of $^*\mathrm{Cr(bpy)_3}^{3+}$ by $\mathrm{I^-}$, a reaction that presumably occurs by electron transfer, but does not yield the expected products.[36] Unlike $\mathrm{I^-}$, the $\mathrm{Co(tmc)^{2+}}$ cannot effectively ion-pair with the cationic chromium complex, but the driving force for back-electron-transfer is quite large, so that it might take place before the initial products of the quenching reaction diffuse apart.

Quenching experiments were also carried out with several of the other cobalt(II) macrocycles. The quenching rate constants for $\mathrm{Co([14]aneN_4)^{2+}}$, Co(*C-meso*-$\mathrm{Me_6[14]aneN_4)^{2+}}$, *meso*-Co($\mathrm{Me_6[14]4,11\text{-}dieneN_4)^{2+}}$, and $\mathrm{Co([15]aneN_4)^{2+}}$ are $(1.4 \pm 0.2) \times 10^8$, $(5.1 \pm 0.4) \times 10^7$, $(2.85 \pm 0.05) \times 10^7$, and $(1.55 \pm 0.06) \times 10^8$ $\mathrm{M^{-1}\,s^{-1}}$, respectively. Plots of k_{obsd} versus [Co(II)] are linear. In each of these cases, quenching is accompanied by buildup of $\mathrm{Cr(bpy)_3}^{2+}$ as monitored at 560 nm. We conclude, therefore, that electron-transfer quenching occurs in all of these cases.

Discussion

Application of the Marcus equation for outer-sphere electron transfer to this series of reactions is useful, since all of the partners (except $\mathrm{Co(tmc)^{2+}}$) have known electrode potentials and self-exchange rate constants. The equations used are[41]

$$k_{\mathrm{CoRu(calc)}} = (k_{\mathrm{CoCo}}k_{\mathrm{RuRu}}K_{\mathrm{CoRu}}f)^{1/2} \tag{5}$$

$$\log f = [\log (K_{\mathrm{CoRu}})]^2/4 \log [k_{\mathrm{CoCo}}k_{\mathrm{RuRu}}/Z^2] \tag{6}$$

The results for the four complexes for which all of the requisite parameters are known are then as follows:

complex	$E^\circ_{3/2}$	k_{CoCo}/ $\mathrm{M^{-1}\,s^{-1}}$	log k_{CoRu} obs	log k_{CoRu} calc
$\mathrm{Co([14]aneN_4)^{2+}}$	0.42	8×10^{-4}	7.5	8.4
meso-Co($\mathrm{Me_6[14]4,11\text{-}dieneN_4)^{2+}}$	0.56	4.5×10^{-5}	6.2	7.2
$\mathrm{Co(tim)^{2+}}$	0.56	5×10^{-2}	7.3	8.2
$\mathrm{Co([15]aneN_4)^{2+}}$	0.66	6×10^{-3}	7.2	7.4

The agreement, although not superb, is within about 1 log unit for each rate constant. The application of the Marcus theory can be reversed to estimate a value for the self-exchange rate constant of the pair Co(*C-meso*-$\mathrm{Me_6[14]aneN_4)^{3+/2+}}$; k_{CoCo} is estimated to be 2×10^{-5} $\mathrm{M^{-1}\,s^{-1}}$.

Because the electrode potential and self-exchange rate constant for $\mathrm{Co(tmc)^{2+}}$ are not known, no further analysis is feasible. It is noted, however, that the two ruthenium(III) complexes with nearly the same electrode potentials react at nearly the same rate, whereas the reaction with $\mathrm{Ru(4,7\text{-}Me_2phen)_3}^{3+}$, with a driving force some 0.15 V smaller, occurs about 30 times more slowly, in qualitative agreement with the Marcus theory.

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Registry No. $\mathrm{Ru(bpy)_3}^{2+}$, 18955-01-6; $\mathrm{(H_2O)_2Co([14]aneN_4)^{2+}}$, 65554-13-4; $\mathrm{(H_2O)_2Co}$(*C-meso*-$\mathrm{Me_6[14]aneN_4)^{2+}}$, 68170-27-4; $\mathrm{(H_2O)_2Co(tim)^{2+}}$, 38337-82-5; $\mathrm{(H_2O)_2Co([15]aneN_4)^{2+}}$, 74093-13-3; $\mathrm{(H_2O)_2Co(tmc)^{2+}}$, 126543-79-1; $\mathrm{Ru(phen)_3}^{3+}$, 23633-32-1; $\mathrm{Ru(4,7\text{-}Me_2phen)_3}^{3+}$, 79747-03-8.

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(41) The Marcus equation is used in the simple form given by eqs 5 and 6, using Z as the gas-phase collision frequency of 10^{11} $\mathrm{M^{-1}\,s^{-1}}$, without allowance for work terms, since each pair of reactants, $\mathrm{RuL^{3+}}$ and $\mathrm{Co(N_4mac)^{2+}}$, have the same ionic charges.

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Theoretical Study of the Intramolecular Cis-Trans Isomerization Mechanism in $\mathrm{Cr(CO)_5X}$ (X = CO, $\mathrm{PH_3}$, $\mathrm{PPh_3}$)

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The reaction mechanism for intramolecular cis-trans isomerization in $\mathrm{Cr(CO)_5X}$ (X = CO, $\mathrm{PH_3}$, $\mathrm{PPh_3}$) was explored. The approximate molecular orbital method PRDDO (partial retention of diatomic differential overlap) was used to optimize the geometries of $\mathrm{Cr(CO)_6}$, $\mathrm{Cr(CO)_5PH_3}$, and $\mathrm{Cr(CO)_5PPh_3}$ and to estimate the transition-state structures resulting from nondissociative cis-trans isomerization mechanisms. The Bailar twist, Ray and Dutt, and bicapped tetrahedron nondissociative mechanisms were investigated. With monodentate ligands, all three mechanisms lead to identical transition states, clearly identifiable as trigonal prisms. Ab initio theory including MP2 perturbation theory was used to evaluate the energy barrier for $\mathrm{Cr(CO)_6}$ and $\mathrm{Cr(CO)_5PH_3}$. The calculated barrier in both systems is ~40 kcal/mol. PRDDO calculations for the same systems yield a slightly higher value of ~47 kcal/mol. For $\mathrm{Cr(CO)_5PPh_3}$, PRDDO predicts a barrier of ~40 kcal/mol. Although the predicted energy of activation for a nondissociative mechanism occurring via a trigonal-prism transition state in $\mathrm{Cr(CO)_5PPh_3}$ is 7 kcal/mol lower (at the PRDDO level) than that observed in the two previous systems, the barrier is still slightly higher than the triphenylphosphine ligand dissociation energy of 32 kcal/mol.

Introduction

Stereomobility of ligands occurring in six-coordinate octahedral complexes has important implications in synthetic organometallic chemistry and has been the focus of numerous experimental studies.[1-7] The mechanisms by which stereochemical rearrangements occur provide useful information about the configurational stability of the complex with respect to cis-trans isomerization. Cis-trans isomerization can occur in either of two ways. First, dissociation of a ligand can be followed by rearrangement of the resultant five-coordinate coordinatively unsaturated intermediate. Second, rearrangement may occur via a nondissociative intramolecular mechanism. At least three possible path-

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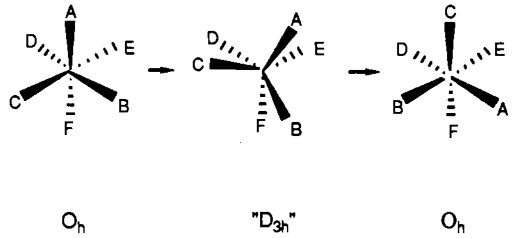
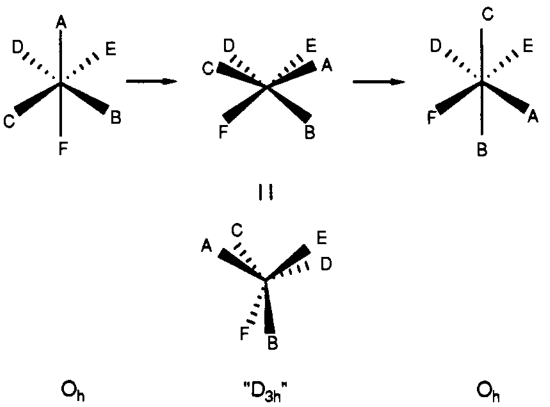
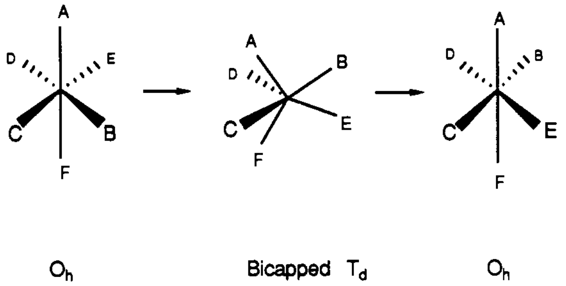
ways have been suggested for the intramolecular rearrangement: the Bailar twist mechanism,[2] the Ray and Dutt mechanism,[3] and a mechanism that proceeds through a bicapped tetrahedron transition state.[4] The Bailar twist mechanism involves a twist of three metal–ligand bonds about one of the C_3 axes.



In the Ray and Dutt mechanism, two adjacent carbonyls remain fixed and the remaining two carbonyl pairs are involved in 90° rotations in opposing directions. For complexes containing monodentate ligands only, these two mechanisms actually lead to identical permutations of the ligands but can be operationally distinguished by the required symmetry of the transition state: The Bailer twist requires idealized D_{3h} symmetry, while the Ray–Dutt twist requires only C_{2v} symmetry.



The bicapped tetrahedron transition state is produced by a 90° rotation of two adjacent carbonyls and the angular relaxation of the remaining carbonyl pairs.



Octahedral group 6B metal carbonyls are known to exhibit fluxionality via both ligand dissociation and intramolecular nondissociative mechanisms. For instance, cis–trans isomerization has been studied in both $Mo(CO)_4(PPh_3)_2$ and $Mo(CO)_4(PEt_3)_2$.[5,6] In the first system, isomerization proceeds via dissociation of PPh_3, while in the second system, a nondissociative rearrangement with an energy barrier of 24.5 kcal/mol occurs. If a nondissociative mechanism is to occur as in the latter case, the energy of activation must be less than the ligand dissociation energy (e.g., <32 kcal/mol for PPh_3).[7] Experimentally, ligand dissociation has been confirmed by the subsequent incorporation of labeled carbon monoxide from a saturated ^{13}CO environment. This type of experimental evidence is consistent with cis–trans isomerization in $Cr(CO)_4(PPh_3)_2$ occurring via a dissociative mechanism; however, the less sterically crowded $Cr(CO)_5PPh_3$ system appears to exhibit fluxionality via a nondissociative mechanism.[7] An experimental value for the activation energy of this process has not yet been determined but has been estimated to be between 32 and 16 kcal/mol. The upper bound is obtained from the ligand dissociation energy of PPh_3 and the lower value is consistent with the absence of line broadening in the ^{13}C NMR spectra.[7] The purpose of this study is to explore the mechanism of nondissociative cis–trans isomerization in $Cr(CO)_5PPh_3$, $Cr(CO)_5PH_3$, and $Cr(CO)_6$ at the highest practical theoretical level. We demonstrate that the Bailar twist and Ray and Dutt mechanisms result in an energetically and geometrically identical trigonal-prism transition state and that the bicapped tetrahedron itself is not a true transition state but is more likely a point on a surface which must still pass through the trigonal-prism transition state to complete the isomerization. For $Cr(CO)_6$ and $Cr(CO)_5PH_3$ the energy barrier (~40 kcal/mol) for isomerization through a trigonal-prismatic transition state is significantly higher than the probable energy of activation for a dissociative process. Although the predicted barrier is somewhat lower for $Cr(CO)_5PPh_3$, the resultant trigonal-prismatic transition state appears to be energetically competitive with a dissociative rearrangement mechanism.

Table I. Experimental versus Calculated Geometries for Ground-Sate Structures

geometric param[e]	$Cr(CO)_6$ exp[a]	$Cr(CO)_6$ calc	$Cr(CO)_5PH_3$ exp[b]	$Cr(CO)_5PH_3$ calc	$Cr(CO)_5PPh_3$ exp[c]	$Cr(CO)_5PPh_3$ calc
C–O	1.14	1.16	1.16	1.16	1.15	1.16
C–Cr	1.91	1.91	1.88	1.91	1.84,[d] 1.88	1.89,[d] 1.90
P–Cr			2.35	2.30	2.42	2.39
R–P–Cr				118.9	115.6 ± 2.5	116.5
R–P				1.37	1.83	1.82
R–P–R				98.7	102.6	101.6

[a] Whitaker, A.; Jeffery, J. W. *Acta. Crystallogr.* **1967**, *23*, 977. [b] Hattner, G.; Schelle, S. *J. Organomet. Chem.* **1973**, *7*, 383. [c] Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265. [d] Trans carbonyl. [e] Units are in Å and deg (bond distances represent the average with an error of ±0.01 Å).

Method

The method of partial retention of diatomic differential overlap[8,9] was used to optimize the ground-state geometries of $Cr(CO)_6$, $Cr(CO)_5PH_3$, and $Cr(CO)_5PPh_3$. Geometry optimizations utilizing PRDDO were carried out on the Cray X-MP/24 computer made available through the University of Texas Center for High Performance Computing. The basis set on the metal for PRDDO calculations is described elsewhere.[10] Optimization of $Cr(CO)_6$ included all degrees of freedom while octahedral symmetry was maintained. Optimization of $Cr(CO)_5PH_3$ and $Cr(CO)_5PPh_3$ included all degrees of freedom except that the internal Ph ring parameters were held constant (C–H = 1.08 Å, C–C = 1.40 Å, C–C–C = 120.0°, C–C–H = 120.0°). Results of PRDDO geometry optimizations are presented in Table I. The average errors associated with the C–Cr, P–Cr, and C–O bond distances are ±0.03, ±0.04, and ±0.01 Å, respectively. As in our previous work on similar systems, the PRDDO optimized geometries are in good agreement with experiment.[11-14]

Geometries for points along the potential surface for the Bailar twist, the Ray and Dutt, and the bicapped tetrahedron mechanisms were found by the linear synchronous transit/orthogonal optimization approach.[15] The application of this approach to organometallic reaction mechanisms has been previously described in some detail[12,13] and will only be described briefly here. First, the reactant and product geometries are placed at maximum coincidence.[16] Intermediate structures with a unique path coordinate are then found by linear interpolation of the internuclear distances between identical atoms. Various permutations of the ligands in the product with respect to those of the reactant define the mechanism of the reaction pathway. The maximum energy structure along each pathway is then found by successive path coordinate constrained or-

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thogonal optimizations of trial structures. This method has been very successful in examining reaction surfaces.[12-14,17] It provides estimates of transition-state structures and energies without the evaluation of force constants, which would be difficult to calculate in the large systems studied here.

For $Cr(CO)_6$, all geometric parameters were optimized for several structures along the reaction paths arising from the three different mechanisms. The potential energy surface for $Cr(CO)_5PH_3$ was determined in the same fashion. Again, all geometric parameters were optimized. For the much larger and complex triphenylphosphine system, the PH_3 fragment in the $Cr(CO)_5PH_3$ transition-state structure was substituted with PPh_3. The $Cr(CO)_5$ fragment was then held fixed, but the PPh_3 ligand was optimized including the R–P–R and R–P–Cr angles, the P–Cr distance, and the P–Cr twist angle. The resulting energy barrier at the PRDDO level was 53 kcal/mol, much higher than predicted for a nondissociative mechanism. We therefore orthogonally optimized this structure including all parameters with the exception of the internal Ph ring parameters. The barrier was lowered by 13 kcal/mol, and there was a 0.10 Å shortening of the P–Cr bond distance, demonstrating the importance of a complete geometry optimization in this system. Because an essentially continuous series of structures connecting product and reactant are found, the maximum energy structure is necessarily an upper bound to the true transition-state energy at the PRDDO level. Total energies for both the ground states and transition states were determined by using ab initio methods including MP2 correlation corrections for both $Cr(CO)_6$ and $Cr(CO)_5PH_3$. The complexity of the $Cr(CO)_5PPh_3$ structures made ab initio calculations with a reasonable basis set impossible. Instead, PRDDO values generated for $Cr(CO)_5PPh_3$ were compared to the results of PRDDO and ab initio theory for $Cr(CO)_6$ and $Cr(CO)_5PH_3$ and were used to estimate the approximate energy of activation. While higher levels of correlation corrections would of course be desirable, MP2 energetics are likely to produce reasonable estimates of correlation effects in these systems. The ground and transition states of all of these systems have similar HOMO–LUMO gaps (within 0.03 au, or 8% in all cases). Additionally, the calculated MP2 corrections are very small (1–3 kcal/mol) relative to the computed barriers.

The basis set on the metal for ab initio calculations consisted of a Gaussian expansion of a Slater orbital basis set optimized for the ground state of the neutral metal. The basis set is triple-ζ in the 3d space, double-ζ in the 4s/4p region, and single-ζ for the 3p orbitals and the inner shells. A more detailed description of this basis has appeared elsewhere.[18] The basis set on the ligands consisted of a double-ζ 6-31G[19] basis with polarization functions on the phosphorus. Addition of polarization functions on the carbonyls did not affect the calculated energies of activation for $Cr(CO)_6$, and they were therefore not included in ab initio/MP2 calculations presented here for both $Cr(CO)_6$ and $Cr(CO)_5PH_3$. The total energies for the ground-state structures were calculated with the ab initio program GAMESS[20] and MP2[21] contributions were determined by using GRADSCF.[22]

Empirical force field calculations were used to determine the nonbonded van der Waals interactions with the software package CHEM-X.[23]

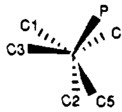
Results and Discussion

To explore the mechanism for nondissociative isomerization in pentacarbonyl(triphenylphosphine)chromium, it is convenient to initially study the identical process in much smaller but more computationally tractable systems such as hexacarbonylchromium and pentacarbonyl(phosphine)chromium.

Table II. Calculated Geometries for Transition-State Structures

geometric param[a]	X = CO	X = PH_3	X = PPh_3
Cr–X	1.91	2.32	2.32
Cr–C	1.91	1.90	1.91
C–O	1.16	1.16	1.16
C_1–Cr–C_2	83.1	83.7	82.6
C_1–Cr–C_3	80.0	79.1	76.7
C_1–Cr–C_4	83.1	83.2	83.8
C_1–Cr–C_5	135.0	135.0	132.5
C_1–Cr–X	135.0	134.7	136.5
C_2–Cr–C_3	135.0	135.0	129.6
C_2–Cr–C_4	83.1	83.2	82.2
C_2–Cr–C_5	80.0	78.6	76.7
C_2–Cr–X	135.0	134.7	135.8
C_3–Cr–C_4	135.0	134.2	138.8
C_3–Cr–C_5	83.1	85.3	84.7
C_3–Cr–X	83.1	83.8	86.6
C_4–Cr–C_5	135.0	134.2	133.4
C_4–Cr–X	80.0	79.9	83.0
C_5–Cr–X	83.1	83.8	84.3
R–P–R		98.6	104.1
R–P–Cr		118.5	114.8

[a] Units are in Å and deg. The numbering system is



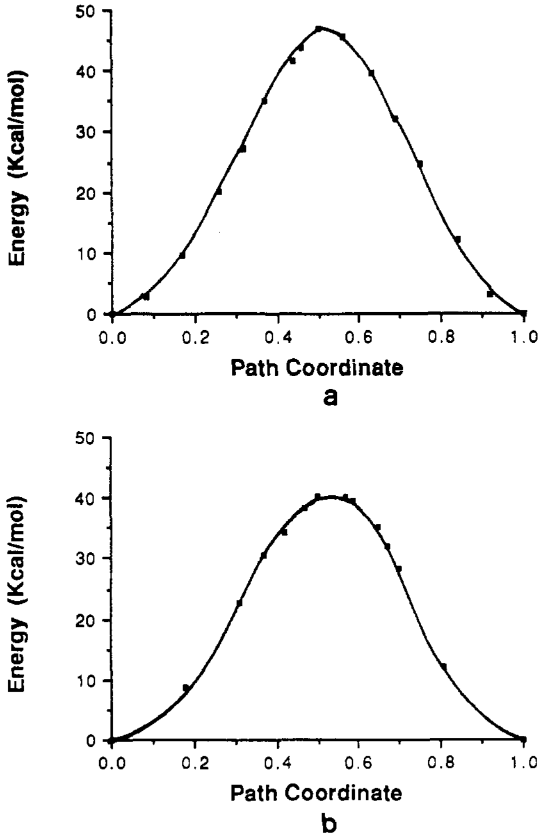


Figure 1. Potential energy surface for intramolecular cis–trans isomerization in (a) $Cr(CO)_6$ and (b) $Cr(CO)_5PPh_3$. Both surfaces are presented at the PRDDO level.

$Cr(CO)_6$. With the linear synchronous transit (LST) approach within PRDDO, we are able to show that, although the symmetry of the initial guess for the transition state is different for the Bailar twist and the Ray and Dutt mechanisms (D_{3h} and C_{2v} for Bailar twist and Ray–Dutt twist, respectively), the calculated transition states are geometrically and energetically identical trigonal prisms with geometrical parameters given in Table II. This should be true for other systems with monodentate ligands, and indeed similar trigonal-prism transition states are produced from both mechanisms in $Cr(CO)_5PH_3$, which will be discussed below. Partial orthogonal optimization of the bicapped tetrahedron structure results in a distorted octahedron, energetically similar to the original starting octahedral geometry. If a LST is constructed between this distorted octahedron and the product structure, the resultant mechanism passes through a trigonal-prism

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(17) Maximum coincidence is defined as the relative orientation of the reactant and product that maximizes the sum of the distances between identical atoms in the two species.

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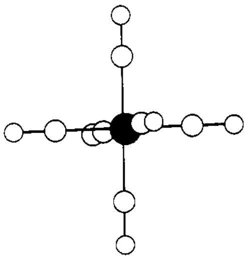
Table III. Calculated Energy of Activation for Cis–Trans Isomerization via a Trigonal-Prism Nondissociative Mechanism

complex	basis	energy, kcal/mol
$Cr(CO)_6$	PRDDO	47
	6-31G	43
	4-31G*	43
	6-31G + MP2	40
$Cr(CO)_5PH_3$	PRDDO	47
	6-31G	41
	6-31G + MP2	40
$Cr(CO)_5PPh_3$	PRDDO	40

transition state. Because both the Bailar twist and the Ray and Dutt mechanisms result in identical transition states for monodentate ligands and the bicapped tetrahedron is not a true transition state, we will drop the distinction between mechanisms and limit our discussion to the Bailar twist.

The PRDDO potential energy surface for cis–trans isomerization via a nondissociative rearrangement is presented in Figure 1a, and the structures of the ground state and transition state are shown as follows:



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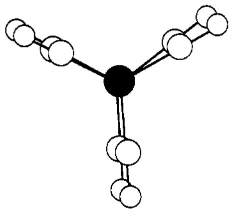
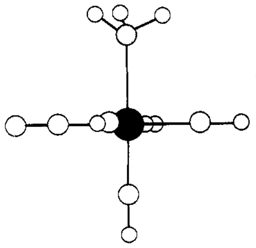


b

The PRDDO energy of activation is 47 kcal/mol. At the ab initio level with a 6-31G basis on the ligands, the corresponding energy barrier is 43 kcal/mol (Table III). Polarization functions were then added to a similar 4-31G[24] basis to enhance the description of π donation to the ligands, and the resulting energy barrier did not change. The effects of electron correlation were determined with MP2 perturbation theory on the smaller 6-31G basis (142 basis functions), and the resulting energy barrier was lowered to 40 kcal/mol. In this instance, a fully polarized basis set calculation, which would consist of 214 basis functions, was not feasible.

In our model system, the energy barrier for cis–trans isomerization through a trigonal-prism transition state is approximately 40 kcal/mol, much higher than the estimated value for the $Cr(CO)_5PPh_3$ but significantly close to the first dissociation energy of CO at 37 kcal/mol.[25] In light of this, we chose to examine a better model system, $Cr(CO)_5PH_3$, and explore the energetics associated with the Bailar twist (trigonal prism) mechanism.

$Cr(CO)_5PH_3$. The potential energy surface for cis–trans isomerization via the Bailar twist mechanism resembles in all respects the potential energy surface generated for $Cr(CO)_6$. The ground-state and transition-state structures for $Cr(CO)_5PH_3$ are shown as follows:



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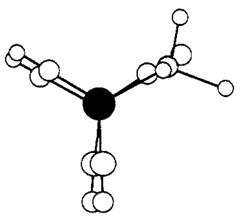
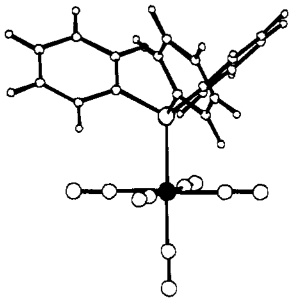


b

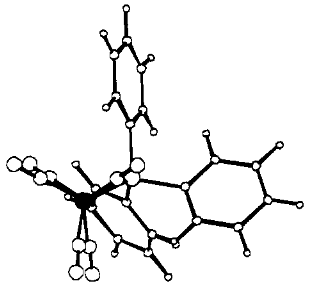
The PRDDO energy of activation is 47 kcal/mol. At the ab initio level, with a 6-31G basis on the ligands and polarization functions on the phosphorus, the corresponding energy barrier is 41 kcal/mol. The addition of correlation effects decreases the barrier to 40 kcal/mol (Table III). On the basis of these results, it would appear that the surface is remarkably insensitive to ligand substitution (i.e. substitution of CO with PH_3). But because there are marked differences in the electronic and steric properties of CO, PH_3, and PPh_3, it was necessary to include the highly complex experimental system $Cr(CO)_5PPh_3$ in this study.

$Cr(CO)_5PPh_3$. Two very obvious differences are encountered when a CO or PH_3 ligand is substituted with PPh_3. First, the triphenylphosphine ligand introduces the possibility of additional steric interactions, and second, the electronic properties are quite different. For example, the proton affinity, a measure of the gas-phase basicity, is much smaller for PH_3 compared to PPh_3: triphenylphosphine has a proton affinity 40 kcal/mol greater than that for phosphine.[26] σ- and π-bonding character also differ. These differences may account for a lower energy barrier in the $Cr(CO)_5PPh_3$. Unfortunately, this system is much too large to study with ab initio methodology (182 orbitals at the minimum basis set level); therefore, we are limited to calculating the potential energy surface with PRDDO. However, PRDDO parallels the results obtained from the ab initio work on the smaller systems, with only a slightly higher calculated barrier, so it should be very useful in determining substituent effects. In this work we provide the first estimates of transition-state structures in systems of this size and complexity.

For $Cr(CO)_5PPh_3$, the PRDDO value for the activation energy associated with cis–trans isomerization through the trigonal-prism transition state is 40 kcal/mol. The ground-state and transition-state structures appear as follows:



a



b

The complete potential energy surface appears in Figure 1b. The calculated barrier is 7 kcal/mol less at the PRDDO level than that observed in the previous two systems. One would predict a slightly lower barrier at the ab initio level, since PRDDO slightly overestimated the calculated energy of activation for the first two systems. If, as with $Cr(CO)_6$ and $Cr(CO)_5PH_3$, the ab initio value is 7 kcal/mol lower than the PRDDO energy barrier, the extrapolated barrier for $Cr(CO)_5PPh_3$ would be ~33 kcal/mol. Because the ligand dissociation energy for PPh_3 is estimated to be 32 kcal/mol,[7] it appears that the nondissociative mechanism via a trigonal-prismatic transition state is energetically competitive with ligand dissociation. Further experimental work in this area would obviously be helpful.

Substituent Effects. As mentioned previously, the obvious differences in the CO, PH_3, and PPh_3 substituents are their electronic and steric characteristics. In $Cr(CO)_6$ and $Cr(CO)_5PH_3$, these differences do not affect the calculated energy barrier for cis–trans isomerization through a trigonal-prism transition state.

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Table IV. Mulliken Charges, d-Orbital Population, Degree of Bonding, and Overlap Population for Transition-State Structures

complex	Cr Mulliken charge	d-orbital pop.	Cr–X deg of bonding	overlap pop.
$Cr(CO)_6$				
O_h	0.342	4.99	0.907	0.245
D_{3h}	0.329	4.89	0.907	0.248
$Cr(CO)_5PH_3$				
O_h	0.208	5.04	0.669	0.317
D_{3h}	0.204	4.93	0.652	0.308
$Cr(CO)_5PPh_3$				
O_h	0.252	5.02	0.611	0.318
D_{3h}	0.234	4.93	0.667	0.335

Substitution with PPh_3, however, results in a 7 kcal/mol decrease in the energy barrier determined at the PRDDO level. In $Cr(CO)_5PPh_3$, electronic and/or steric factors must be contributing to the stabilization or destabilization of either or both the octahedral and trigonal-prism geometries.

Table IV summarizes the Mulliken charges, overlap population, d orbital population, and degree of bonding for the X–Cr bond in both the octahedral and trigonal-prism geometries as determined at the PRDDO level. The CO ligand exhibits the strongest degree of bonding, presumably a reflection of the π-accepting ability of the CO group relative to the other ligands. Although the relative π-accepting ability for the substituents would be predicted to be $CO > PH_3 > PPh_3$, there are no clear trends evident in the population analysis. For instance, the total d orbital populations for the octahedrons of $Cr(CO)_5X$ for X = CO, PH_3, and PPh_3 are 4.99, 5.04, and 5.02 e^-, respectively. These differences do not reflect the relative π-accepting strength of PH_3 and PPh_3. A more detailed population analysis that differentiates between σ and π effects also yields no clear trends. Differences in π-accepting abilities have been used to explain the noticeably shorter Cr–P bond distance in $Cr(CO)_4(PH_3)_2$ compared to $Cr(CO)_5PPh_3$ (2.32 versus 2.42 Å).[30] Indeed, the P–Cr bond distance is calculated to be 0.09 Å shorter in $Cr(CO)_5PH_3$ than in $Cr(CO)_5PPh_3$. However, the 0.09-Å difference for P–Cr in $Cr(CO)_5PH_3$ and $Cr(CO)_5PPh_3$ no longer exists in the transition-state structures (the bond distances are now equivalent).

The d orbital populations for the transition-state structures are all approximately 0.10 e^- less than the octahedrons. The reduced d orbital populations in all systems would suggest that the trigonal prism facilitates more efficient π back-donation, but again a detailed population analysis yields no obvious trends in the π-accepting or σ-donating abilities of PH_3 relative to PPh_3. Therefore, we attribute the difference in bond lengths for the ground-state structures to factors other than the σ-donating or π-accepting abilities of PH_3 relative to PPh_3.

As alluded to previously, the octahedral geometry may not always be optimum for minimizing the ligand–ligand repulsions.[31] In the octahedron, the triphenylphosphine ligand is adjacent to four carbonyls, while in the trigonal prism, only three carbonyls are adjacent. The triphenylphosphine ligand has C_3-like symmetry, and consequently, it is easier to fit the three phenyl rings into a configuration that minimizes the steric interactions with only three nearest-neighbor carbonyls with P–Cr–CO bond angles of ~84° rather than four carbonyls with P–Cr–CO angles of ~90°. The Cr–P bond is longer in the ground state due to the steric interactions between the phenyl groups and the adjacent carbonyls. These interactions are minimized somewhat in the transition state, and the shorter bond distance reflects the reduced nonbonded strain. This is beautifully confirmed by a simple van der Waals calculation[23] of the differences in nonbonded energy for the ground state versus the transition state for the two systems with X = PH_3 and PPh_3: 19.3 and 12.0 kcal/mol, respectively. The octahedron can be thought of as being destabilized by 7 kcal/mol when X = PPh_3 as a result of steric nonbonded interactions. Consequently, the barrier through the trigonal-prism transition state is calculated to be approximately 7 kcal/mol lower for $Cr(CO)_5PPh_3$ versus $Cr(CO)_6$ and $Cr(CO)_5PH_3$.

Conclusion

The LST approach coupled with PRDDO-optimized geometries and ab initio energetics suggests that intramolecular cis–trans isomerization in six-coordinate monodentate species proceeds via a trigonal-prism transition state. The bicapped tetrahedron is not a true transition state but, more probably, is a point on the surface that must still pass through a trigonal-prism transition state. PRDDO predicts a 40 kcal/mol energy of activation associated with a nondissociative mechanism for cis–trans isomerization in $Cr(CO)_5PPh_3$. If $Cr(CO)_5PPh_3$ does undergo isomerization via a nondissociative trigonal-prismatic mechanism, the process is probably only slightly favored over rearrangement via ligand dissociation.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5PPh_3$, 14917-12-5; $Cr(CO)_5PH_3$, 18116-53-5.

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