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Experimental and computational investigations of phosphine exchange in 15-electron [$CrCpCl_2(PR_3)$] systems by stopped-flow and density functional calculations: a single-state S_N2 mechanism

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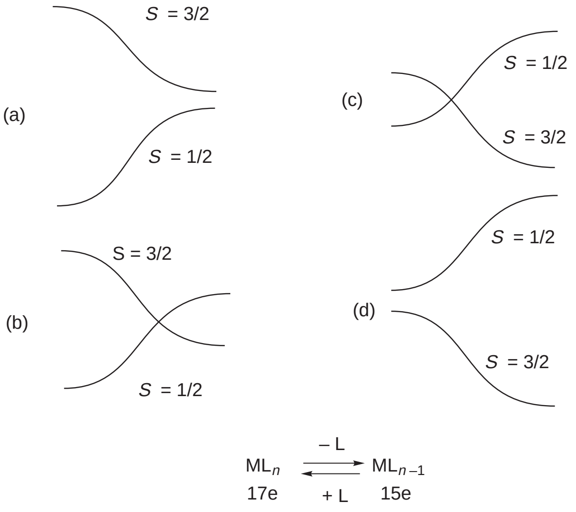
The exchange of the phosphine ligand on the half-sandwich 15-electron, spin quartet [$CrCpCl_2L$] system has been investigated experimentally by stopped-flow kinetics with visible detection and theoretically by calculations with DFT methods on the PH_3 self-exchange model system. The exchange of $PMePh_2$ with PMe_3 follows clean second-order kinetics with the activation parameters $\Delta H^{\ddagger} = 7.0(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24.3(8)$ cal K^{-1} mol^{-1}, consistent with an associative exchange. The rate constant for the exchange of L with PMe_3 in [$CrCpCl_2L$] at room temperature varies only within a factor of 8 for the series of complexes with L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, or η^1-dppe. The computational work showed that the PH_3 self-exchange process occurs *via* a symmetric transition state along the spin quartet hypersurface, without crossover to the spin doublet state. The optimized transition state corresponds to a first-order saddle point with Cr–P distances of 3.190 and 3.174 Å, located 7.6 kcal mol^{-1} above the [$CrCpCl_2(PH_3)$] (spin quartet) + PH_3 combination, or 13.6 kcal mol^{-1} below the [$CrCpCl_2(PH_3)_2$] doublet minimum. Thus, the phosphine exchange reaction can be classified as a classical S_N2 process.

Introduction

The organometallic chemistry of Cr^{III} has boomed in recent years, in large part because of its implication in the Phillips process for ethylene polymerization.[1] The first reported chromium(III) organometallic complex was the pseudo-octahedral complex [$CrEt(H_2O)_5$]$^{2+}$,[2] followed only a few years later by half-sandwich derivatives of types $CrCpX_2L$ and $CrCpX_3^-$ (X = Cl, Br or I; L = py, THF or PPh_3).[3] Subsequently, many other similar half-sandwich complexes containing alkyl groups, phosphines, Cp*, and other ligands were described by several groups including ours.[1,4–14] The dicationic aqua complexes [$CrCp(H_2O)_3$]$^{2+}$ and [$CrCp^*(H_2O)_3$]$^{2+}$ have also been described.[15,16] Apart from particular cases where the formation of dinuclear compounds with metal–metal bonds is favored,[17–19] these systems are overwhelmingly seen to adopt an open shell, spin quartet, 15-electron configuration which can be related to the ubiquitous octahedral configuration of classical Werner-type complexes. They strongly resist co-ordination by another 2-electron donor which would bring the electron count to 17, *i.e.* closer to the closed-shell configuration, but also necessarily involve an energetically quite costly (for chromium) pairing of electrons. This behavior is opposite from that of the neighbouring molybdenum, which prefers a spin-paired 17-electron configuration in view of stronger metal–ligand bonds and reduced electron pairing energies. These considerations, which have been backed-up by computational studies at both the *ab initio* and density functional levels,[20,21] may be generalized to all open-shell organometallic systems.[22,23] In the absence of steric effects, the relative stability of 15- and 17-electron systems for Cr^{III} and Mo^{III} relative to the association/dissociation of a 2-electron donor ligand may be qualitatively summarized as illustrated in the reaction co-ordinates (a) through (d) of Scheme 1,[23] corresponding to an increasing degree of electron pairing energy.

Bulky ligands and/or ligands that establish relatively weak bonds lead to the stabilization of even less saturated (13-electron) configurations. Examples are [$Na(OEt_2)_2$][$Na(OEt_2)(THF)$][$CrPh_5$][24] or, for half-sandwich complexes, [$CrCp^*Cl(CH_2SiMe_3)$] and [$CrCp^*(CH_2SiMe_3)_2$].[1,25] Also, the activity of [$CrCp^*R(THF)_2$]$^+$, [$CrCp^*R(OEt_2)_2$]$^+$, and [$CrCp^*(CH_2Ph)_3Li$] as polymerization catalysts has been attributed to dissociation equilibria with 13-electron species which can bind and activate the olefin substrate.[1] On the other hand, we have recently shown that the use of the strongly bonding and highly nephelauxetic CN^- ligand allows the stabilization, *in solution*, of the spin-paired, 17-electron complexes [$Cr(ring)(CN)_4$]$^{2-}$ (ring = Cp or Cp*) and [$CrCp(CN)_2L_2$] (L = tertiary phosphine).[26] Another 17-electron complex of Cr^{III}, albeit stable only at low temperatures, is [$CrCp(\eta^3$-$C_3H_5)_2$].[27] On the basis of all the above it is clear that the chromium(III) center in organometallic systems has the ability to accommodate a variety of different co-ordination spheres and electron counts.



Scheme 1

In view of the relevance that the half-sandwich chromium(III) system has to the olefin polymerization process, we considered it of interest to probe the mechanism of fundamental chemical transformations on model compounds in this electronic configuration. The reaction that we have chosen for our initial studies is the exchange of a phosphine ligand on the [$CrCpCl_2(PR_3)$] system. A dissociative exchange process would parallel the dissociation of L from [$CrCp^*RL_2$]$^+$ (L = THF or Et_2O) to generate the proposed active species in ethylene polymerization catalysis. An associative process, on the other hand, could generate a species having the same configuration as the stable 17-electron [$MoCpCl_2(PR_3)_2$] or the cyano-substituted chromium(III) derivatives mentioned above. The latter process could involve a spin flip from a quartet state in the starting material to a doublet in the intermediate, and then back to a quartet in the product, thus representing a new case of the so-called two-state reactivity (TSR),[28,29] namely a reaction occurring on two different spin surfaces.[30–32]

The phosphine exchange process on the 17-electron molybdenum(III) complexes [$Mo(ring)Cl_2(PMe_3)_2$] (ring = Cp or Cp*) was conveniently investigated by monitoring the growth of the ^{31}P NMR resonance of free PMe_3 upon treatment with a large excess of PMe_3-d^9 ($t_{1/2}$ of the order of hours at room temperatures), allowing the establishment of a first order (dissociative) process. Preliminary studies of the analogous exchange for the [$CrCpCl_2(PMe_3)$] system have shown that the reaction is complete within the time necessary to record the first NMR spectrum, thus the reaction is too fast for classical monitoring kinetics studies.[33] On the other hand, the addition of PMe_3 to a solution of [$CrCpCl_2(PMe_3)$] does not significantly affect the line shape of the resonances of free and co-ordinated PMe_3,[33] thus the reaction is too slow for the application of NMR line broadening kinetic studies. Consequently, we turned to non-degenerate, quantitative phosphine exchange reactions and to the use of the stopped-flow kinetics methodology. We report here our experimental investigations of various [$CrCpCl_2(PR_3)$] + PMe_3 reactions, and a parallel computational study along the reaction coordinate for the model [$CrCpCl_2(PH_3)$] + PH_3 system.

Experimental

All operations were carried out under an atmosphere of dinitrogen. Solvents were dehydrated by conventional methods and distilled directly from the dehydrating agent prior to use (THF from sodium–benzophenone and toluene from Na). Compounds [$CrCpCl_2L$] (L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, or η^1-dppe) were prepared as previously described.[5,12,13] Solutions of PMe_3 [1 M in THF and 1 M in toluene (Aldrich)] were used as received.

The stopped-flow kinetic investigations were carried out with a Hi-Tech DX2 apparatus, equipped with a xenon lamp (75 W) and a KinetaScan diode array UV-visible detector. The data were analysed with the SPECFIT global analysis package[34] on a Pentium PC.

Theoretical calculations were carried out by GAUSSIAN 94[35] on a SGI Origin 200 workstation. The three-parameter form of the Becke, Lee, Yang and Parr functional (B3LYP)[36] was employed. The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H and C[37] and the relativistic electron core potential (ECP) sets of Hay and Wadt[38–40] for the heavy atoms. Electrons outside the core were all those of H and C atoms, the 3s, 3p electrons in Cl and P, and the 3s, 3p, 3d and 4s electrons in Cr. A C_s symmetry arrangement was imposed for the [$CrCpCl_2(PH_3)_n$] systems ($n = 1$ or 2) at each fixed $Cr \cdots P$ distance. The transition state calculation was carried out with a Synchronous Transit-Guided Quasi-Newton (QST2) algorithm. The energies shown in the Results section correspond to unrestricted B3LYP (UB3LYP) calculations. The value of $\langle S^2 \rangle$ at convergence was in the range 0.7503–0.7504 for all spin doublet calculations and in the range 3.7527–3.7630 for all spin quartet calculations.

Results and discussion

The exchange reaction (1) (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, PEt_3

$$[CrCpCl_2(PR_3)] + PMe_3 \longrightarrow [CrCpCl_2(PMe_3)] + PR_3 \quad (1)$$

or η^1-dppe) is quite rapid and quantitative at room temperature and is therefore amenable to kinetics investigations by the stopped-flow technique. The thermodynamic drive for the reaction is provided by the stronger bonds established by PMe_3 with the chromium(III) center relative to the other phosphine ligands, presumably because of a combination of the stronger donating ability and the less stringent steric requirements of the PMe_3 ligand.[41] A similar trend of relative stability was observed for the related half-sandwich complexes of Mo^{III}.[31,42]

The $PMePh_2$ derivative was selected for carrying out detailed rate law and activation parameter investigations. Although both starting and final complexes are blue, the visible absorption spectra differ sufficiently, especially in the 450–700 nm region, to allow an accurate determination of kinetic parameters on the basis of variations up to 0.1 absorbance unit. The instrument background noise (and the residuals of the final data fittings) are below 1 milliabsorbance unit. Various kinetic runs were carried out under pseudo-first order conditions. Initial investigations were carried out in THF. The global analysis of the data obtained in this solvent, however, did not yield a satisfactory fit to a common single exponential for all absorption frequencies. An acceptable fit was obtained instead for an A $\longrightarrow$ B $\longrightarrow$ C model. The absorption spectra calculated with the SPECFIT global analysis program for A, B and C were qualitatively similar and suggest that all species are 15-electron half-sandwich derivatives of Cr^{III}. The most reasonable structural assignment of the different species appears to be the product of phosphine exchange, [$CrCpCl_2(PMe_3)$], to B and the ionic product [$CrCpCl(PMe_3)_2$]$^+Cl^-$, derived from substitution of a chloride ligand by a second PMe_3 molecule, to C. Under the above assumption, we reasoned that the second exchange process could be strongly retarded or completely suppressed upon carrying out the kinetic study in a less polar solvent, *e.g.* toluene.

Indeed, the investigation in toluene afforded clean single exponential decays, leading to the pseudo-first-order rate constants in Table 1. The graphic representation of the constants obtained at 25 °C as a function of the phosphine concentration (runs 1–4, see Fig. 1) immediately establishes a second-order rate law for this phosphine exchange reaction. From the slope of the straight line, the second-order rate constant $k = 223 \pm 5$ M^{-1} s^{-1} is obtained at this temperature.

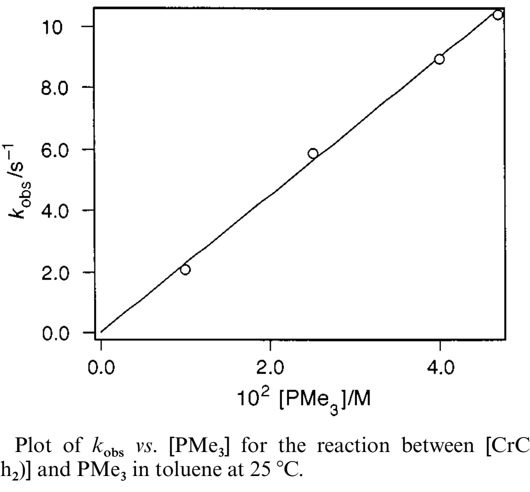


Fig. 1 Plot of k_{obs} *vs.* [PMe_3] for the reaction between [$CrCpCl_2(PMePh_2)$] and PMe_3 in toluene at 25 °C.

Table 1 Rate constants for the [$CrCpCl_2(PMePh_2)$] + PMe_3 reaction in toluene

Run	10^{-2} [PMe_3]/M	T/K	k_{obs}/s^{-1}	10^{-2} k/M^{-1} s^{-1}
1	1.00	298	2.075(8)	
2	2.50	298	5.9(1)	
3	4.00	298	8.9(1)	
4	4.70	298	10.39(7)	
5	2.10	278	1.88(3)	0.89(1)
6	2.10	288	3.09(3)	1.47(1)
7	2.10	298	4.66(4)	2.22(2)
8	2.10	308	7.29(6)	3.47(3)

Complex concentration = 1.23×10^{-3} M.

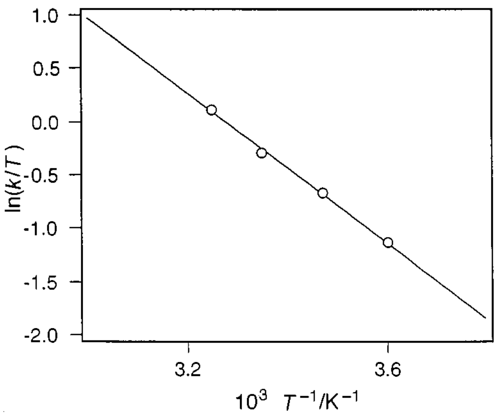


Fig. 2 Eyring plot for the reaction between [$CrCpCl_2(PMePh_2)$] and PMe_3 in toluene.

An investigation of the same reaction at the constant [PMe_3]:[Cr] ratio of 17:1 and at different temperatures in the 5–35 °C range (runs 5–8) yields a linear ln(k_{obs}/T) *vs.* 1/T plot (Fig. 2), leading to the calculations of the activation parameters for the reaction: $\Delta H^{\ddagger} = 7.0(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24.3(8)$ cal K^{-1} mol^{-1}. The large negative activation entropy, together with the established second order rate law, is consistent with an associative mechanism involving a high degree of ordering in the transition state.

Kinetic investigations were also carried out for other starting materials as shown in eqn. (1). These were only determined at a single [PMe_3]:[Cr] ratio and at a single temperature. The second order rate constants (see Table 2) were derived under the reasonable assumption that all these reactions occur by the same mechanism as the $PMePh_2$/PMe_3 exchange. The results are themselves further evidence in favor of a common associative mechanism for all these exchange reactions. For a pure dissociative process, the Cr–PR_3 bond would be broken in the slow step of the reaction. Consequently, the rate contants should be very sensitive to the nature of the phosphine ligand, the more weakly bonded phosphine ligands leading to faster exchange processes. Other systems that have previously been established to follow a dissociative ligand exchange, such as the 18-electron complex *cis*-[$Mo(CO)_4L_2$], afford first order rate constants over 3 orders of magnitude smaller for PMe_2Ph relative to PPh_3.[43] On the other hand, a pure associative process would involve the formation of the new Cr–PMe_3 bond, which is essentially the same for all systems. Consequently, the rate should only experience a slight dependence on the nature of the outgoing phosphine, the faster rates being expected for the *least sterically encumbering* and/or *least electron donating* phosphines. For the present system, the data in Table 2 show that the pseudo-first-order rate constant varies over a factor of only 8 on going from PPh_3 to PMe_2Ph. In addition, the slower reaction is given by the PPh_3 complex, consistent with a sterically controlled associative process and in strong disagreement with a dissociative process.

Table 2 Rate constants for the [$CrCpCl_2(PR_3)$] + PMe_3 reaction in toluene at 25 °C

PR_3	k_{obs}/s^{-1}	10^{-2} k/M^{-1} s^{-1}
PPh_3	1.03(4)	1.03(4)
η^1-dppe	17(1)	17(1)
PMe_2Ph	9(1)	9(1)
PEt_3	1.8(1)	1.8(1)

Complex concentration = 5.00×10^{-4} M, [PMe_3] = 1.00×10^{-2} M.

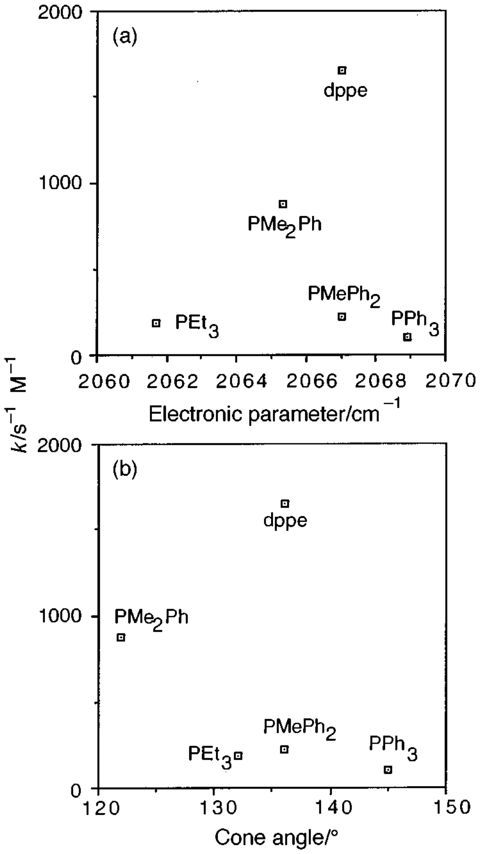


Fig. 3 Correlation between the second-order rate constant of the [$CrCpCl_2(PR_3)$] + PMe_3 reaction and Tolman's electronic and steric parameters.

Fig. 3 shows the correlation between the second-order rate constants and Tolman's electronic and steric parameters.[41] There is a poor correlation with both parameters for the entire series of compounds investigated. The three systems based on the homologous PMe_nPh_{3-n} series (n = 0, 1 or 2) show a linear correlation with both parameters, but the electronic parameters would be expected to lead to the opposite trend of reactivity (PPh_3 > $PMePh_2$ > PMe_2Ph). Thus, these phosphine ligands influence the exchange rate mostly by virtue of their steric encumberance. The PEt_3 ligand shows an unusually slow rate when its steric requirements are compared with those of the PMe_nPh_{3-n} systems. The reason for this discrepancy may be either an important contribution of the electronic factor [PEt_3 is a much stronger donor than the PMe_nPh_{3-n} phosphines, see Fig. 3(a)], or by the gross underestimation of the actual steric encumberance of PEt_3 by Tolman's cone angle,[44,45] or a combination of the two effects. A discrepancy that cannot be easily rationalized is the relatively fast exchange rate for the η^1-dppe complex. This ligand, when co-ordinated in a monodentate fashion, has electronic and steric parameters identical with those of $PMePh_2$, yet it leads to an exchange rate constant *ca.* 7.5 times bigger than that furnished by $PMePh_2$.

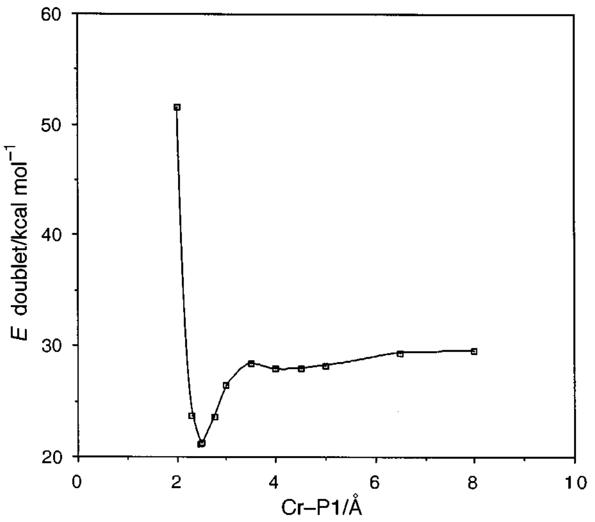


Fig. 4 Energy of the [CrCpCl$_2$(PH$_3$)] + PH$_3$ system in the doublet spin state at various fixed distances between the Cr atom and the P atom of the incoming PH$_3$ ligand. The energy (kcal mol^{-1}) is relative to the [CrCpCl$_2$(PH$_3$)] (S = 3/2) + PH$_3$ system at infinite distance.

Although the rate law and the activation entropy strongly suggest an associative mechanism, these experimental data cannot distinguish between the formation of a distinct 17-electron intermediate and an interchange transition state, nor whether a spin state change occurs along the reaction coordinate, namely whether this is a one-state or a two-state reaction. To help clarify this point, we have complemented our experimental studies with theoretical calculations.

Previous calculations with full geometry optimization on [CrCpCl$_2$(PH$_3$)] (in the doublet and quartet states) and [CrCpCl$_2$(PH$_3$)$_2$] (doublet state) at various levels of theory indicated that the combination of quartet [CrCpCl$_2$(PH$_3$)] and free PH$_3$ is at least 13.6 kcal mol^{-1} more stable than doublet [CrCpCl$_2$(PH$_3$)$_2$].[20,21] This is a substantially greater number than the measured activation enthalpy for the [CrCpCl$_2$(PMePh$_2$)] + PMe$_3$ system, thus suggesting that the formation of a 17-electron intermediate having a doublet configuration may not occur.

Additional calculations on the spin doublet curve at various fixed distances between the Cr and the P atom of the entering PH$_3$ ligand, with complete optimization of all other parameters, yield the results shown in Fig. 4. The minimum of this curve corresponds to the previously fully optimized spin doublet adduct which is located at 0.03375 hartree (21.2 kcal mol^{-1}) above the [CrCpCl$_2$(PH$_3$)] (spin quartet) + PH$_3$ combination at the chosen level of theory.

An analogous study along the quartet curve revealed the expected repulsive interaction upon approach of the incoming PH$_3$ ligand, after an initial slight energy decrease. However, the energy of the system remained low relative to the bound doublet minimum and an elongation of the bond between Cr and the already co-ordinated PH$_3$ ligand accompanied the approach of the incoming PH$_3$ ligand. An attempt to optimize a structure with Cr$\cdots$P < 3 Å led to the expulsion of the other PH$_3$ ligand. A transition state calculation for the PH$_3$ exchange provided a relatively symmetric geometry with Cr–P distances of 3.190 and 3.174 Å, at an energy only 0.0122 hartree (7.6 kcal mol^{-1}) above the [CrCpCl$_2$(PH$_3$)] (spin quartet) + PH$_3$ combination, or 13.6 kcal mol^{-1} below the bound doublet minimum. A frequency calculation confirms that this geometry corresponds to a first-order saddle point. The single imaginary frequency corresponds to the normal mode illustrated in Fig. 5, featuring the motion of one P atom toward the Cr atom and the other one away from it. The translation movement of the two PH$_3$ ligands is accompanied by a slight rocking motion, tilting the C_{3v} symmetry axis of the PH$_3$ ligands from a direction collinear with the Cr–P bond in the bonded geometry toward a direction collinear with the Cr–Cp axis in the non-bonded geometry.

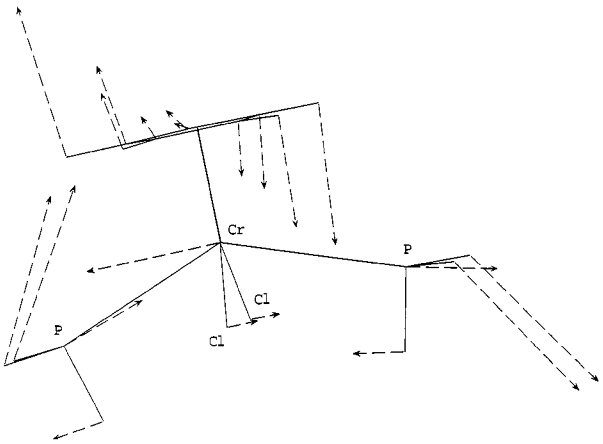


Fig. 5 Normal mode corresponding to the imaginary frequency of the first-order saddle point for the PH$_3$ exchange reaction coordinate of the [CrCpCl$_2$(PH$_3$)] + PH$_3$ system.

When extrapolated to the PMe$_3$ system the calculation results indicate that the associative phosphine exchange is likely proceeding entirely on the spin quartet surface *via* a single symmetric transition state without crossover to the spin doublet surface, namely the reaction can be classified as a classical S$_N$2 exchange, and corresponds to the situation represented in part (d) of Scheme 1. The calculated activation barrier for the associative self-exchange in the PH$_3$ system is quite close to the measured enthalpic barrier to the exchange of PMePh$_2$ by PMe$_3$. These results may be relevant to the intimate mechanism of CpCr^{III}-catalysed olefin polymerization.

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