

A Molecular Mechanics Model of Ligand Effects. 5. Ligand Repulsive Energy Values for Phosphines and Phosphites Bound to CpRh(CO) and the Crystal Structure of CpRh(CO)(PPh₃)

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Received January 22, 1993*

Molecular mechanics methods have been employed to compute energy-minimized structures of a series of CpRh(CO)(PX₃) complexes, where PX₃ is CO, trialkylphosphine, trialkyl phosphite, mixed alkyl/arylphosphine, or mixed alkyl/aryl phosphite. The energy-minimized structures are applied to compute the ligand repulsive energy, E'_R . Values of E'_R are compared with relative values of E_R (Brown, T. L. *Inorg. Chem.* 1992, 31, 1286) in Cr(CO)₅ in which the geometric character of the metal center is substantially different from CpRh(CO). The values of E'_R in CpRh(CO) and E_R in Cr(CO)₅ correlate reasonably well ($r_{\text{corr}} = 0.93$). The slope of the linear regression of E'_R vs E_R is 1.4. The magnitude of the slope indicates that the CpRh(CO) metal center is less crowded than the Cr(CO)₅ metal center with respect to the ligands PX₃. The correlation of E'_R with cone angle is also fairly good ($r_{\text{corr}} = 0.82$). The trend in molecular mechanics energy changes of CpRh(CO) with ligand cone angle follows the same general pattern observed in Cr(CO)₅. The structure of CpRh(CO)(PPh₃) has been determined by X-ray diffraction measurement at 0 °C with $R_w = 0.033$. The crystals belong to the triclinic space group $P\bar{1}$, with $a = 10.024(2)$ Å, $b = 10.589(2)$ Å, $c = 11.282(2)$ Å, $\alpha = 72.06(1)^\circ$, $\beta = 81.42(1)^\circ$, $\gamma = 62.57(1)^\circ$, $Z = 2$, and $V = 1011.2(3)$ Å³.

Introduction

Quantitative measures of ligand steric requirements have great potential value.¹ They might be employed in semiquantitative or comparative ways: e.g., in choosing ligands for their capacity to alter the geometry of a metal-centered reaction site or to control the coordination number at a metal center. They find use in various quantitative applications, such as linear free energy relationships² that correlate and predict rates, equilibria,³ or product distributions.⁴

Despite the obvious attractions of establishing quantitative steric measures, there are many inherent limitations on any scale that might be devised. These arise from several sources, among them the following:

1. Ligands, such as phosphines, phosphites and amines, may exist in any number of several conformational configurations when the groups attached to the central, coordinating atom are flexible. The lowest energy conformation may differ in the coordinated ligand from that for the free ligand, and may vary from one coordination environment to another.

2. The reaction context affects which aspect of a ligand's steric characteristics are of importance. Thus, two ligands acting as attacking reagents in a substitution process may exert relatively different steric effects from when the two are "spectator" ligands; that is, bound to or near a center at which reaction is occurring.

3. The character of the rate-determining step affects which aspect of a ligand's total steric requirements are important in a reaction. For some reactions involving spectator ligands, the bulk of the ligand at a distance from the site of coordination may influence the approach of a reagent to the metal; for others, the repulsive interactions between ligands in the coordination sphere may represent the most important manifestation of ligand steric properties.

The various measures of ligand steric requirement that have been proposed over the past two decades can be roughly grouped into two classes: one in which the steric requirement is evaluated for the free ligand, and the other in which it is evaluated for the ligand coordinated to a metal center. The cone angle, θ , first proposed by Tolman and co-workers,^{1a} is the best known of the former type. The recently introduced *Ligand Repulsive Energy*⁵ parameter, E_R , is an example of the latter kind.

Efforts to evaluate the variability in ligand steric requirement with change in coordination environment using the cone angle concept have taken various forms. Evaluations of cone angles from X-ray crystal structure data⁶ reveals a significant range of cone angle values, even for ligands that are fairly compact. Most recently, computations of solid cone angles for ligands in varying conformational states promise to lead to further insights as to the variations occasioned by the particulars of the environment.⁷

The computation of E_R provides for a means of evaluating in a quantitative way the steric repulsive interactions between a ligand and the rest of the molecular system to which it is bound. E_R is defined as the gradient of the van der Waals repulsive energy between the ligand and the rest of the molecule to which it is bound, multiplied by the equilibrium ligand–metal distance, eq 1.

$$E_R = r_e[-dE_{\text{vdW(repulsive)}}/dr_{\text{M-L}}] \quad (1)$$

The computation takes as its point of departure the minimum energy structure computed via molecular mechanics, using the

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- Abstract published in *Advance ACS Abstracts*, October 15, 1993.
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MMP2 force field, with added parameters as needed to describe the metal complex and metal–ligand interaction.

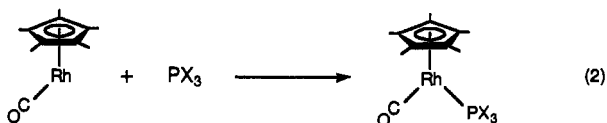
The E_R values computed to date have been calculated for ligands bound to the prototypical metal complex $\text{Cr}(\text{CO})_5$.⁵ This species was chosen for the fact that it is more or less intermediate among organometallic metal centers in terms of the degree of crowding of ligands about the metal, because the nominal C_{4v} symmetry at the metal precludes large energy variations upon rotation of the ligand about the metal–ligand axis, and because the known vibrational data⁸ and force field analysis⁹ for $\text{Cr}(\text{CO})_6$ provide a good basis for selection of reasonable parameters for the molecular mechanics computations.

In this contribution we compute the ligand repulsive energy values for a series of phosphorus ligands bound to $\text{CpRh}(\text{CO})$ using the methodology previously employed to compute ligand repulsive energy values in $\text{Cr}(\text{CO})_5$ complexes.⁵ Coordinatively-unsaturated ($\eta^5\text{-C}_5\text{R}_5$) ML ($\text{M} = \text{Rh, Ir}$; $\text{R} = \text{H, CH}_3$; $\text{L} = \text{CO, PR}_3$, olefin) compounds are considered key intermediates in several chemical processes,¹⁰ including C–H activation of hydrocarbon molecules.¹¹ The major focus of the present work has been to determine how much variation in relative values of E_R occurs among the ligands chosen for study as a result of the substantial differences in geometrical character of the metal complex to which the ligand is bound. The $\text{CpRh}(\text{CO})$ –ligand interaction in this series differs from that in the $\text{Cr}(\text{CO})_5\text{L}$ complexes,^{5,12} in that the degree of steric crowding about the metal is not the same, the nominal symmetry along the metal–ligand axis is much lower, and the Cp ring differs considerably from an electronically equivalent number of CO groups. The results of the study are of importance in providing insight into the generality of E_R values as ligand steric parameters, and into the level of precision that can be attached to E_R values, or other measures of ligand size, in linear free energy or other quantitative applications.

Molecular Mechanics Methods

All molecular mechanics calculations were carried out on a Stardent Titan computer, using BIOGRAF (Version 2.21), a comprehensive package of molecular programs developed by Molecular Simulation, Inc. The force field model employed is MMP2. The components of the energy terms in the calculations are described in detail elsewhere.^{12a,13}

To apply the molecular mechanics model, we consider the binding of a phosphorus ligand, PX_3 at the prototypical metal center, $\text{CpRh}(\text{CO})$:



We want to estimate the change in molecular mechanics energy in this process, ΔE :

$$\Delta E = E_{\text{Rh-P}} - E_{\text{Rh}} - E_{\text{PX}_3} \quad (3)$$

Here, $E_{\text{Rh-P}}$, E_{Rh} and E_{PX_3} are the molecular mechanics energies of $\text{CpRh}(\text{CO})(\text{PX}_3)$, $\text{CpRh}(\text{CO})$, and PX_3 , respectively.

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Table I. Added Parameters for MMP2 Force Field Calculations

A. Force Constants for Bond Stretching			
bond	$k_s,^a$ mdyn \AA^{-1}	$r_0, \text{\AA}$	
Cp–Cp	2.780	1.42	
Cp–H	2.606	1.08	
Cp–Cp _c ^b	10.425	1.21	
Rh–Cp _c	3.000	1.90	
Rh–C	2.100	1.81	
Rh–P	2.085	2.25	
B. Force Constants for Bond Angle Deformation			
bond angle type	k_b , mdyn $\text{\AA} \text{rad}^{-2}$	θ , deg	
Cp–Cp–Cp	0.695	108	
Cp–Cp–H	0.208	126	
Cp _c –Cp–H ^b	0.208	180	
Cp–Cp _c –Cp	0.000	72	
Cp–Cp–Cp _c	0.000	54	
Cp–Cp _c –Rh	0.348	90	
Cp _c –Rh–C	0.500	135	
Cp _c –Rh–P	0.500	135	
P–Rh–C	0.500	90	
C–Rh–C	0.500	90	
Rh–C–O	0.500	180	
Rh–P–C(sp ³)	0.209	112	
Rh–P–C(sp ²)	0.209	112	
Rh–P–O	0.278	118	
C. Force Constants for Torsional Angle Deformation			
torsional type	$K_{\phi,n}$, kcal/mol	periodicity	phase factor
H–Cp–Cp–H	1.5	2	1
Cp–Cp–Cp–H	4	2	–1
Cp–Cp–Cp–Cp	6	2	1

^a Multiply by 143.88 to convert from mdyn \AA^{-1} to kcal mol^{–1} \AA^2 . ^b Cp_c = Cp_{centroid}.

To evaluate $E_{\text{Rh-P}}$ and E_{Rh} , we must assume geometric models for $\text{CpRh}(\text{CO})$ and $\text{CpRh}(\text{CO})(\text{PX}_3)$ and values for all bond stretching, bond bending, and torsional modes. The force field model, MMP2, does not contain parameters for many of the bonds in these fragments. The treatment of the metal–Cp ring interaction presents particular difficulties. In one way of viewing the bonding, the Rh atom is bonded individually to the five carbon atoms of the Cp ring. Alternatively, a massless dummy atom, Cp_c, can be placed at the center of the Cp ring and the metal atom bonded to the dummy atom. The former model presents great difficulties in defining an appropriate force constant description;¹⁴ we have therefore chosen the latter approach.

In the model we have chosen, the dummy atom in the center of the Cp ring has one bond to the metal and to each of the five carbon atoms of the Cp ring. These bonds are assigned force constants for the appropriate stretch, angle bends and torsions. The values of the relevant force constants were chosen to maintain Cp_c at or near the center of the ring, and to provide a chemically reasonable interaction with the metal. The Rh–Cp_c force constant and strain-free distance were chosen to provide empirical agreement with key experimental data (*vide infra*).

Molecular mechanics force fields for a series of linear metallocenes have been derived by Doman, Landis, and Bosnich¹⁴ from analysis of vibrational data. They find that force field parameters internal to the Cp are insensitive to the environment of the Cp and essentially transferable from metal to metal.^{14,15} We have employed their force constant values (Table I). In addition to the internal cyclopentadienyl constants, the stretching force constant and equilibrium distance for the dummy atom–carbon (Cp_c–Cp) interaction were set at 10.425 mdyn/ \AA and 1.21 \AA , respectively.

The strain-free equilibrium value for the Rh–Cp_c distance was chosen to be 1.895 \AA , based on the average of 53 Rh–Cp_c distances reported in

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the literature.¹⁶ A value of 3.00 mdyn/Å was chosen for the stretching force constant.

The Rh–CO force constant was set to be 2.10 mdyn/Å, slightly larger than for Cr–CO, based on a slightly lower IR $\nu(\text{CO})$ frequency for CpRh(CO)(L) (L = phosphine) as compared with Cr(CO)₅(L) (L = phosphine). For example, the IR $\nu(\text{CO})$ stretching frequency in CpRh(CO)(PPh₃) (1957 cm⁻¹)¹⁷ is about 30 cm⁻¹ lower than the average value (1987 cm⁻¹) of the four CO bands in Cr(CO)₅(PPh₃).^{8c}

The strain-free Rh–P distance was set at 2.25 Å. The average Rh–P distance in the X-ray structures is estimated to be 2.27 Å for a variety of phosphorus ligands.¹⁶ Use of 2.25 Å in the molecular mechanics calculation yields a computed equilibrium Rh–P distance of 2.257 Å for CpRh(CO)(PPh₃), which is close to [2.2445(6)Å], the value observed in the X-ray structure.

Added bond angle force constants are listed in Table I; all dihedral angle torsional barriers involving Rh were set equal to zero. In addition to the parameters presented in Table I, we also assumed the following van der Waals parameters for Rh: $r_0 = 2.30$ Å and $D_0 = 0.510$ kcal mol⁻¹.

The energy-minimization computations for a series of 30 phosphines, 8 phosphites, and their CpRh(CO) complexes were carried out using procedures similar to those described earlier.^{12a} A Monte Carlo search strategy was used to find the global energy minimum when the conformational space is large. Typically 300–400 conformations were generated by variations of any of a set of key dihedral angles, then each was partially energy-minimized. The 10–15 lowest energy structures were selected and fully minimized. The lowest energy structure of the fully-minimized set was then assumed to represent the global energy minimum. In addition, energy minimizations were also performed on conformations which seemed intuitively to be promising of representing the global minimum.

The procedure for calculations E'_R values for the CpRh(CO)(PX₃) complexes was similar to that employed for Cr(CO)₅(phosphine) complexes, described previously.⁵ In brief, it is as follows.

(1) Obtain the global energy-minimized structure for CpRh(CO)(PX₃).

(2) Change the form of the van der Waals potential to a purely repulsive one, eq 4. Here D_0 represents the potential well depth in the full

$$E_{\text{vdw}}(\text{repulsive}) = \sum D_0 \exp[\gamma\{(r_0 - r)/r_0\}] \quad (4)$$

exponential-six expression, γ is typically 12.5, r is the interaction distance and r_0 is the sum of the two scaled van der Waals radii for the interacting atoms.¹⁸

(3) With all other internal coordinates of the energy-minimized structure frozen, compute the van der Waals repulsive energy with respect to the Rh–P distance in the region about the equilibrium Rh–P distance, r_e . In practice, the computed energy varies linearly with respect to the Rh–P distance over about 0.08 Å on each side of r_e . The negative of the computed gradient is then multiplied by r_e to give the *ligand repulsive energy*, E'_R (eq 1).

X-ray Crystal Structure Determination of CpRh(CO)(PPh₃)

The compound, CpRh(CO)(PPh₃), was prepared according to a literature procedure.¹⁹ A single crystal suitable for X-ray diffraction study was obtained by recrystallization from hexane solution at –20 °C. An orange prismatic crystal with well-developed faces was mounted to a thin glass fiber. Diffraction data were collected at 0 °C on an Enraf-Nonius CAD4 diffractometer. The diffraction data were corrected for Lorentz, polarization, anomalous dispersion, and absorption effects (SHELX-76).^{20a} No decay corrections were necessary and no change in the appearance of the crystal occurred during data collection. Scattering

Table II. Crystallographic Data for CpRh(CO)(PPh₃)

formula	C ₂₄ H ₂₀ OPRh
fw	458.30
space group	P1
a, Å	10.024(2)
b, Å	10.589(2)
c, Å	11.282(2)
α , deg	72.06(1)
β , deg	81.42(1)
γ , deg	62.57(1)
V, Å ³	1011.2(3)
Z	2
d_{calc} , g/cm ³	1.505
cryst size, mm	0.2 × 0.3 × 0.4
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	9.18
radiation (monochromator)	MoK α ($\lambda = 0.71073$ Å)
temp, °C	0(1)
scan method	ω/θ
data calcn range (2θ), deg	2.0–40.0 and 40.0–52.0
tot. no. of unique rflns	3954
no. of unique rfln obsd [$F_o^2 > 2.6\sigma(F_o^2)$]	3616
no. of params refined	338
transm factor: max; min	0.837; 0.724
R^a	0.026
R_w^b	0.033
R_{int}^c	0.018
quality-of-fit indicator ^d	2.02
largest shift/esd, final cycle	<0.05
largest peak, e/Å ³	0.7(1)

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c 227 equivalent intensities measured as non-unique data. ^d Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$.

factor were taken from ref 21. Relevant crystallographic and structure determination data are given in Table II.

The positions for non-hydrogen atoms including the Rh and P atoms were obtained by direct method (SHELXS 86).^{20b} Subsequent least-squares refinement and difference Fourier calculations revealed positions of the disordered cyclopentadienyl and hydrogen atoms. The disordered cyclopentadienyl ring was refined as an ideal rigid group in two orientations. In the final refinement stages, the major orientation converged to an occupancy of 60%; the carbon atoms of Cp and all hydrogen atoms were refined with isotropic thermal parameters. All remaining atoms were given anisotropic thermal parameters, and an empirical isotropic coefficient converged to 6.8×10^{-7} . The highest peaks in the final difference Fourier map were in the vicinity of the disordered Cp ring atoms with no chemical meaning. The final difference Fourier map had no other significant features.

Results

Molecular mechanics calculations were carried out for a series of phosphines and phosphites, and their CpRh(CO)(PX₃) complexes. Table III lists the calculated total molecular mechanics energies, E_T , of the free phosphorus ligands and complexes, and the values for the bond stretch (E_b), bond bend (E_θ), dihedral angle torsion (E_ϕ), and van der Waals (E_{vdw}) energy components of the total energy. The molecular mechanics energy differences (eq 3) corresponding to complex formation (eq 2) are presented in Table IV. The energy terms corresponding to the energy minimized structure for CpRh(CO) are $E_T = -2.16$, $E_b = 5.47$, $E_\theta = -11.36$, $E_\phi = 0.34$, and $E_{\text{vdw}} = 3.40$ kcal mol⁻¹. The E'_R values of the CpRh(CO)(L) (L = phosphine or phosphite) complexes are also given in Table IV.

It should be noted that neither the energy terms nor E'_R values computed vary significantly in relative values with moderate variation in assumed values for Rh–Cp_e bond stretching force constant and other force field variables.

Selected bond distances and angles of X-ray crystallographically determined CpRh(CO)(PPh₃) are presented in Tables V and VI. Table VII lists comparisons of key bond distances and angles in the computed and X-ray structures for CpRh(CO)(PPh₃). An

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Table III. Calculated Minimum Molecular Mechanics Energies (kcal mol⁻¹) of Free Phosphorus Ligands and Corresponding CpRh(CO)(PX₃) Complexes

ligand	free PX ₃ ^a					CpRh(CO)(PX ₃)				
	E _T	E _b	E _θ	E _φ	E _{vdw}	E _T	E _b	E _θ	E _φ	E _{vdw}
CO						1.17	2.10	-3.45	0.29	2.23
PMe ₃	0.32	0.00	0.46	0.91	-1.05	-2.23	2.14	-2.98	0.96	-2.36
PEt ₃	3.92	0.17	1.32	1.27	1.17	-0.29	2.30	-1.94	1.49	-2.14
P(<i>n</i> -Bu) ₃	7.53	0.61	1.96	1.32	3.63	4.12	2.79	-0.62	2.44	-0.48
P(<i>i</i> -Bu) ₃	8.04	0.86	2.73	1.34	3.11	6.67	3.05	2.43	3.04	-1.85
P(<i>i</i> -Pr) ₃	12.16	0.61	5.51	3.25	2.80	7.16	2.99	2.17	2.67	-0.67
PCy ₃	26.20	1.34	6.30	9.65	8.90	23.86	3.73	5.10	10.08	4.94
P(<i>t</i> -Bu) ₃	28.49	2.31	14.82	3.90	8.09	28.65	7.93	8.28	4.83	7.62
PMe ₂ Et	1.48	0.05	0.70	1.06	-0.33	-1.62	2.13	-2.59	1.10	-2.26
PMe ₂ (<i>i</i> -Pr)	2.82	0.23	0.95	1.19	0.45	-1.33	2.28	-2.39	1.22	-2.44
PMe ₂ (<i>t</i> -Bu)	5.55	0.58	2.54	1.28	1.15	0.61	2.70	-1.65	1.38	-1.82
PEt ₂ Me	2.64	0.11	1.00	1.18	0.34	-1.39	2.17	-2.35	1.19	-2.39
PEt ₂ (<i>i</i> -Pr)	6.16	0.30	2.95	1.45	1.47	1.55	2.55	-1.40	2.26	-1.86
PEt ₂ (<i>t</i> -Bu)	9.21	0.74	3.19	2.31	2.97	3.54	3.08	-0.88	2.58	-1.23
P(<i>i</i> -Pr) ₂ Me	6.40	0.42	2.83	1.51	1.64	1.08	2.59	-1.33	1.60	-1.79
P(<i>i</i> -Pr) ₂ Et	8.77	0.49	3.78	2.03	2.47	2.95	2.75	-0.36	2.11	-1.56
P(<i>i</i> -Pr) ₂ (<i>t</i> -Bu)	16.64	1.10	7.85	3.27	4.42	13.11	4.21	3.35	4.14	1.42
P(<i>t</i> -Bu) ₂ Me	14.38	1.22	6.92	2.63	3.62	8.79	3.84	1.63	2.89	0.42
P(<i>t</i> -Bu) ₂ Et	17.28	1.39	8.01	3.01	4.87	11.87	4.50	2.72	3.29	1.37
P(<i>t</i> -Bu) ₂ (<i>i</i> -Pr)	21.93	1.38	11.80	3.85	4.90	18.83	5.08	6.52	4.01	3.21
PPh ₃	2.53	0.50	2.50	-14.71	14.24	-2.07	2.67	-1.48	-14.47	11.21
PPh ₂ Me	2.04	0.36	1.48	-9.32	9.52	-2.46	2.45	-2.25	-9.13	6.47
PPh ₂ Et	2.72	0.42	1.78	-9.53	10.05	-2.17	2.56	-2.09	-9.18	6.54
PPh ₂ (<i>n</i> -Bu)	3.79	0.56	2.04	-9.53	10.72	-1.53	2.67	-1.83	-9.21	6.84
PPh ₂ (<i>i</i> -Bu)	3.91	0.65	2.18	-9.45	10.52	-1.48	2.81	-1.05	-9.13	5.89
PPh ₂ (<i>i</i> -Pr)	4.98	0.63	2.75	-9.33	10.92	-1.47	2.63	-0.83	-9.59	6.31
PPh ₂ (<i>t</i> -Bu)	9.01	1.01	5.37	-9.37	12.00	2.31	3.31	0.55	-9.17	7.61
PPhMe ₂	2.04	0.19	1.60	-4.21	4.46	-1.41	2.34	-2.48	-4.04	2.78
PPhEt ₂	3.19	0.26	0.08	-4.51	5.36	-1.29	2.39	-1.67	-4.30	2.30
PPh(<i>n</i> -Bu) ₂	5.47	0.53	2.44	-4.37	6.89	0.29	2.64	-1.25	-4.29	3.18
PPh(<i>t</i> -Bu) ₂	16.06	1.20	10.56	-3.57	7.87	11.55	4.71	3.91	-3.32	6.25
P(OCH ₂) ₃ CCH ₃	20.31	0.89	1.74	9.30	8.38	18.41	2.99	-1.75	9.76	7.40
P(OMe) ₃	9.91	0.42	2.47	1.73	5.29	9.27	2.83	-0.79	4.56	2.67
P(OEt) ₃	10.94	0.61	2.30	1.85	6.17	13.41	3.07	0.19	8.00	2.16
P(O- <i>i</i> -Pr) ₃	21.78	0.97	4.48	10.40	5.93	20.42	3.37	3.50	12.98	0.57
P(O- <i>i</i> -Pr) ₂ (O- <i>t</i> -Bu)	25.68	1.22	4.78	14.11	5.57	27.00	3.92	4.49	18.58	0.02
P(O- <i>i</i> -Pr)(O- <i>t</i> -Bu) ₂	29.72	1.46	5.20	18.19	4.88	32.84	4.35	6.70	22.63	-0.85
P(OPh) ₃	8.17	1.31	6.11	-18.45	19.20	10.35	4.05	5.30	12.68	13.68
P(O- <i>t</i> -Bu) ₃	34.51	1.74	6.09	22.49	4.13	36.17	4.49	6.98	26.50	-1.80

^a Alkylphosphines and alkyl phosphites from ref 12.

ORTEP drawing of CpRh(CO)(PPh₃) (showing the major orientation of the Cp ring) is given in Figure 1.

Discussion

Structure Comparisons. Comparative values of key computed and X-ray structural bond distances and angles in CpRh(CO)(PPh₃) and in (1-CH₃CO-2-CH₃Cp)Rh(CO)(PPh₃)²² are listed in Table VII. The parameters associated with the structure of CpIr(CO)(PPh₃) are closely similar.²³ The good agreement is evidence that the parameter values chosen for the MMP2 computations are appropriate. In the CpRh(CO)(PX₃) (PX₃ = phosphine or phosphite) complexes, the lowest energy conformations of the ligands may differ significantly from those of the free ligand. Figure 2 illustrates the substantial change in conformation of P(*n*-Bu)₃ on complex formation. The computed energy-minimized structure of free P(*n*-Bu)₃ has nominal 3-fold axial symmetry. In the complex, one of the butyl groups is in approximately the orientation seen in the free ligand, (Figure 2), but another butyl group is rotated about 45° around the C-C-C dihedral angle and the third is rotated about 90°, to relieve steric repulsion with the CpRh(CO) fragment.

In the free phosphites, the dihedral angle between the plane defined by the pseudo-3-fold axis through the phosphorus and P-O bond and that defined by the P-O-C plane is a prominent

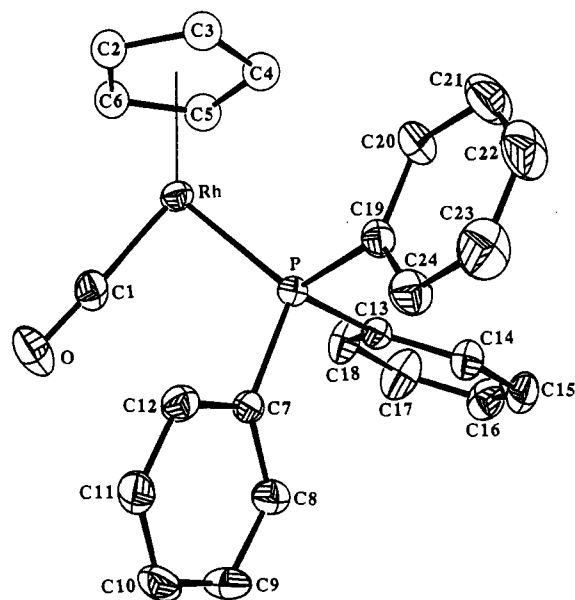


Figure 1. X-ray structure drawing of CpRh(CO)(PPh₃).

feature. This dihedral angle was referred to previously as the group dihedral.^{12a} In the free phosphite ligands, group dihedrals are close to 0°, corresponding to a vertical orientation of the P-O-C plane, with the organic group up, as shown in Figure 3b. This means that the oxygen lone pairs are directed "down" and

(22) Bitterwolf, T. E.; Hubler, T. L.; Reingold, A. L. *J. Organomet. Chem.* **1992**, *431*, 199.

(23) Bennett, M. J.; Pratt, J. L.; Tuggle, R. M. *Inorg. Chem.* **1974**, *13*, 2408.

Table IV. Energy (kcal mol⁻¹) Differences Calculated via Molecular Mechanics upon Complex Formation (ΔE in eq 3) and the Ligand Repulsive Energy, E_R .

ligand	ΔE_T	ΔE_b	ΔE_θ	ΔE_ϕ	ΔE_{vdw}	E'_R	E_R^a	θ	$r(\text{Rh}-\text{Cp}_c)$	$r(\text{Rh}-\text{L})^b$
CO						5	7	95	1.932	1.811
PMe ₃	-4.47	0.05	0.01	-0.24	-4.29	26	39	118	1.932	2.252
PEt ₃	-6.13	0.05	0.19	-0.07	-6.29	44	61	132	1.932	2.260
P(<i>n</i> -Bu) ₃	-5.32	0.09	0.86	0.83	-7.10	49	64	132	1.933	2.260
P(<i>i</i> -Bu) ₃	-3.28	0.11	3.15	1.41	-7.94	50	83	143	1.931	2.260
P(<i>i</i> -Pr) ₃	-6.91	0.30	0.10	-0.86	-6.45	65	109	160	1.934	2.275
PCy ₃	-4.25	0.31	2.24	0.15	-6.95	67	116	170	1.933	2.275
P(<i>t</i> -Bu) ₃	-1.75	3.54	-2.46	0.64	-3.46	114	154	182	1.943	2.326
PMe ₂ Et	-5.01	-0.01	0.17	-0.25	-4.91	33	48	123	1.931	2.254
PMe ₂ (<i>i</i> -Pr)	-6.06	-0.04	0.11	-0.26	-5.87	35	57	132	1.931	2.254
PMe ₂ (<i>t</i> -Bu)	-6.85	0.04	-0.74	-0.19	-5.95	40	66	139	1.931	2.256
PEt ₂ Me	-5.94	-0.03	0.10	-0.28	-5.72	33	57	127	1.930	2.252
PEt ₂ (<i>i</i> -Pr)	-6.53	0.17	-0.90	0.53	-6.31	46	75	141	1.931	2.259
PEt ₂ (<i>t</i> -Bu)	-7.58	0.25	-0.62	-0.03	-7.18	53	90	149	1.932	2.264
P(<i>i</i> -Pr) ₂ Me	-7.23	0.09	-0.71	-0.19	-6.41	48	78	146	1.932	2.261
P(<i>i</i> -Pr) ₂ Et	-7.73	0.18	-0.70	-0.20	-7.01	51	91	151	1.932	2.263
P(<i>i</i> -Pr) ₂ (<i>t</i> -Bu)	-5.44	1.02	-1.05	0.58	-5.99	80	123	167	1.937	2.287
P(<i>t</i> -Bu) ₂ Me	-7.50	0.54	-1.84	-0.02	-6.18	62	113	161	1.932	2.272
P(<i>t</i> -Bu) ₂ Et	-7.32	1.02	-1.84	-0.01	-6.49	76	125	165	1.935	2.283
P(<i>t</i> -Bu) ₂ (<i>i</i> -Pr)	-5.01	1.62	-1.84	-0.12	-4.67	91	127	175	1.937	2.297
PPh ₃	-6.51	0.08	-0.53	-0.04	-6.02	43	75	145	1.932	2.258
PPh ₂ Me	-6.41	0.00	-0.28	-0.10	-6.04	33	57	136	1.931	2.253
PPh ₂ Et	-6.81	0.05	-0.42	0.06	-6.49	45	66	140	1.932	2.259
PPh ₂ (<i>n</i> -Bu)	-7.23	0.02	-0.42	0.04	-6.87	42	66	140	1.932	2.256
PPh ₂ (<i>i</i> -Bu)	-7.30	0.07	0.22	0.04	-7.62	45	71	144	1.932	2.258
PPh ₂ (<i>i</i> -Pr)	-8.36	-0.09	-0.14	-0.55	-7.59	43	75	150	1.931	2.256
PPh ₂ (<i>t</i> -Bu)	-8.61	0.22	-1.38	-0.08	-7.37	56	97	157	1.932	2.264
PPhMe ₂	-5.35	0.06	-0.64	-0.11	-4.66	36	44	122	1.932	2.259
PPhEt ₂	-6.39	0.04	1.70	-0.08	-6.05	44	57	136	1.931	2.259
PPh(<i>n</i> -Bu) ₂	-7.09	0.03	-0.24	-0.19	-6.69	44	77	136	1.931	2.259
PPh(<i>t</i> -Bu) ₂	-6.43	1.42	-3.20	-0.04	-4.61	86	124	170	1.936	2.291
P(OCH ₂) ₃ CCH ₃	-3.82	0.01	-0.04	0.18	-3.96	19	25	101	1.932	2.248
P(OMe) ₃	-2.55	0.32	0.18	2.55	-5.60	48	52	107	1.932	2.264
P(OEt) ₃	0.56	0.37	1.34	5.86	-7.00	52	59	109	1.933	2.264
P(O- <i>i</i> -Pr) ₃	-3.28	0.32	2.46	2.29	-8.34	48	74	130	1.928	2.260
P(O- <i>i</i> -Pr) ₂ (O- <i>t</i> -Bu)	-0.59	0.61	3.15	4.18	-8.54	57	78	144	1.932	2.264
P(O- <i>i</i> -Pr)(O- <i>t</i> -Bu) ₂	1.21	0.80	4.95	4.16	-8.71	62	90	158	1.933	2.267
P(OPh) ₃	0.26	0.65	2.63	5.48	-8.50	72	65	128	1.933	2.275
P(O- <i>t</i> -Bu) ₃	-0.26	0.66	4.33	3.73	-8.91	61	99	172	1.930	2.263

^a E_R values for Cr(CO)₅. ^b L = C or P.**Table V.** Selected Bond Distances (Å) from X-ray Structure of CpRh(CO)(PPh₃)

Rh-C1	1.808(2)	C8-C9	1.387(3)
Rh-P	2.2445(6)	C9-C10	1.372(4)
Rh-C2	2.274(2)	C10-C11	1.373(4)
Rh-C3	2.293(2)	C11-C12	1.379(3)
Rh-C4	2.297(2)	C12-C7	1.400(3)
Rh-C5	2.280(2)	C13-C14	1.391(3)
Rh-C6	2.266(2)	C14-C15	1.383(3)
Rh-Cp _c ^a	1.936(2)	C15-C16	1.369(4)
C1-O	1.158(3)	C16-C17	1.375(4)
C2-C3	1.420(3)	C17-C18	1.389(3)
C2-C6	1.420(3)	C19-C20	1.386(3)
C3-C4	1.420(3)	C20-C21	1.380(4)
C4-C5	1.420(3)	C21-C22	1.368(5)
C5-C6	1.420(3)	C22-C23	1.370(4)
P-C7	1.830(2)	C23-C24	1.388(4)
P-C13	1.832(2)	C24-C19	1.387(4)
P-C19	1.838(2)		
C7-C8	1.386(3)		

^a Cp_c = Cp_{centeroid}.

outward with respect to the 3-fold axis that passes through phosphorus.²⁴ In the CpRh(CO)(P(OEt)₃) complex, one of the alkoxy groups is oriented in approximately the position characteristic of the free ligand, but the other two are substantially twisted (Figure 3). Inspection of the data for the group dihedrals of other phosphite ligands shows that this is a characteristic of several of the complexes.

Table VI. Selected Bond Angles (deg) for CpRh(CO)(PPh₃)

Cp _c -Rh-P ^a	134.78(6)	C6-C2-C3	108.2(2)
Cp _c -Rh-C1	135.1(1)	C7-C8-C9	120.3(2)
C1-Rh-P	89.98(8)	C8-C9-C10	120.5(2)
Rh-C1-O	177.8(2)	C9-C10-C11	119.9(2)
Rh-P-C7	114.65(7)	C10-C11-C12	120.4(2)
Rh-P-C13	113.80(7)	C11-C12-C7	120.5(2)
Rh-P-C19	118.84(8)	C12-C7-C8	118.5(2)
P-C7-C8	122.9(2)	C13-C14-C15	120.3(2)
P-C7-C12	118.5(2)	C14-C15-C16	120.6(2)
P-C13-C14	122.4(2)	C15-C16-C17	119.5(2)
P-C13-C18	118.7(2)	C16-C17-C18	120.4(3)
P-C19-C20	118.6(2)	C17-C18-C13	120.3(2)
P-C19-C24	122.9(2)	C18-C13-C14	118.8(2)
C7-P-C13	103.1(1)	C19-C20-C21	120.7(3)
C7-P-C19	103.2(1)	C20-C21-C22	120.3(3)
C13-P-C19	101.16(10)	C21-C22-C23	120.1(3)
C2-C3-C4	108.0(2)	C22-C23-C24	120.0(3)
C3-C4-C5	108.0(2)	C23-C24-C19	120.5(3)
C4-C5-C6	108.0(2)	C24-C19-C20	118.4(2)
C5-C6-C2	108.0(2)		

^a Cp_c = Cp_{centeroid}.

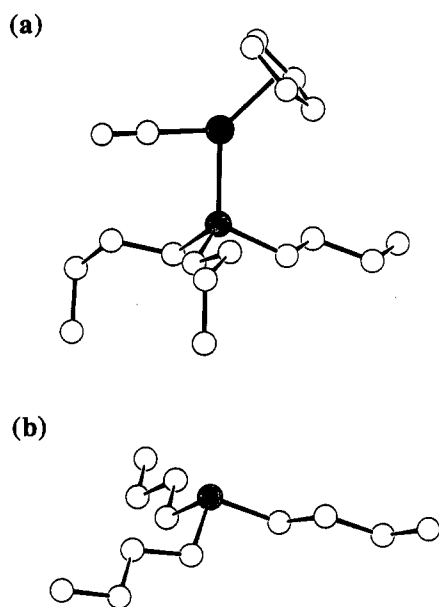
As the size of groups bound to phosphorus increase in the trialkyl phosphine CpRh(CO)(PX₃) complexes, the steric repulsions increase, resulting in an increase in the P-C bond distance from 1.85 Å for the smallest ligand to 1.88 Å for the largest. Similarly, the X-P-X (X = C or O) angles in both the free ligands and in the complexes increase with increasing bulk of the alkyl group. Additional evidence for increasing steric repulsion between the ligand and CpRh(CO) complex is observed in a small but steady increase in Rh-P distance with increasing ligand cone angle (Figure 4) from 2.247 Å for CpRh(CO)(P(OCH₂)₃-

(24) (a) Borovikov, Y. Y. *Ukr. Khim. Zh.* 1986, 52, 974. (b) Arshinova, R. P.; Zverev, V. V.; Villem, Y. Y.; Villem, N. V. *Zh. Obshch. Khim.* 1981, 51, 1757.

Table VII. Comparison of the Key Bond Distances (Å) and Angles (deg) for the X-ray Crystal Structure of CpRh(CO)(PPh₃) with Its Computed Structure Using MMP2

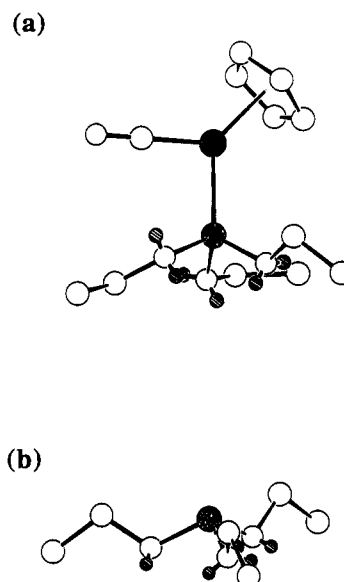
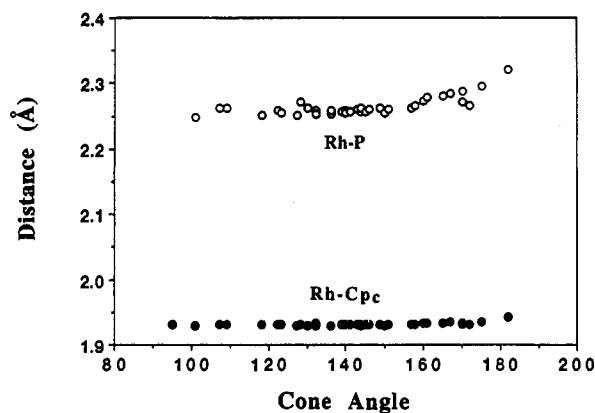
bond distance or angle	X-ray	calcd	Cp'Rh(CO)(PPh ₃) ^c X-ray
Rh-Cp _c ^a	1.936(2)	1.931	1.940(3)
Rh-P	2.2445(6)	2.257	2.263(1)
Rh-C1	1.808(2)	1.811	1.829(4)
Rh-C2	2.274(2), 2.286(3) ^b	2.297	
Rh-C3	2.293(2), 2.308(4)	2.294	
Rh-C4	2.297(2), 2.285(3)	2.297	
Rh-C5	2.280(2), 2.247(3)	2.297	
Rh-C6	2.266(2), 2.248(3)	2.295	
C1-O	1.158(3)	1.160	
P-C7	1.830(2)	1.836	
P-C13	1.832(2)	1.842	
P-C19	1.838(2)	1.839	
Cp _c -Rh-P	134.78(6)	133.6	134.2(1)
Cp _c -Rh-C1	135.1(1)	134.0	133.5(2)
P-Rh-C1	89.98(8)	88.6	92.3(1)
Rh-C1-O	177.8(2)	179.7	175.3(1)
Rh-P-C7	114.65(7)	113.7	
Rh-P-C13	113.80(7)	112.1	
Rh-P-C19	118.84(8)	119.6	
C7-P-C13	103.1(1)	104.3	
C7-P-C19	103.2(1)	105.4	
C13-P-C19	101.16(10)	100.1	

^a Cp_c = Cp_{centroid}. ^b Two values are presented because of Cp ring disordering. ^c Cp' = (1-CH₃CO-2-CH₃)cyclopentadienyl.

**Figure 2.** Energy-minimized structures for (a) CpRh(CO)(P(*n*-Bu)₃) and (b) P(*n*-Bu)₃.

CCH₃) to 2.321 Å for CpRh(CO)(P(*t*-Bu)₃). These changes are due to the effects of repulsive interactions on bond distance and angles as the system seeks a minimum energy configuration; the assumed strain-free values of the parameters are the same throughout the series. The Cp_c-Rh distance is essentially constant through the series (Figure 4). Thus, bond stretching due to steric repulsion occurs along Rh-P rather than in the Rh-Cp ring distance.

It is interesting to compare the variations in metal-phosphorus distances in the Cr(CO)₅ and CpRh(CO) systems. As the cone angle of the phosphine increases in the complexes, the metal-phosphorus distance increases in both systems. However, the metal-phosphorus distance variation is much smaller in the CpRh(CO) system (0.07 Å) than in Cr(CO)₅ system (0.28 Å), and there is no discontinuous increase in the computed metal-ligand distance for extremely bulky ligands, as was computed for

**Figure 3.** Energy-minimized structures for (a) CpRh(CO)(P(OEt)₃) and (b) P(OEt)₃. Hatched circles = lone pairs.**Figure 4.** Variations in Rh-Cp_c and Rh-P distances with ligand cone angle (θ) for PX₃ complexes of CpRh(CO).

the Cr(CO)₅ system.^{12b} These results imply that the CpRh(CO) metal center is sterically less crowded than Cr(CO)₅.

Energy Changes. The variations in the total energy change, ΔE_T , and components of the energy change are graphed as a function of the cone angle in Figure 5; the energy scale is the same for each component.

Irregular trends are seen in all cases except ΔE_b . The bond stretch energy change is more or less independent of cone angle up to a value of about 160°, then increases with cone angle. However, the overall change in ΔE_b for all ligands studied is smaller than that for any other component. The phosphite ligands exhibit energy changes somewhat higher overall than the phosphines for both the bond angle bend and torsional components of ΔE . With respect to bond angle bending, the phosphites show the same general trend in this series as they do in the Cr(CO)₅ complexes.^{12a}

The van der Waals component of the energy change shows a somewhat irregular decrease with increasing cone angle, to a value in the vicinity of 150°, and then an upward trend with increasing cone angle. As with the Cr(CO)₅ complexes, it appears that the attractive terms in the exponential-six expression for the van der Waals energy grow more rapidly than the repulsive terms, until a point is reached at which the ligand-metal center steric repulsions overcome the attractive terms and the trend reverses.

The sum of the various contributions to ΔE_T results in a generally higher value for this quantity for phosphites than for

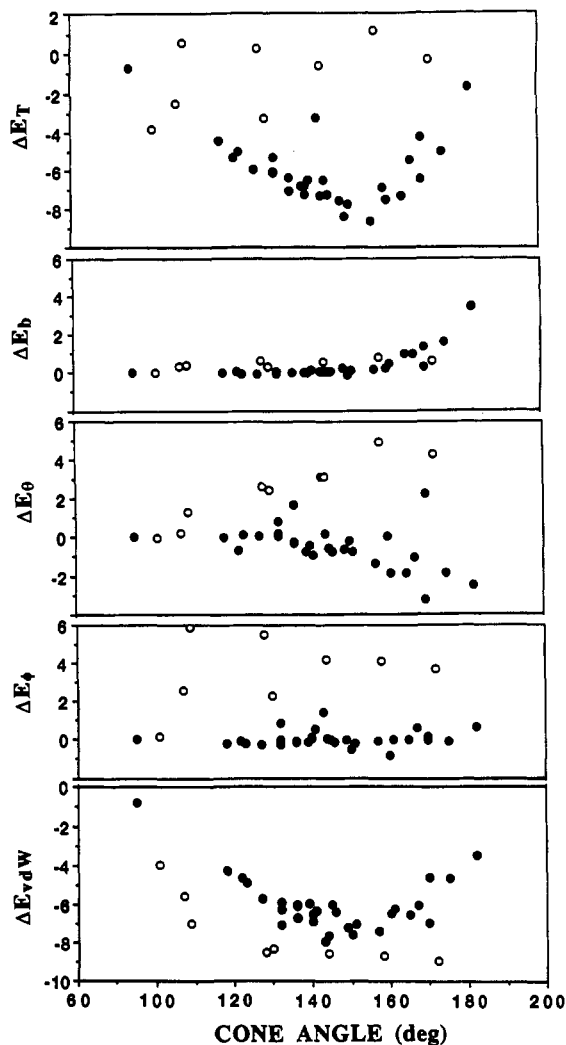


Figure 5. Total molecular mechanics energy change upon complex formation, ΔE_T , and the components of ΔE as a function of increasing cone angle (θ) of the ligand, for PX_3 complexes of $CpRh(CO)$: (●) phosphine; (○) phosphite.

phosphines of a comparable steric requirement. Among the phosphines, the overall trend is of a decreasing ΔE_T with increasing ligand cone angle, to a value of about 160° and then a reversal of the trend for still larger cone angles. It is noteworthy that $P(i-Bu)_3$ is anomalous in this series, just as in the $Cr(CO)_5$ series, presumably for reasons associated with steric interactions peculiar to β -branching, as discussed elsewhere.^{12b,25}

Thus, in general, the trends in energy changes with ligand cone angle follow the same general pattern observed when the metal center is $Cr(CO)_5$.^{12a,b} It is encouraging that, for two quite different metal centers, the same factors seem to affect the components of energy change upon complex formation modeled by molecular mechanics.

The Ligand Repulsive Energy, E'_R . The correlation of E'_R with cone angle is fair, as shown in Figure 6. The close correlation between E'_R and θ for trialkylphosphines is remarkable, because the conformations of several of the ligands in this series are different in the molecular mechanics calculations and cone angle measurements. In measuring the cone angles of phosphines, the conformer that yields the lowest cone angle is usually chosen.^{1a} By contrast, in computing E'_R values, the ligand conformation characteristic of the lowest energy conformer is used. As illustrated in Figures 2 and 3, this conformation may be different from that used in measuring the cone angle.

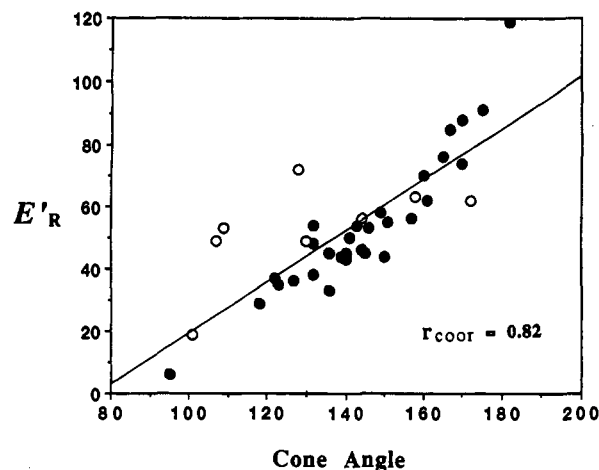


Figure 6. E'_R vs cone angle (θ) for PX_3 complexes of $CpRh(CO)$: (●) phosphine; (○) phosphite.

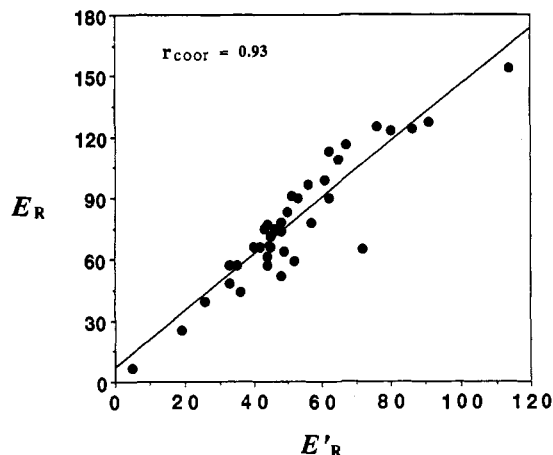


Figure 7. E'_R of $CpRh(CO)(PX_3)$ vs E_R of $Cr(CO)_5(PX_3)$.

When phenyl-containing phosphines are added to the trialkylphosphines, the correlation remains fairly good except for a few ligands. The generally good fit indicates that phenyl-containing ligands correlate well using the small empirical modification of the van der Waals radius for sp^2 carbon.¹⁸ Some of the departures from linearity arise because the cone angles for unsymmetrical ligands are assumed to be weighted-average values, whereas the E'_R values are calculated for each ligand. For PR_2R' and PRR'_2 ligands, the computed E'_R values are often lower than predicted from a weighted average of the values for PR_3 and PR'_3 ligands, because the ligand can accommodate in binding to the metal by tilting with respect to the Rh-P bond.

The data for phosphites are superimposed on the phosphine correlation in Figure 6. The phosphites behave in relationship to the phosphines in the same manner as seen for the $Cr(CO)_5(PR_3)$ complexes.⁵ At lower cone angle values, the phosphites have comparatively higher E'_R values, because the lone pairs are more prominently weighted in the molecular mechanics calculation than in the CPK models of these ligands. On the other hand, for phosphites of larger cone angle, the E'_R values are lower, because the phosphites are comparatively flexible ligands, more capable than the phosphines of distortions that relieve strong repulsive interactions.

The E'_R values for $CpRh(CO)$ are graphed vs the E_R values for $Cr(CO)_5$ in Figure 7. When all ligands are included, the correlation coefficient for the linear regression is 0.93. When the outlier $P(OPh)_3$ ligand is dropped, giving rise to the linear regression shown in Figure 7, the correlation coefficient is 0.95. The slope of the correlation is 1.4. The magnitude of the slope

(25) Brown, H. C.; Bartholomay, H. Jr.; Taylor, M. D. *J. Am. Chem. Soc.* 1944, 66, 435.

implies that the $\text{Cr}(\text{CO})_5$ metal center is more crowded than the $\text{CpRh}(\text{CO})$ metal center with respect to the ligands included in this study.

The origin of the anomalously high E'_R value for $\text{P}(\text{OPh})_3$ lies in repulsive interactions between one of the phenyl rings and the Cp ring. The steric requirements of the lone pairs on oxygen promote a configuration for each OPh group in which the group dihedral angle is small. Indeed, group dihedral angles near zero are computed for free $\text{P}(\text{OPh})_3$. In the $\text{Cr}(\text{CO})_5$ complex, the $\text{P}(\text{OPh})_3$ ligand can accommodate to the $\text{Cr}(\text{CO})_5$ by a 180° twisting of one OPh group, and approximately 90° twists of the other two. In $\text{CpRh}(\text{CO})$ the three group dihedral angles are -37.6 , -65.9 , and $+29.6^\circ$. In this configuration, one of the phenyl rings experiences substantial steric interaction with the Cp ring, giving rise to the anomalously large value of E'_R .

It is noteworthy that the correlation between E'_R and θ (Figure 6) for phosphine ligands has a nonzero intercept, E'_R at $\theta = 76^\circ$. The intercept for the phosphine ligand series in $\text{Cr}(\text{CO})_5$ complexes, referred to previously as the absolute steric threshold, was found to be 86° . Thus in terms of this measure, the onset of a ligand steric effect occurs at an even smaller value of θ for the $\text{CpRh}(\text{CO})$ complex than for $\text{Cr}(\text{CO})_5$. There is, however, a fairly high uncertainty in the values of the intercept in both series. Comparison of the slopes of E_R vs θ plots for different metal centers may be a better way to measure the relative crowdedness of the metal center for a given series of ligands.

Another steric threshold, reflected in the variation in total energy change, ΔE_T , for the $\text{CpRh}(\text{CO})$ -ligand interaction as a function of ligand size, also provides an indication of the crowding at the metal center. For the phosphine ligands, the graph of ΔE_T vs θ exhibits a negative slope at smaller values of θ , because the attractive component of the van der Waals term increases more rapidly than the repulsive one. However, there is a turning point at around 160° (Figure 5). The analogous apparent steric threshold occurs at about 145° for the $\text{Cr}(\text{CO})_5$ metal center.^{12b} Thus, on this basis as well as from the slope of the E'_R vs E_R graph, Figure 7, it is clear that $\text{CpRh}(\text{CO})$ is the more open metal center.

There have been attempts to measure ligand cone angles in specific metal complexes on the basis of X-ray structural data.⁶ These studies provide evidence that variations in ligand conformation from one complex to another result in variations in their effective steric requirements. However, there has been no method of assessing the variations in ligand steric requirements for a wide range of ligands and metal centers, nor has there been a

method applicable to the isolated complex; that is, free of the intermolecular forces that operate in the solid state. The computation of E_R values provides such an opportunity.

The results displayed in Figure 7 show first of all that, except for one outlier ligand, there is a generally good correlation between the E'_R values computed for $\text{CpRh}(\text{CO})$ complexes and the E_R values computed for $\text{Cr}(\text{CO})_5$ complexes. The $\text{CpRh}(\text{CO})$ metal center was chosen for this study in part because it differs substantially from $\text{Cr}(\text{CO})_5$, both in terms of the local symmetry experienced by the ligand along the ligand-metal bond, and in terms of the degree of crowding about the metal center. The fact that a generally good correlation between E'_R and E_R values is seen means that the E_R values derived from computations of the $\text{Cr}(\text{CO})_5$ complexes should be generally applicable as measures of relative ligand steric effects in a variety of situations.

At the same time, the departures from the linear relationship that are observed provide a measure of the uncertainty that attaches to E_R as a measure of ligand steric requirement. This uncertainty does not reside in some deficiency in E_R as a steric parameter that is somehow absent in another measure, such as the cone angle. Because the cone angle is measured on the ligand in isolation, or is based on an assumed conformation for the ligand, it has the appearance of an invariant quantity, but the variations in ligand conformations seen in X-ray structures demonstrate that even fairly compact ligands have variable steric requirements. Those that have the capacity to adopt multiple conformations, with differing steric properties (e.g., $\text{P}(\text{OEt})_3$, $\text{P}(\text{CH}_2\text{Ph})_3$), can be expected to exhibit even larger variations. Among other things, this means that in the use of any ligand steric parameter in linear free energy correlations, the interpretations must be colored by an appreciation of the variability inherent in the parameter.

Acknowledgment. This research was supported by the National Science Foundation through Grants NSFCHE89-12773 and NSFCHE92-13531. BIOGRAF was made available through an academic grant from Molecular Simulations, Inc. The Stardent Titan computer on which the calculations were carried out was obtained through a University Research Initiative award from the Defense Advanced Research Projects Agency. The crystal structure determination of $\text{CpRh}(\text{CO})(\text{PPh}_3)$ was carried out in the X-ray Diffraction Center of the School of Chemical Sciences by Dr. Scott Wilson.

Supplementary Material Available: ORTEP drawings and tables of bond distances, bond angles, positional and thermal parameters (7 pages). Ordering information is given on any current masthead page.