stretching frequency ν(Pt-P) for the PH_3 trans to $SnCl_3$ (259 cm^{-1}) in the Cis isomer is shifted 114 cm^{-1} to the low frequency region, compared with the ν(Pt-P) for the Pt-P bond cis to $SnCl_3$. It is interesting to note that the ν(Sn-Cl) and ν(Pt-Cl) appear in the same region of the spectra which makes difficult its experimental attribution[35]. The calculated frequencies show that the most important vibrational frequencies are present in the low frequency region of the infrared (I.R) spectrum, which makes difficult the experimental identification of the Cis and Trans isomers by infrared spectroscopy. The transition state TS has one negative eigenvalue of 80 cm^{-1} and the normal mode associated with this frequency is shown in Figure 2. We have re-optimized the geometry of the TS structure as a minimum energy point on the PES in an attempt to verify if it optimizes to one of the isomers or to a probable intermediate. We found that the initial structure is already a stationary point on the PES and when harmonic frequency analysis is performed we found one small imaginary frequency characterizing a first-order TS

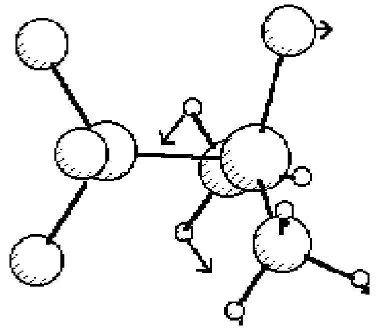


Figure 2. Normal mode exhibiting one negative eigenvalue in the Hessian matrix of TS. The figure shows a pseudorotation of the Cl-Pt-P1 angle (see Figure 1).

Table 1. Main vibrational stretching frequencies for the $[Pt(Cl)(SnCl_3)(PH_3)_2]$ compound *.

Isomer	ν(Pt-Cl)		ν(Pt-P)		ν(Pt-Sn)		ν(Sn-Cl)	
	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
Cis	334	328[c]	259[a] 373[b]	442[e] 427[e]	201	184-230[g]	345	408, 396[h]
Trans	312	206[d]	313	415[f]	206		367	

*All values in cm^{-1}. [a]Pt-P bond trans to $SnCl_3$, [b]Pt-P bond cis to $SnCl_3$. [c]in compound *cis*-$[Pt(Cl)_2(NH_3)_2]$[35], [d]in compound *trans*-$[Pt(Cl)_2(NH_3)_2]$[35]. [e]in compound *cis*-$[Pt(Cl)_2(PEt_3)_2]$[35], [f]in compound *trans*-$[Pt(Cl)_2(PEt_3)_2]$[35], [g]ref. 35, [h]in compound $SnCl_4$[35].

Table 2. Total amount of charge donation, charge backdonation and bond energy obtained by the CDA method, using the MP2 wavefunction.

Fragment		Σ Donation	Σ Backdonation	Interaction energy (kcal mol^{-1})
A	B			
PH_3[a]	$Pt(Cl)(SnCl_3)(PH_3)$	0.577 e	0.202 e	50.9
PH_3[b]	$Pt(Cl)(SnCl_3)(PH_3)$	0.565 e	0.075 e	24.6
PH_3[c]	$Pt(Cl)(SnCl_3)(PH_3)$	0.603 e	0.139 e	44.5

[a] PH_3 cis to $SnCl_3$ in the *cis*-[Pt(Cl)(SnCl3)$(PH_3)_2$], Cis, isomer. [b] PH_3 trans to $SnCl_3$ in the *cis*-[Pt(Cl)$(SnCl_3)(PH_3)_2$], Cis, isomer. [c] PH_3 trans to another PH_3 group in the Trans isomer. [o] 1cal = 4.18J.

structure, in spite of being on a flat region of the PES.

Electronic effects of the ligands

The nature of the M-L interactions was analyzed through the Charge Decomposition Analysis, CDA[28], using the MP2 wavefunction. The results are shown in Table 2. There are several interesting points to be addressed here. First, as can be seen from Table 2, in all combinations analyzed, the magnitude of the charge donation from the PH_3 fragment to the platinum fragment, [Pt(Cl)$(SnCl_3)(PH_3)$], is greater than is the backdonation term, which indicates that the PH_3 fragment is a poor π-acceptor ligand. The comparisons of the extent of backdonated charges of the two PH_3 ligands in the *cis*-[Pt(Cl)$(SnCl_3)(PH_3)_2$], (Cis isomer) can give some ideas, indirectly, about the amount of backdonation of the $SnCl_3$ ligand. For example, the extent of backdonation from the PH_3 fragment trans to the $SnCl_3$ group in the Cis isomer (0.075 e) is lower than backdonation from the PH_3 fragment cis to $SnCl_3$ (0.202 e). This indicates that the $SnCl_3$ fragment is withdrawing electron density from the platinum atom, which in turn, reduces the electron density available for donating to the PH_3 group. So, The PH_3 is competing unevenly with the $SnCl_3$ group to withdraw electron density from the platinum and this explains quantitatively why the isomerization does occur. In fact, the backdonation from the platinum fragment, [Pt(Cl)$(SnCl_3)(PH_3)$], to the PH_3 fragment trans to another PH_3 ligand in the Trans isomer (0.139 e), gives support to this assertion.

A quantitative measurement of the trans effect of the $SnCl_3$ group can be seen through the M-L interaction energy quoted in Table 2. As can be seen, the Pt-P bond energy evaluated for the PH_3 fragment cis to $SnCl_3$ in the Cis isomer (50.9 kcal mol^{-1}) is 26.3 kcal mol^{-1} higher than the Pt-P bond energy calculated for the PH_3 fragment trans to $SnCl_3$ (24.6 kcal mol^{-1}) in this same isomer. That is, the $SnCl_3$ ligand can weaken the Pt-P bond trans to it by ca. 26 kcal mol^{-1}.

Relative energies

The relative energies obtained for the gas phase PES are quoted in Table 3 and the relative thermodynamic properties are shown in Table 4. As can be seen from Table 3, the activation energy, DE$^{\#}$, for the Cis→Trans isomerization is 26.9 kcal mol^{-1} and, the Trans isomer is *ca.* 7.0 kcal mol^{-1} more stable than the Cis one in gas phase. Table 3 also shows that there is no significant change in energy when the electron correlation level is augmented up to fourth order of perturbation theory. The thermodynamic properties, evaluated at room temperature, shown in Table 4 give the following activation parameters for the gas phase Cis→Trans isomerization reaction: $\Delta S^{\#} = 2.0$ cal K^{-1} mol^{-1}, $\Delta H^{\#} = 26.7$ kcal mol^{-1} and $\Delta G^{\#} = 26.1$ kcal/mol. The reaction proceeds with $\Delta G_{Cis\rightarrow Trans}$ of -7.7 kcal mol^{-1}, $\Delta H_{Cis\rightarrow Trans}$ of -7.0 kcal mol^{-1} and $\Delta S_{Cis\rightarrow Trans}$ of 2.8 cal K^{-1} mol^{-1}. From these data, it seems that the enthalpy changes will favor the Trans isomer much more than the entropy changes. This energetic favoring of the Trans isomer in gas phase may be due to internal bond energy changes in the Trans isomer.

Table 3. Relative energies (in kcal mol^{-1})* for the three stationary points located on the gas phase PES for the isomerization reaction.

	Cis[a]	TS	Trans
ΔE_{MP2}	0	27.8	-6.9
Δ_{MP2} + ZPE	0	26.9	-6.9
$\Delta E_{MP4(SDQ)}{}^{b}$	0	27.7	-7.0

[a] Total energies for the Cis isomer are E_{MP2}=-2645.528958 a.u, Zero Point Energy (ZPE)=0.063639 a.u, $E_{MP4(SDQ)}$=-2645.618237 a.u. [b] Single-point energy calculation on the MP2 optimized structures (see text). *1cal=4.18J

Table 4. Zero point energies (ZPE), relative entropies (ΔS), relative energies (ΔE), relative enthalpies (ΔH) and relative free-energy in gas phase for the Cis, Trans and TS structures* (T=298K)

	Cis	TS	Trans
ZPE	39.9	39.1	40.0
ΔS	0	2.0	2.8
ΔH	0	26.7	-6.8
ΔE_{MP2}	0	27.7	-6.9
ΔG [a]	0	26.1	-7.7

*All values are in kcal mol^{-1}, except for the ΔS where cal K^{-1} mol^{-1} is used. (1cal=4.18J) [a] Evaluated including electronic contribution and thermal correction at 298K.

Solution results

The solvation energy of Cis, TS and Trans are shown in Table 5. As can be seen, the SCRF results lead to higher stabilization energies in solution compared with the IPCM results. This can be explained by the fact that in the SCRF approach the solute-solvent interaction is modeled as a dipole-dipole interaction and so, this method has a marked dependence on the solute dipole moment (a quadratic dependence, μ^2), as can be seen in eq. 7. The SCRF results agree with the expected trend in solvation energy, where the species having higher dipole moment will be more stabilized in solution. That is, the Cis isomer ($\mu = 11.684$ debye) is more stabilized than Trans ($\mu = 3.015$ debye) and TS ($\mu = 6.875$ debye). The IPCM gave different stabilization energies in solution, where the Trans isomer is more stabilized than TS. This is because in the IPCM model we do not assume a homogeneous solute charge distribution as in the SCRF method. The more proper atomic charge distribution in IPCM may give atomic charge polarization effects, which give rise to deviations from what would be expected if only the solute total dipole moment is considered. Thus, a species with the smallest overall dipole moment may still have the largest solvent stabilization energy, as in this case. Of course, this different solvent stabilization energies obtained by these two methods, will be reflected on the relative stability of the Cis and Trans isomer in solution, ΔG^0_{sol} (Cis→Trans), as can be seen in the relative free energy in solution, shown in Table 6. In the SCRF model the Trans isomer is 4.8 kcal mol^{-1} more stable than the Cis isomer. The IPCM model gave a reverse stability order, where the Cis isomer is 2.1 kcal mol^{-1} more stable than Trans. These IPCM results are in accordance with the experimental studies of Redfield and Nelson[6]. These authors evaluated the cis→trans relative stability of $[Pd(Cl)_2\{PPh(CH_3)_2\}_2]$ in eleven different solvents and found that the cis isomer was more stable in all solvents analyzed. The assumption of a homogeneous charge distribution, the symmetric form to the cavity and the marked dependence on the solute dipole moment appear to make the SCRF approach more inconsistent than the IPCM. The sensitivity of the SCRF to the cavity radius (with a dependence of a_0^{-3}) is another problem. Different procedures to estimate a_0 can lead to different results. In fact, we have some results showing that in order to reproduce the IPCM results, we have to use explicitly some solvent molecules in the SCRF treatment, an approach called Super-Molecule + SCRF (SM +SCRF)[36]. The two methods agree only on the free energy of activation in solution, where we have an increase, compared with the gas phase results, in both methods (30.1 kcal mol^{-1} in the SCRF approach and 38.9 kcal mol^{-1} in IPCM).

Assuming that the IPCM is our best solution result, we have two factors competing with each other: the strong trans effect of the $SnCl_3$ ligand, which avoids placing the PH_3 ligand trans to it and determines more stabilization of the *trans*-$[Pt(Cl)(SnCl_3)(PH_3)_2]$ isomer in gas phase, and the high dipole moment of the Cis isomer which makes it more stable in solution.

Table 5. Solvation energy of Cis, Ts and Trans obtained by the SCRF and IPCM methods*.

	SCRF[a]	IPCM[b]
Cis (μ = 11.684 debye)	-21.3	-22.5
TS (μ = 6.875 debye)	-17.3	-9.7
Trans (μ = 3.015 debye)	-18.4	-12.7

* All values in kcal mol^{-1} (1cal=4.18J); [a] Cavity radius a_0 of 4.472Å for Cis, 4.099 Å for Trans and 4.196 Å for TS; [b] Isodensity of 0.001e

Table 6. Relative free energies in solution*

	SCRF	IPCM
$DG^{0\#}_{sol}$ (Cis→TS)	30.1	38.9
DG^{0}_{sol} (Cis→Trans)	-4.8	2.1

* all values in kcal mol^{-1} (1cal=4.18J)

As was said before, several mechanisms can explain the cis→trans isomerization reaction in square planar compounds[12]. Most of these mechanisms are solvent assisted. The activation free energy found in this work for the Cis→Trans isomerization of $[Pt(Cl)(SnCl_3)(PH_3)_2]$, without the assistance of specific interactions of the solvent, seems to be high in gas phase ($\Delta G^{\#} = 26.1$ kcal mol^{-1}) and in solution ($\Delta G^{\#}_{SCRF} = 30.1$ kcal mol^{-1}, $\Delta G^{\#}_{IPCM} = 38.9$ kcal mol^{-1}) to explain this isomerization process. Combining the strong trans influence of the $SnCl_3$ ligand, as was shown in this work, and the ability of the Pt-Sn bond to stabilize penta-coordinated intermediates[11], another route for this isomerization reaction could be the displacement of the PH_3 ligand trans to $SnCl_3$ by a solvent molecule, which catalyze the isomerization of another molecule (see Scheme 4)

$$\textit{cis}\text{-}[Pt(Cl)(SnCl_3)(PH_3)_2] \xrightarrow{\text{Solvent}} [Pt(Cl)(SnCl_3)(S)(PH_3)] + PH_3$$

$$\textit{cis}\text{-}[Pt(Cl)(SnCl_3)(PH_3)_2] \xrightarrow{PH_3} \textit{trans}\text{-}[Pt(Cl)(SnCl_3)(S)(PH_3)]$$

Scheme 4

Despite the fact that CH_2Cl_2 is a weakly coordinating solvent, the ability of such kind of solvents to displace strongly coordinated ligands from the transition metal can not be ruled out. For example, the loss of a PPh_3 from Wilkinson's catalyst, $[RhCl(PPh_3)_3]$[37], is a crucial step in the catalytic cycle. Another example where this autocatalytic pathway takes place is in the isomerization of $[PtCl_2(CO)L]$[38], which proceeds spontaneously in several solvents of the weakly coordinating type.

As can be seen, this is the challenge of treating solvent effects in organonometallic reactions, that is, even weakly coordinating solvents can affect drastically the reaction pathway and in fact, all sort of specific interactions (coordination of the solvent, interactions with coordinated ligands through hydrogen bond etc.) must be taken into account and so, the continuum approaches can not explain these phenomena.

Conclusions

In this work we investigated the energetic and reaction mechanism for the gas-phase cis→trans isomerization reaction of $[Pt(Cl)(SnCl_3)(PH_3)_2]$, at the MP4(SDQ)//MP2 level of theory. The solvent effects on the reaction energetic were evaluated using the Self Consistent Reaction Field (SCRF) approach and the Isodensity Polarizable Continuum Model (IPCM). All the stationary points located on the gas-phase potential energy surface were fully optimized. The transition state (TS) structure obtained indicates that this reaction may proceed through a pseudorotation mechanism, leading to a quasi-tetrahedral structure for TS. The activation free energy obtained for the gas-phase reaction was 26.1 kcal mol^{-1}. No significant change in energy was observed when the correlation level is increased up to fourth order. The electronic effects of the ligands on the isomerization reaction were evaluated through the analysis of the MP2 wavefunction with the aid of the Charge Decomposition Analysis (CDA) method. This analysis indicates that $SnCl_3$ is a strong trans director capable of weakening the Pt-P bond trans to it by 26.3 kcal mol^{-1}. The CDA results gave explanation about why this isomerization does occur.

The solvent effects on the energetic of the gas phase reaction were evaluated using the SCRF and IPCM continuum approaches. In both cases an increase in the free energy of activation was observed ($DG^{\#} = 30.1$ kcal mol^{-1} using the SCRF approach and $DG^{\#} = 38.9$ kcal mol^{-1} with the IPCM method). The IPCM results gave an inverse thermodynamic stability order, compared to the gas phase stability, which can be attributed to charge polarization effects on the stabilization of the Trans isomer. Combining the strong trans influence of the $SnCl_3$ ligand and the ability of the Pt-Sn to stabilize the penta-coordinated geometry, we proposed an autocatalytic mechanism for this reaction, which is solvent assisted. Based on the results presented here and on the facts that even weakly coordinating solvents can significantly change the reaction pathway through specific interactions, we believe that other treatments, taking into account all these interactions, are necessary to study organometallic reactions in solution. Our group is currently engaged in developing new tools for studying these reactions in solution. Despite the fact that the solvent dynamics was not explicitly included in the present study, work is in progress aiming to model the dynamic effects.

We are interested in understanding the substitution and isomerization reactions of square planar compounds, and other results will be available in future publications.

Acknowledgements

The authors would like to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for support. We would like to thank Dr. Hélio F. Dos Santos for useful discussions. This work was partially supported by PADCT (Programa de Apoio ao Desenvolvimento Científico e Tecnológico, Proc. No. 620241/95.0) from the Science and Technology Ministry (MCT) of Brazil and FAPEMIG (Fundação de Amparo à Pesquisa no Estado de Minas Gerais). W.B. De Almeida would like to thank the Pró-Reitoria de Pós-Graduação e Pesquisa (PROPP), Universidade Federal de Juiz de Fora, for a Visiting Professor Fellowship.

References

1. Tolman, C.A. *Chem. Soc. Rev*. **1972**, *1*, 337.
2. Braterman, P. S.; Cross, R. *J. Chem. Soc. Rev*. **1973**, *2*, 271.
3. Basolo, F.; Pearson, G. *Mechanism of Inorganic Reactions*, 2nd edn., Wiley: New York, 1967.
4. (a) Farrel, N. *Transition Metal Complexes as Drug and Chemotherapeutic Agents*, Kluwer Academic, Dordrecht, 1989. (b) Gill, D. S. *Platinum Coordination Complexes in Cancer Chemotherapy*; Martinus Nijhoff: Boston, 1984. (c) Fricker, S. P. *Metal Compounds in Cancer Therapy*, Chapmann&Hall: London, 1994.
5. (a) Chatt, J.; Wilkins, R. G. *J. Chem. Soc*. **1952**, 273. (b) Chatt, J.; Wilkins, R. G. *J. Chem. Soc*. **1952**, 4300. (c) Chatt, J.; Wilkins, R. G. *J. Chem. Soc*. **1953**, 70. (d) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1956**, 525.
6. Redfield, D. A.; Nelson, J. H. *Inorg. Chem*. **1973**, *12*, 15.
7. (a) Verstuyft, A. N.; Nelson, J. H. *Inorg. Chem*. 1975, 14, 1501. (b) Louw, W. *J. Inorg. Chem.* **1977**, *16*, 2147.
8. (a) Scrivanti, A.; Berton, A.; Toniolo, L.; Bottteghi, C. *J. Organomet. Chem*. **1986**, *314*, 369. (b) Parrinelo, G.; Stille, J. K. *J. Am. Chem. Soc*. **1987**, *109*, 7122. (c) Kóllar, L.; Consiglio, G.; Pino, P. *J. Organomet. Chem.* **1987**, *330*, 305. (d) Kóllar, L.; Bagos, J.; Tóth, I.; Heil, B. *J. Organomet. Chem.* **1988**, *350*, 277. (e) Gómez, M.; Muller, G.; Sainz, D.; Sales, J. *Organometallics* **1991**, *10*, 4036. (f) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev*. **1989**, *89*, 11.

9. Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1978**, *61*, 1848.
10. Rocha, W. R.; De Almeida, W. B. *Int. J. Quantum Chem.* **1997**, *65*, 643.
11. Rocha, W. R.; De Almeida, W. B. *Organometallics* **1998**, *17*, 1961.
12. Anderson, G. K.; Cross, R. *J. Chem. Soc. Rev.* **1980**, *9*, 185.
13. Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
14. (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 1868. (b) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc*. **1982**, *104*, 3529.
15. Jorgensen, W. L. *Acc. Chem. Res*. **1989**, *22*, 184.
16. Aqvist, J.; Warshel, A. *Chem. Rev*. **1993**, *93*, 2523.
17. (a) Field, M. J.; Bash, P. A.; Karplus, M. *J. Comp. Chem*. **1990**, *11*, 700. (b) Singh, U. C.; Kollman, P. A. *J. Comp. Chem.* **1986**, *7*, 718. (c) Gao, J. in *Reviews in Computational Chemistry*, Lipkowitz, K. B.; Boyd, D. B., Eds., VCH: New York, **1996**, *7*, 119.
18. (a) Rivail, J. L.; Terryn, B.; Ruiz-Lopez, M. F. *J. Mol. Struct.: Theochem* **1985**, *120*, 387. (c) Tapia O. in *Molecular Interactions*; Orville-Thomas, W. J., Ed., Wiley: New York, 1982, vol. 3, chapter 2. (d) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. (e) Born, M. *Z. Phys*. **1920**, *1*, 45. (f) Onsager, L. *J. Am. Chem. Soc*. **1936**, *58*, 1486.
19. Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.
20. Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frish, M. J. *J. Phys. Chem.* **1996**, *100*, 16098.
21. Truong, T. N.; Nguyen, U. N.; Stefanovich, E. V. *Int. J. Quantum Chem*. **1996**, *60*, 1615.
22. (a) Duffy, E. M.; Severance, D. L.; Jorgensen, W. L. *J. Am. Chem. Soc*. **1991**, *114*, 7535. (b) Straub, J. E.; Borkovel, M.; Berne, J. B. *J. Chem. Phys*. **1988**, *89*, 4833. (c) Truong, T. N.; Truong, T. T.; Stefanovich, E. V. *J. Chem. Phys.* **1997**, *107*, 1881. (d) Chandraskar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc*. **1984**, *106*, 3049. (e) Gao, J.; Xia, X. *J. Am. Chem. Soc.* **1993**, *115*, 9667. (f) Warshel, A. *J. Phys. Chem*. **1982**, *86*, 2218. (g) Barder, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501. (h) Pérez, V.; Liuch, J.; Bertrán, L. *J. Comp. Chem.* **1992**, *13*, 1057. (i) Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc*. **1991**, *113*, 7430.
23. Muguruma, C.; Koga, N.; Kitaura, K.; Morokuma, K. *J. Chem. Phys.* **1995**, *103*, 9274.
24. Honda, K.; Kitaura, K. *Chem. Phys. Lett.* **1987**, *140*, 53.
25. Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 270.
26. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
27. Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A.; Gobbi, A.; Jonas,V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.
28. Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352.
29. (a) Antes, I.; Frenking, G. *Organometallics* **1995**, *14*, 4263. (b) Dapprich, S.; Frenking, G.; *Angew, Chem*. **1995**, *107*, 383. *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 354. (c) Frenking, G.; Pidum, U. *J. Chem. Soc., Dalton Trans*., 1997, 1653.
30. De Almeida, W. B.; Dos Santos, H. F.; Rocha, W. R.; Zerner, M. C. *J. Chem. Soc., Dalton Trans.* **1998**, *15*, 2531.
31. GAUSSIAN 94 *(revision A.1)*. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahan, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J.A. Gaussian, Inc., Pittsburgh, PA, 1995.
32. Wisner, J. M.; Bartchak, T. J.; Ibers, J. A.; Low, J. J.; Goddard III, W. A. *J. Am. Chem. Soc*. **1986**, *108*, 347.
33. Albinati, A.; Gunten, U. N.; Pregosin, P. S.; Ruegg, H. J. *J. Organomet. Chem.* **1985**, *295*, 239.
34. Del Pra, A.; Forsellini, E.; Bomberi, G.; Michelin, R. A.; Ros, A. *J. Chem. Soc., Dalton Trans*. **1979**, 1862.
35. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley: New York, 1986.
36. Dos Santos, H. F.; O'Malley, P. J.; De Almeida, W. B. *Theor. Chem. Acc*. **1998**, *99*, 301.
37. Tolmann, C. A.; Meakin, P. Z.; Lindwer, D. L.; Jesson, J. P. *J. Am. Chem. Soc*. **1974**, *96*, 2762.
38. Anderson, G. K.; Cross, R. *J. Inorg. Chim. Acta*, **1979**, *38*, L21.

Received: June 14, 1999