

# A Simple Representation of Steric Bulk for Ligands by a Modified van der Waals Energy Expression

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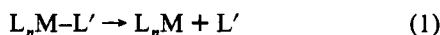
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The van der Waals interaction energy,  $\Delta E_{\text{vdw}}$ , between  $\text{PX}_3$  and the three metal fragments  $\text{Cr}(\text{CO})_5$ ,  $\text{Pd}(\text{PX}_3)_3$ , and  $\text{Pd}(\text{PX}_3)_2$  has been studied by a modified all-repulsive van der Waals energy term,  $E_{\text{vdw}}(\text{mod})$ , within the framework of molecular mechanics. The interaction energy,  $\Delta E_{\text{vdw}}(\text{mod})$ , provides a much better correlation with the Tolman cone angle than  $\Delta E_{\text{vdw}}(\text{rep/att})$  from the original van der Waals energy expression employed by the MMP2 force field,  $E_{\text{vdw}}(\text{rep/att})$ . The original  $E_{\text{vdw}}(\text{rep/att})$  term has an attractive component, and in many cases affords  $\Delta E_{\text{vdw}}(\text{rep/att})$  interaction energies that are increasingly stabilizing as the steric bulk of  $\text{PR}_3$  grows. The replacement of  $E_{\text{vdw}}(\text{rep/att})$  by  $E_{\text{vdw}}(\text{mod})$  in the MMP2 energy expression does not significantly change the optimized structures. It is finally suggested that the total difference in the MMP2 energy between  $\text{L}_n\text{M}-\text{L}'$  on the one hand and  $\text{L}'$  and  $\text{L}_n\text{M}$  on the other might provide a good measure in absolute terms for the steric ligand interaction energy between  $\text{L}'$  and  $\text{L}_n\text{M}$ , provided that  $E_{\text{vdw}}(\text{rep/att})$  is replaced by  $E_{\text{vdw}}(\text{mod})$ .

## I. Introduction

It is useful and customary<sup>1</sup> to discuss the metal–ligand bond dissociation energy  $D(\text{M}-\text{L}')$  for the process



in terms of steric and electronic effects:

$$D(\text{M}-\text{L}') = -(\Delta E_{\text{elec}} + \Delta E_{\text{steric}}) \quad (2)$$

The electronic part,  $\Delta E_{\text{elec}}$ , and the steric contribution,  $\Delta E_{\text{steric}}$ , can be defined quantum mechanically in various ways.<sup>2</sup> The steric<sup>2h</sup> and destabilizing part originates basically from repulsive two-orbital four-electron interactions between occupied orbitals on  $\text{L}'$  and the metal fragment  $\text{ML}_n$ . The stabilizing electronic contribution<sup>2h</sup> is on the other hand the result of interactions between occupied and empty orbitals on  $\text{L}'$  and  $\text{ML}_n$ . The electronic part gives rise<sup>2</sup> to covalent bonding, transfer of charge between  $\text{ML}_n$  and  $\text{L}'$ , and charge polarization on each of the two fragments.

It is often assumed that  $\Delta E_{\text{elec}}$  and  $\Delta E_{\text{steric}}$  are separable and that  $\Delta E_{\text{elec}}$  is the same for a series of ligands  $\text{L}'$ . In that case trends in  $D(\text{M}-\text{L}')$  can be discussed in terms of  $\Delta E_{\text{steric}}$  which is related to the steric bulk of  $\text{L}'$ . The correlation between  $\Delta E_{\text{steric}}$  and steric bulk is conveniently discussed in terms of a free energy relationship<sup>3</sup>

$$\Delta E_{\text{steric}} = \alpha\gamma \quad (3)$$

where  $\gamma$  is an index for steric bulk and  $\alpha$  an empirical proportionality factor common for all  $\text{L}'$  in the series.

Tolman<sup>4</sup> has rationalized trends in phosphine and phosphite dissociation energies utilizing the so-called cone angle  $\theta$  as the index  $\gamma$  of eq 3. Brown<sup>1</sup> and co-workers have more recently attempted to relate  $\Delta E_{\text{steric}}$  to the van der Waals interaction term of molecular mechanics (MM),  $E_{\text{vdw}}$ , for some of the same  $\text{PR}_3$  dissociation processes studied by Tolman. The van der Waals interaction energy is conceptually related to the cone angle  $\theta$  and should thus serve well as an index for steric bulk. However, the studies by Brown<sup>1</sup> and co-workers revealed a remarkably poor correlation between the  $E_{\text{vdw}}$  term of MM and  $\theta$ . Instead, Brown<sup>1</sup> *et al.* constructed a useful index in terms of the ligand repulsive energy  $E_{\text{R}}$  which correlates well with the cone angle  $\theta$ .

The main objective of our study is to find a modified expression for  $E_{\text{vdw}}$  which will provide a good correlation with  $\theta$ . Such a modified expression could serve as an approximation to real strain energies and as an index  $\gamma$  for the large class of ligands  $\text{L}'$  where a cone angle may not be useful (such as polydentate ligands). Additionally, we shall also briefly discuss how one might determine  $\Delta E_{\text{steric}}$  in absolute terms from molecular mechanics calculations.

## II. Methods

All molecular mechanics calculations were performed on an IBM RISC/6000 workstation, using POLYGRAF by Molecular Simulations, Inc. POLYGRAF's implementation and modifications of the MMP2 force field were employed. Molecular mechanics force fields, including that used in MMP2, are the subject of a number of reviews.<sup>5a,c</sup> We shall only give a brief description of the MMP2 energy terms and parameters here.

The total MMP2 molecular mechanics energy of a molecule,  $E_{\text{T}}$ , consists of a bond stretching component,  $E_{\text{b}}$ , as well as bond bending,  $E_{\theta}$ , bond torsion,  $E_{\phi}$ , and nonbonded components,  $E_{\text{nb}}$ :

$$E_{\text{T}} = E_{\text{b}} + E_{\theta} + E_{\phi} + E_{\text{nb}} \quad (4)$$

In MMP2 the bond stretching component is represented by a cubic term:

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$$E_b = \frac{K_b}{2}(r - r_0)^2[1 - 2(r - r_0)] \quad (5)$$

Here  $r$  is the bond distance,  $r_0$  is the intrinsic bond distance, and  $K_b$  is the bond stretching force constant.

The bond bending component of the MMP2 molecular mechanics energy is a function of the bond angle  $\theta$ :

$$E_\theta = \frac{K_\theta}{2}(\theta - \theta_0)^2[1 - d_\theta(\theta - \theta_0)^4] \quad (6)$$

Here  $\theta_0$  is the intrinsic angle and  $K_\theta$  represents the bond bending force constant. The constant  $d_\theta$  has a default value of 0.754. Various bond stretching and bending cross terms are also present.

The torsional energies are represented as a truncated Fourier expansion:

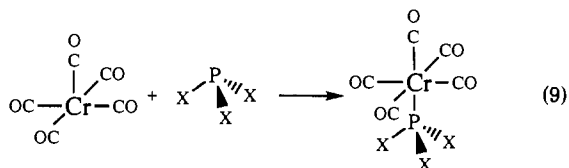
$$E_\phi = \frac{\nu_1}{2}(1 + \cos \phi) + \frac{\nu_2}{2}(1 - \cos 2\phi) + \frac{\nu_3}{2}(1 + \cos 3\phi) \quad (7)$$

The van der Waals interactions are represented by a repulsive/attractive exponential-6 potential as shown in eq 8.  $D_0$  is the well depth of the potential energy minimum,  $r_0$  is the interatomic distance at the minimum, and  $\gamma$  is a scaling factor; see Figure 1.

$$E_{vdw} = D_0 \left\{ \left( \frac{6}{\gamma - 6} \right) e^{(\gamma(1-r/r_0))} - \left( \frac{\gamma}{\gamma - 6} \right) \left( \frac{r_0}{r} \right)^6 \right\} \quad (8)$$

### III. Tolman's Cone Angle and Brown's Ligand Repulsive Energy

In a series of papers by Brown<sup>1</sup> and co-workers an attempt was made to quantify steric bulk by molecular mechanics. The study focused on the steric contribution of the metal-ligand interaction in the binding of phosphine and phosphite ligands to  $\text{Cr}(\text{CO})_5$ . The process is shown in eq 9.



Presently the most widely used index for steric bulk in phosphorus and related ligands is the so-called Tolman<sup>4</sup> cone angle. The cone angle,  $\theta$ , is defined as the apex angle of the cylindrical cone centered 2.28 Å above the P atom, measured along the 3-fold axis of the ligand. The corresponding conical surface is tangent to the outermost van der Waals surface of a space filling model of the ligand. Cone angles were originally based on measurements of CPK space-filling molecular models and have subsequently been measured by some from crystal structures.

Brown applied the molecular mechanics method to the binding of a phosphorus ligand  $\text{PX}_3$  to a  $\text{Cr}(\text{CO})_5$  fragment according to the process of eq 9. In the calculations by Brown<sup>1</sup> *et al.* use was made of the MMP2 force field<sup>5,6</sup> with the unknown force field parameters derived from crystal structures and vibrational studies of  $\text{Cr}(\text{CO})_6$ . The change in molecular mechanics energy for this process is given by

$$\Delta E_T = E_T(\text{Cr}(\text{CO})_5\text{PX}_3) - E_T(\text{Cr}(\text{CO})_5) - E_T(\text{PX}_3) \quad (10)$$

Here  $E_T(\text{Cr}(\text{CO})_5\text{PX}_3)$ ,  $E_T(\text{Cr}(\text{CO})_5)$ , and  $E_T(\text{PX}_3)$  are the total molecular mechanics energies defined in eq 4 for  $\text{Cr}(\text{CO})_5\text{PX}_3$ ,  $\text{Cr}(\text{CO})_5$ , and  $\text{PX}_3$ , respectively. The total change in energy,  $\Delta E_T$  (eq 10), can be separated into individual components  $\Delta E_b$ ,

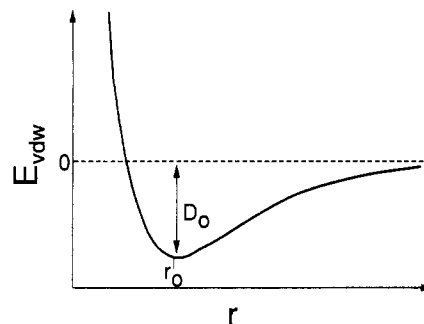


Figure 1. van der Waals potential for  $E_{vdw}(\text{rep/att})$  of eq 8.

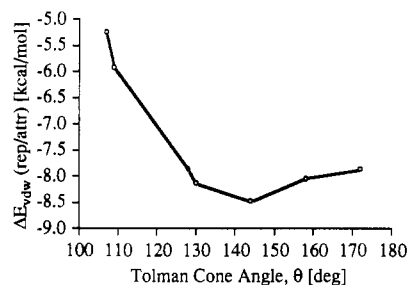


Figure 2.  $\Delta E_{vdw}(\text{rep/att})$  as a function of the Tolman cone angle for a series of phosphite ligands as determined in ref 1a.

$\Delta E_\theta$ ,  $\Delta E_\phi$ , and  $\Delta E_{nb}$ . For example,  $\Delta E_{vdw}$ , which is presented in eq 11, represents the change in the van der Waals energy as the  $\text{Cr}(\text{CO})_5$  and  $\text{PX}_3$  fragments are brought together to form  $\text{Cr}(\text{CO})_5\text{PX}_3$ .

$$\Delta E_{vdw} = E_{vdw}(\text{Cr}+\text{P}) - E_{vdw}(\text{Cr}) - E_{vdw}(\text{P}) \quad (11)$$

Changes in energy due to deformation of the  $\text{Cr}(\text{CO})_5$  and  $\text{PX}_3$  fragments as they are complexed are also proportioned among the bond stretching terms,  $\Delta E_b$ , bond bending terms,  $\Delta E_\theta$ , and bond torsion terms,  $\Delta E_\phi$ .

Brown<sup>1</sup> *et al.* have argued that an effective computational index for steric bulk must take into account that steric forces are short ranged, repulsive, and nonbonded. Bonded electronic effects should not be included in such a measurement. Thus, Brown argued that the total energy change,  $\Delta E_T$ , would be an inappropriate measure of the steric bulk because both steric,  $\Delta E_{vdw}$ , and electronic components,  $\Delta E_b + \Delta E_\theta + \Delta E_\phi$  are intermingled within it.

It was initially expected that the change in the van der Waals energy,  $\Delta E_{vdw}$ , could provide a measure for steric bulk. However, the results obtained by Brown<sup>1c</sup> using  $\Delta E_{vdw}$  show no clear correlation to the Tolman cone angle. In fact, for a series of phosphites, it was found that the  $\Delta E_{vdw}$  term became progressively smaller as the steric bulk increased. These results<sup>1c</sup> are presented in Table 1 and plotted for a series of phosphites in Figure 2. In other words, as the phosphite ligand increased in size, the complexes became more stabilized by the van der Waals interaction. This trend is somewhat counterintuitive since one would expect the complex to be destabilized as the ligands become more bulky.

The origin of the counterintuitive trend in  $\Delta E_{vdw}$ , Table 1, has been analyzed.<sup>1</sup> It can be traced to the fact that the MMP2 van der Waals interaction has both a destabilizing repulsive term and a stabilizing attractive component, Figure 1 and eq 8. The relatively small attractive contributions are encountered at larger interatomic distances whereas the larger repulsive interactions occur at a shorter range. In a metal complex with many atoms crowded together the large number of attractive contributions add up to a considerable stabilization. The attractive contributions come in particular from interactions between atoms on the  $\text{PX}_3$  group and the CO ligands.

Table 1. Brown's Steric Parameters for Phosphorus Ligands<sup>1</sup>

ligand	Tolman cone angle (deg)	$\Delta E_T^a$	$\Delta E_b^a$	$\Delta E_\rho^a$	$\Delta E_\phi^a$	$\Delta E_{vdw}(\text{rep/attr})^a$	Brown's $E_R^a$
P(O- <i>t</i> -Bu) <sub>3</sub>	172	6.29	0.64	9.76	3.82	-7.86	99
P(O- <i>t</i> -Bu) <sub>2</sub> (O- <i>i</i> -Pr)	158	4.48	0.57	8.34	3.57	-8.04	90
P(O- <i>i</i> -Pr) <sub>2</sub> (O- <i>t</i> -Bu)	144	1.72	0.39	5.59	4.21	-8.47	78
P(O- <i>i</i> -Pr) <sub>3</sub>	130	0.29	0.34	4.07	4.00	-8.12	74
P(OPh) <sub>3</sub>	128	4.80	0.30	4.55	8.15	-7.86	57
P(OEt) <sub>3</sub>	109	-1.52	0.16	1.79	2.46	-5.92	59
P(OMe) <sub>3</sub>	107	0.45	0.19	1.12	3.47	-5.24	52
P( <i>t</i> -Bu) <sub>3</sub>	182	9.56	9.31	-0.31	1.42	-0.86	154
P( <i>i</i> -Pr)( <i>t</i> -Bu) <sub>2</sub>	175	4.66	7.34	-0.12	-0.05	-2.51	127
P( <i>i</i> -Pr) <sub>2</sub> ( <i>t</i> -Bu)	167	0.67	2.44	0.42	0.95	-3.14	123
P( <i>i</i> -Pr) <sub>3</sub>	160	-0.75	1.50	0.91	0.24	-3.40	109
P( <i>i</i> -Pr) <sub>2</sub> (Et)	151	-2.95	0.89	0.96	0.03	-4.83	91
P( <i>i</i> -Pr) <sub>2</sub> (Me)	146	-4.18	0.49	0.35	-0.01	-5.01	78
P(Et) <sub>2</sub> ( <i>i</i> -Pr)	141	-4.60	0.32	0.40	0.09	-5.44	75
P( <i>i</i> -Pr)(Me) <sub>2</sub>	132	-4.50	0.12	0.72	-0.12	-5.22	57
P(Et) <sub>3</sub>	132	-4.72	0.10	1.20	-0.02	-6.00	61
P(Et) <sub>2</sub> Me	127	-5.03	0.11	0.49	-0.16	-5.47	57
P(Me) <sub>2</sub> Et	123	-4.83	0.04	0.29	-0.19	-4.97	48
P(Me) <sub>3</sub>	118	-4.40	0.02	0.07	-0.20	-4.29	39

<sup>a</sup> kcal/mol.

The poor correlation between  $\Delta E_{vdw}$  from MMP2 and the Tolman cone angle, Figure 2, lead Brown *et al.* to propose a new measure of steric bulk, the ligand repulsive energy  $E_R$ . The definition of  $E_R$  is given in eq 12. Here,  $R_c$  represents the

$$E_R = R_c \left( \frac{\partial E_{vdw}(\text{rep})}{\partial r(\text{Cr-P})} \right) \quad (12)$$

equilibrium Cr-P distance in the optimized structure and  $E_{vdw}(\text{rep})$  is the repulsive component of the total van der Waals energy term of eq 8. The purely repulsive van der Waals expression,  $E_{vdw}(\text{rep})$ , is shown in eq 13 with the parameters  $D_0$ ,  $\gamma$ , and  $r_0$

$$E_{vdw}(\text{rep}) = D_0 e^{(\gamma(1-r/r_0))} \quad (13)$$

taken from the total van der Waals energy expression. Brown's results using his newly defined ligand repulsive energy,  $E_R$ , are presented in Table 1.

It follows from Table 1 that there is a good correlation between Tolman's cone angle and Brown's  $E_R$  term. Brown's ligand repulsive energy can in addition easily be applied to unsymmetrical  $PX_2X'$  ligands where  $\theta$  is difficult to define. An extension to other types of ligands bound to the metal through a single atom is also straightforward. Thus,  $E_R$  is in many ways an attractive alternative to  $\theta$ .

We shall in the next section provide a different measure of steric bulk based on a modified expression for  $E_{vdw}$  of eq 13. Our work is motivated by the feeling that one must be able to describe steric bulk by repulsive contact terms with a direct bearing on the van der Waals radii, as it is in fact implied in the Tolman cone angle model, rather than on derivatives of  $E_{vdw}$ . We are in addition interested in a measure that can be easily extended to multidentate ligands where  $E_R$  seems less applicable. Finally, we are ultimately interested in an absolute estimate of  $\Delta E_{steric}$  rather than the indices,  $\gamma$ , provided by  $\theta$  and  $E_R$ . The modified expression for  $E_{vdw}$  might afford a first step in that direction.

#### IV. Alternative Representation of the van der Waals Term

The origin of the surprisingly poor correlation between  $\Delta E_{vdw}$  and Tolman's cone angle, Figure 2, is as already mentioned, the attractive part of  $E_{vdw}$ , Figure 1. One might thus try to modify  $E_{vdw}$  of eq 8, which we shall now refer to as  $E_{vdw}(\text{rep/att})$ , by removing the attractive second term of eq 8 altogether. This will lead to the purely repulsive potential  $E_{vdw}(\text{rep})$  given in eq 13. The purely repulsive potential  $E_{vdw}(\text{rep})$  not only lacks the attractive area in the long range region but is also more repulsive

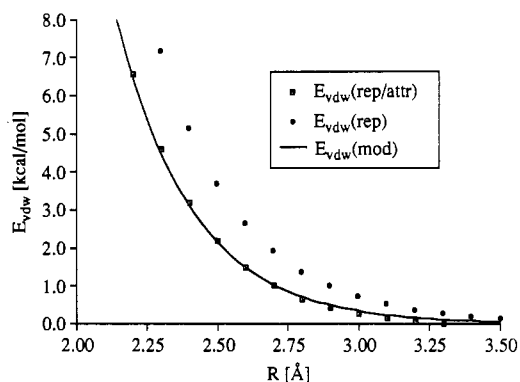


Figure 3. Total van der Waals energy  $E_{vdw}(\text{rep/att})$  compared to Brown's  $E_{vdw}(\text{rep})$  and our  $E_{vdw}(\text{mod})$  for a C-H interaction.

than the net  $E_{vdw}(\text{rep/att})$  at short range as illustrated in Figure 3. Since the MMP2 van der Waals potential is already thought to be too repulsive for short-ranged interactions,<sup>5d</sup> the simple removal of the attractive portion of the potential is expected to exaggerate the steric interactions even further.

We suggest instead a van der Waals term  $E_{vdw}(\text{mod})$  which has the same analytical form as  $E_{vdw}(\text{rep})$  but with the parameters  $D_0$ ,  $\gamma$ , and  $r_0$  chosen from a least-squares fit such that  $E_{vdw}(\text{mod})$  reproduces the repulsive stretch of  $E_{vdw}(\text{rep/att})$ .

Figure 3 shows an example of such a fitted potential for the C-H interaction. The modified parameters  $D_0$ ,  $\gamma$ , and  $r_0$  used in our force field are presented in Table 2. It follows from Figure 3 that the repulsive part of  $E_{vdw}(\text{rep/att})$  is represented reasonably well by  $E_{vdw}(\text{mod})$ . The deviation between  $E_{vdw}(\text{mod})$  and  $E_{vdw}(\text{rep/att})$  in the repulsive region is less than 0.1 kcal mol<sup>-1</sup>, except at interatomic distances far smaller than normal bond length. However, separations considerably shorter than normal bond lengths are not of concern in this study since the corresponding structure will have a prohibitively high  $\Delta E_T$  in any representation of  $E_{vdw}$ .

The attractive component of the van der Waals interaction is real and results from midranged two orbital two electron stabilizing interactions. The MMP2 potential is known to be somewhat too attractive at mid to long distances.<sup>5d</sup> As a simple correction to this, we have removed the attractive portion of the MMP2 van der Waals potential to avoid spurious stabilization. However, in a more refined model where we would expect the van der Waals potential to be more realistic this correction should not be necessary.

**Table 2.** Modified van der Waals Parameters for the  $\Delta E_{\text{vdw}}(\text{mod})$  Expression

interaction	$D_0$ (kcal/mol)	$\gamma$	$r_0$ (Å)
O–O	0.0256	14.243	3.365
H–H	0.0201	14.355	2.948
Lp–Lp <sup>a</sup>	0.0101	13.127	2.373
C–C	0.0238	13.909	3.697
C–O	0.0280	14.094	3.482
C–Lp	0.0155	13.537	3.034
C–H	0.0225	14.229	3.247
C–Cr	0.0434	15.740	3.972
Lp–O	0.0135	13.700	2.923
O–P	0.0340	14.700	3.859
O–Cr	0.0371	15.991	3.868
Lp–P	0.0241	14.191	3.307
H–P	0.0261	15.129	3.658
H–O	0.0207	14.211	3.197
H–Lp	0.0476	12.500	2.425
H–Cr	0.0330	16.523	3.616
C–P	0.0369	14.987	3.928

<sup>a</sup> Lp refers to lone pairs.

Besides the modifications to the van der Waals potential and the parameters  $D_0$ ,  $\gamma$ , and  $r_0$ , the general procedure used to determine  $\Delta E_{\text{vdw}}(\text{mod})$  is very similar to that employed by Brown<sup>1</sup> *et al.*,  $E_{\text{vdw}}(\text{rep/att})$ . The only other notable modification to Brown's procedure involved the minimization technique. Brown adopted a Monte Carlo search of conformational space where between 200 and 300 conformations were randomly generated and the lowest energy structure was chosen as the global minimum. We instead utilized a more efficient scheme which involved three to five cycles simulated annealing between 10 and 500 K followed by minimization. Our own tests showed that the annealing technique not only was time saving but also consistently gave lower minima than the Monte Carlo search strategy. Energy minimizations were carried out using the conjugate gradient method<sup>6</sup> and for the annealing cycles the Nosé–Hoover<sup>7</sup> molecular dynamics method was used. The dynamics runs involved varying the temperature from 10 to 500 K and back down to 10 K in  $10^{\circ}$  steps. The time interval between temperature increments was 0.1 ps and the time step for each time integration cycle was 0.001 ps. Intuitively plausible structures which were minimized were used as starting structures. Our tests revealed that different starting structures (including the Monte Carlo optimal structure) gave structures which varied only slightly in geometry but possessed the same energy within 0.5 kcal/mol.

### V. Application of the Modified van der Waals Term to $\text{Cr}(\text{CO})_5(\text{PX}_3)$

We have applied the MMP2 force field modified with  $E_{\text{vdw}}(\text{mod})$  to the  $\text{Cr}(\text{CO})_5\text{PX}_3$  trialkylphosphine and trialkyl phosphite systems previously studied by Brown<sup>1</sup> *et al.* We shall now demonstrate that steric energies based on  $\Delta E_{\text{vdw}}(\text{mod})$  correlate much better with the Tolman cone angle than those obtained by  $\Delta E_{\text{vdw}}(\text{rep/att})$ . In fact, the correlation is comparable to that achieved by Brown's ligand repulsive energy  $E_{\text{R}}$ .

The structures optimized with the modified van der Waals energy expression involving  $\Delta E_{\text{vdw}}(\text{mod})$  do not differ significantly from those<sup>1</sup> obtained with the original MMP2 van der Waals potential  $\Delta E_{\text{vdw}}(\text{rep/att})$ . Table 3 compares some key geometric parameters from the X-ray crystal structure of  $\text{Cr}(\text{CO})_5\text{PMe}_3$  with the MMP2 minimum energy structure based on  $\Delta E_{\text{vdw}}(\text{rep/att})$  and the structure minimized using the purely repulsive potential  $\Delta E_{\text{vdw}}(\text{mod})$ . For complexes with large steric requirements, such as  $\text{Cr}(\text{CO})_5\text{P}(t\text{-Bu})_3$ , rather large Cr–P distances of  $>2.7$  Å were observed. The origin of these large bond distances is explained by Lee and Brown.<sup>1b</sup>

**Table 3.** Comparison of Key Bond Distances and Angles for  $\text{Cr}(\text{CO})_5\text{PMe}_3$ 

bond or angle <sup>a,b</sup>	crystal structure <sup>c</sup>	MMP2 minimum energy structure <sup>c</sup>	$E_{\text{vdw}}(\text{mod})$ minimum energy structure
Cr–P	2.366	2.360	2.370
P–C6	1.813	1.811	1.814
P–C7	1.815	1.811	1.813
P–C8	1.814	1.810	1.813
Cr–C1	1.850	1.850	1.852
Cr–C2	1.894	1.879	1.882
Cr–C3	1.891	1.879	1.882
Cr–C4	1.888	1.880	1.882
Cr–C5	1.897	1.880	1.882
C6–P–C7	102.6	102.1	102.2
C6–P–C8	102.9	102.6	102.0
C7–P–C8	101.9	102.5	102.6
P–Cr–C2	90.68	90.53	90.06
P–Cr–C3	88.16	89.55	90.21
P–Cr–C4	88.04	90.40	91.30
P–Cr–C5	90.74	91.14	91.42
Cr–P–C6	116.0	115.7	115.9
Cr–P–C7	114.7	115.1	115.2
Cr–P–C8	116.8	116.9	116.8

<sup>a</sup> Atom numbering defined in ref 16. <sup>b</sup> Angles in deg; bond distances in Å. <sup>c</sup> Reference 16.

Table 4 compares  $\Delta E_{\text{vdw}}(\text{mod})$  and  $\Delta E_{\text{vdw}}(\text{rep/att})$  for a number of trialkylphosphine and trialkyl phosphite ligands. It is clear from Table 4 that the steric energies calculated with  $\Delta E_{\text{vdw}}(\text{mod})$  display a clear improvement over  $\Delta E_{\text{vdw}}(\text{rep/att})$  in the correlation with the Tolman cone angle. Correlation coefficients for  $\Delta E_{\text{vdw}}(\text{rep/att})$ ,  $\Delta E_{\text{vdw}}(\text{mod})$ , and  $E_{\text{R}}$  with respect to the Tolman cone angle are given in Table 5. For both trialkylphosphine and trialkyl phosphite ligands,  $\Delta E_{\text{vdw}}(\text{rep/att})$  correlates poorly with the cone angle having a correlation coefficient of only 0.37, and the  $\Delta E_{\text{vdw}}(\text{rep/att})$  values are in most cases negative.

By contrast,  $\Delta E_{\text{vdw}}(\text{mod})$  and  $E_{\text{R}}$  are found to correlate well with the Tolman cone angle for both trialkylphosphines and trialkyl phosphites, Table 5. Figure 4 compares the two measures of steric bulk as a function of the cone angle for the trialkyl phosphites (a), trialkylphosphines (b), and all of the ligands tested (c). For the small group of trialkyl phosphites tested,  $\Delta E_{\text{vdw}}(\text{mod})$  and  $E_{\text{R}}$  have a correlation coefficient of 0.98, Table 5. For the trialkylphosphines, the correlation is also very good, with correlation coefficients of 0.96 and 0.99 for  $\Delta E_{\text{vdw}}(\text{mod})$  and  $E_{\text{R}}$ , respectively. When all of the ligands are considered, both measures of the steric bulk correlate well with the Tolman's cone angle although  $E_{\text{R}}$  does somewhat better. Brown's ligand repulsive energy has a correlation coefficient of 0.92 for all ligands as compared with 0.84 for  $\Delta E_{\text{vdw}}(\text{mod})$ .

Despite of the lower correlation to the cone angle,  $\Delta E_{\text{vdw}}(\text{mod})$  has several advantages over the ligand repulsive energy  $E_{\text{R}}$ . First,  $\Delta E_{\text{vdw}}(\text{mod})$  is simple and more direct than  $E_{\text{R}}$ . A measure of the steric requirements for a ligand upon complexation is more intuitively expressed as the direct change in the Waals energy upon complexation as opposed to the gradient of the van der Waals energy with respect to the metal–ligand distance  $R_{\text{ML}}$  multiplied by  $R_{\text{ML}}$ . In addition,  $\Delta E_{\text{vdw}}(\text{mod})$  is more easily extended to comparing other ligand systems including multi-dentate ligands for which the Tolman cone angle and  $E_{\text{R}}$  may not be useful measures of steric bulk. For example, it would be difficult to procure a measure of steric bulk for crown ethers using either the cone angle concept or  $E_{\text{R}}$ . Also, since  $E_{\text{R}}$  is directly proportional to the (M–L) bond distance, it may underestimate the steric requirements of bulky ligands which form short M–L bonds.

We shall in the next section extend the application of  $\Delta E_{\text{vdw}}(\text{mod})$  to some of the  $d^{10} \text{M}(\text{PR}_3)_n$  complexes which are known to be dominated by steric factors and that have played a crucial role in studies on steric ligand effects.

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**Table 4.** Molecular Mechanics Energies<sup>a</sup> Using  $E_{vdw}(mod)$  Compared to the Tolman Angle and  $E_R$  for Phosphine and Phosphite Complexes of  $Cr(CO)_5$ 

ligand	Tolman cone angle (deg)	$\Delta E_T$	$\Delta E_b$	$\Delta E_\theta$	$\Delta E_\phi$	$\Delta E_{vdw}(mod)$	$E_R^b$	$\Delta E_{vdw}(rep/attr)^c$
P(O- <i>t</i> -Bu) <sub>3</sub>	172	19.03	1.36	9.05	2.73	5.89	99	-7.86
P(O- <i>t</i> -Bu) <sub>3</sub> 2(O- <i>i</i> -Pr)	158	15.44	1.07	7.57	1.88	4.91	90	-8.04
P(O- <i>i</i> -Pr) <sub>2</sub> (O- <i>t</i> -Bu)	144	12.27	0.77	4.46	2.54	4.50	78	-8.47
P(O- <i>i</i> -Pr) <sub>3</sub>	130	9.11	0.75	2.60	1.63	4.14	74	-8.12
P(OPh) <sub>3</sub>	128	14.51	0.55	3.57	6.62	3.77	65	-7.86
P(OEt) <sub>3</sub>	109	7.91	0.46	2.28	1.79	3.37	59	-5.92
P(OMe) <sub>3</sub>	107	7.51	0.39	1.97	2.08	3.07	52	-5.24
P( <i>t</i> -Bu) <sub>3</sub>	182	24.89	5.14	3.90	1.68	14.17	154	-0.86
P( <i>i</i> -Pr)( <i>t</i> -Bu) <sub>2</sub>	175	18.95	3.68	0.66	1.23	13.37	127	-2.51
P( <i>i</i> -Pr) <sub>2</sub> ( <i>t</i> -Bu)	167	14.31	2.37	1.69	1.23	9.02	123	-3.14
P( <i>i</i> -Pr) <sub>3</sub>	160	10.17	1.45	1.52	0.29	6.91	109	-3.40
P( <i>i</i> -Pr) <sub>2</sub> (Et)	151	8.23	0.81	1.55	0.23	5.64	91	-4.83
P( <i>i</i> -Pr) <sub>2</sub> (Me)	146	5.18	0.45	0.87	-0.22	4.07	78	-5.01
P(Et) <sub>2</sub> ( <i>i</i> -Pr)	141	5.29	0.41	0.72	0.13	4.02	75	-5.44
P( <i>i</i> -Pr)(Me) <sub>2</sub>	132	2.88	0.18	0.16	0.08	2.45	57	-5.22
P(Et) <sub>3</sub>	132	5.54	0.41	1.34	0.64	3.15	61	-6.00
P(Et) <sub>2</sub> Me	127	3.55	0.18	0.75	0.20	2.41	57	-5.47
P(Me) <sub>2</sub> Et	123	2.36	0.08	0.40	0.04	1.85	48	-4.97
P(Me) <sub>3</sub>	118	1.77	0.05	0.27	0.00	1.44	39	-4.29

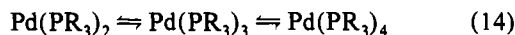
<sup>a</sup> kcal/mol. <sup>b</sup> Reference 1a. <sup>c</sup> Reference 1a,c.

**Table 5.** Correlation Coefficients for the Comparison of  $\Delta E_{vdw}(rep/att)$ ,  $E_R$  and  $\Delta E_{vdw}(mod)$  with the Tolman Cone Angle

	$\Delta E_{vdw}(rep/att)$	$E_R$	$\Delta E_{vdw}(mod)$
phosphites	0.74	0.98	0.98
phosphines	0.83	0.99	0.96
all ligands	0.37	0.92	0.84

## VI. Application of $\Delta E_{vdw}(mod)$ to the Dissociation of Palladium Trialkylphosphine Complexes

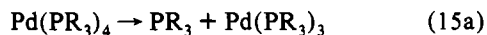
The d<sup>10</sup> M(PR<sub>3</sub>)<sub>n</sub> complexes with M = Pt, Pd, and Ni were among the first to which Tolman<sup>4</sup> applied his cone angle concept. The M(PR<sub>3</sub>)<sub>n</sub> complexes exhibit an equilibrium between tetra-coordinate, tricoordinate, and dicoordinate metal as shown in eq 14 for M = Pd.



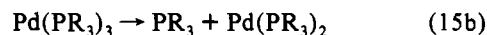
The position of the equilibrium was found to be a function of the steric bulk of the PR<sub>3</sub> ligand and not the basicity of the phosphines.<sup>8</sup> The equilibrium gradually shifted to lower coordination numbers as the cone angle of PR<sub>3</sub> increased.

The palladium systems have primarily been investigated by Musco and co-workers<sup>8</sup> who have shown that the ligand dissociation equilibrium is dominated by the steric bulk of the phosphine ligands. Studies<sup>8d</sup> based on <sup>31</sup>P NMR revealed that tetracoordinated systems were the prevalent species for the small size phosphines PMe<sub>3</sub> and PMe<sub>2</sub>Ph where  $\theta < 130^\circ$ . For larger ligands such as PEt<sub>3</sub>, P(*n*-Bu)<sub>3</sub>, PPh<sub>3</sub>, and P(CH<sub>2</sub>-Ph)<sub>3</sub> tricoordination becomes dominant. Finally for the phosphines P(*i*-Pr)<sub>3</sub>, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>, and P(*t*-Bu)<sub>2</sub>Ph with  $\theta > 155^\circ$  only the dicoordinated species are observed.

We have carried out a MMP2 study on the Pd(PR<sub>3</sub>)<sub>n</sub> species with  $n = 4, 3$ , and 2, using our modified van der Waals potential  $E_{vdw}(mod)$ . Calculations were carried out on the change in the total molecular mechanics energy  $E_T$  of eq 4 for the processes



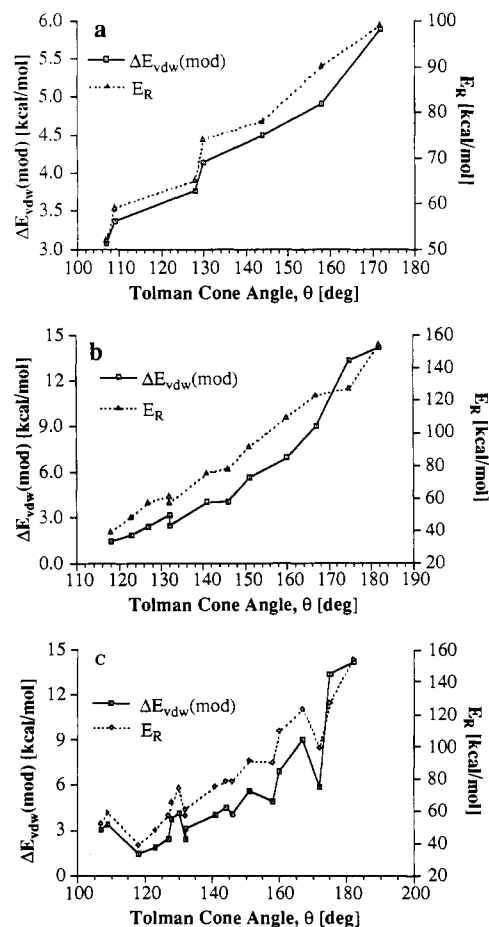
and



The change in energy is given by

$$\Delta E_T((n-1)-n) = E[Pd(PR_3)_n] - E[Pd(PR_3)_{(n-1)}] - E[PR_3] \quad (16)$$

with a similar expression for the change in the modified van der Waals energy.

**Figure 4.** Ligand repulsive energy,  $E_R$ , and  $\Delta E_{vdw}(mod)$  as a function of the Tolman cone angle for (a) trialkyl phosphite, (b) trialkyl phosphine, and (c) trialkyl phosphite and trialkyl phosphine complexes of  $Cr(CO)_5$ .

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**Table 6.** Change in Molecular Mechanics Energy<sup>a,b</sup> for  $\text{Pb}(\text{PR}_3)_2 + \text{PR}_3 \Rightarrow \text{Pd}(\text{PR}_3)_3$  Using the Modified van der Waals Potentials

ligand	cone angle (deg)	$\Delta E_{\tau(2-3)}$	$\Delta E_r(2-3)$	$\Delta E_{\theta(2-3)}$	$\Delta E_{\phi(2-3)}$	$\Delta E_{\text{vdw}(2-3)}$
$\text{PMe}_3$	118	0.67	0.00	0.18	0.00	0.49
$\text{PEt}_2\text{Me}$	127	-0.88	0.05	-1.48	-0.13	0.68
$\text{PEt}_3$	132	1.98	0.08	0.02	0.18	1.70
$\text{P}(n\text{-Pr})_3$	132	4.88	0.08	1.49	0.40	2.90
$\text{P}(t\text{-Bu})\text{Me}_2$	139	7.39	0.50	0.48	1.02	5.39
$\text{P}(i\text{-Bu})_3$	143	11.12	0.49	1.81	2.62	7.20
$\text{P}(i\text{-Pr})_2\text{Et}$	151	8.30	0.64	-0.62	1.38	6.89
$\text{P}(i\text{-Pr})_3$	160	20.80	1.84	3.13	1.22	14.61
$\text{P}(t\text{-Bu})_2\text{Et}_2$	165	45.11	6.05	3.80	5.52	29.30
$\text{P}(t\text{-Bu})_2(i\text{-Pr})$	175	61.96	10.15	4.68	5.74	41.39
$\text{P}(t\text{-Bu})_3$	182	128.32	22.30	23.59	9.39	73.03

<sup>a</sup> Energies in kcal/mol. <sup>b</sup> Energy terms defined in eq 16.

**Table 7.** Change in Molecular Mechanics Energy<sup>a,b</sup> for  $\text{Pd}(\text{PR}_3)_3 + \text{PR}_3 \Rightarrow \text{Pd}(\text{PR}_3)_4$  Using the Modified van der Waals Potentials

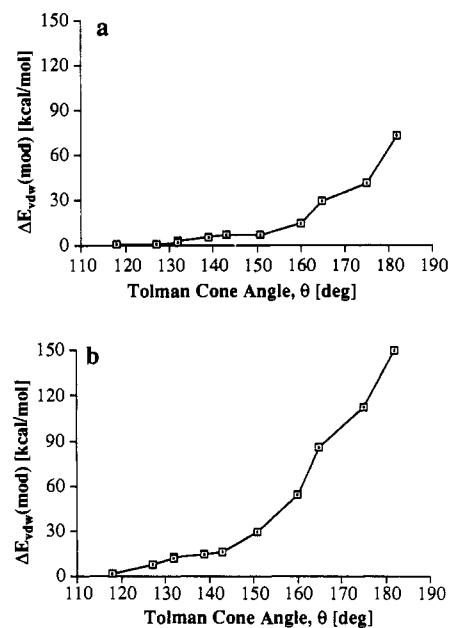
ligand	cone angle (deg)	$\Delta E_{\tau(3-4)}$	$\Delta E_r(3-4)$	$\Delta E_{\theta(3-4)}$	$\Delta E_{\phi(3-4)}$	$\Delta E_{\text{vdw}(3-4)}$
$\text{PMe}_3$	118	1.91	0.00	0.02	0.11	1.77
$\text{PEt}_2\text{Me}$	127	12.10	0.28	2.67	1.41	7.74
$\text{PEt}_3$	132	21.52	0.44	4.38	4.58	12.12
$\text{P}(n\text{-Pr})_3$	132	24.19	0.75	5.89	4.51	13.03
$\text{P}(t\text{-Bu})\text{Me}_2$	139	22.24	2.20	3.24	2.25	14.55
$\text{P}(i\text{-Bu})_3$	143	41.27	1.26	18.21	5.62	16.17
$\text{P}(i\text{-Pr})_2\text{Et}$	151	55.37	4.14	14.72	6.86	29.65
$\text{P}(i\text{-Pr})_3$	160	100.66	12.03	27.27	6.99	54.37
$\text{P}(t\text{-Bu})_2\text{Et}_2$	165	161.69	25.98	44.98	5.03	85.70
$\text{P}(t\text{-Bu})_2(i\text{-Pr})$	175	216.24	36.76	49.07	18.39	112.02
$\text{P}(t\text{-Bu})_3$	182	298.02	63.36	63.76	21.59	149.31

<sup>a</sup> Energies in kcal/mol. <sup>b</sup> Energy terms defined in eq 16.

A procedure similar to that used to determine  $\Delta E$  for the previously discussed chromium trialkylphosphine and phosphite systems was utilized. For lack of good parameters, the geometries of the  $\text{Pd-L}_n$  skeleton were fixed. The  $\text{PdL}_2$  complexes were confined to a linear geometry. There are accounts of  $\text{Pd}(\text{PR}_3)_2$  systems having nonlinear geometries<sup>8,9</sup> but most crystallographic structures and NMR data exhibit linear or nearly linear structures.<sup>8a,b,10</sup> The  $\text{PdL}_3$  complexes were restrained to a perfect trigonal planar conformation, while the  $\text{PdL}_4$  species were fixed in a tetrahedral geometry. The  $\text{Pd-P}$  distances in the  $\text{Pd}(\text{PR}_3)_n$  complexes were frozen at 2.33 Å for  $n = 4$ , 2.30 Å for  $n = 3$ , and 2.27 Å for  $n = 2$ .<sup>8a,b,10,11</sup> The  $\text{Pd-P-C}(\text{sp}^3)$  bending parameters were not available, so the  $\text{Cr-P-C}(\text{sp}^3)$  bending parameters from Brown's work<sup>1</sup> were adopted as an approximation. As in the chromium calculations, all torsions involving the metal center were assumed to have zero barrier. It was felt that the van der Waals parameters used for the chromium center could be used for palladium without modification (Table 2) since this parameter appeared to have little effect on  $\Delta E$ . Brown found with his calculations that as much as a 30% variation in the  $r_0$  parameter for Cr had little effect on  $\Delta E_{\text{vdw}}(\text{rep/att})$ .

Tables 6 and 7 display the changes in molecular mechanics energies for the two processes in described in eqs 15a and 16b, respectively. The corresponding changes in  $E_{\text{vdw}}(\text{mod})$  and  $E_{\text{total}}(\text{mod})$  are given in Figures 5 and 6, respectively, as a function of the cone angle.

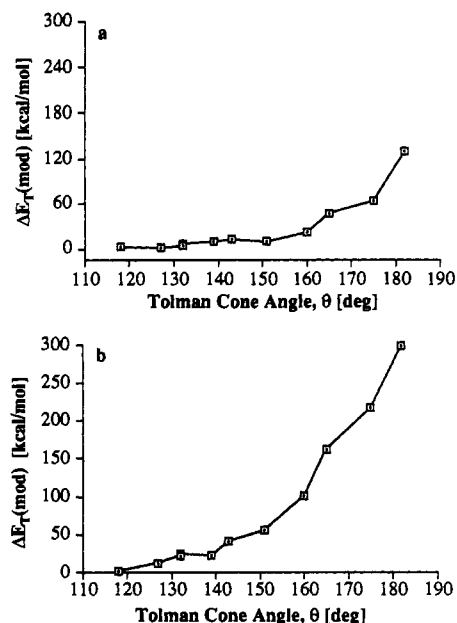
The two graphs in Figure 5 illustrate that  $\Delta E_{\text{vdw}}(\text{mod})$  increases with the cone angle. However, the relationship between  $\Delta E_{\text{vdw}}(\text{mod})$  and  $\theta$  is not linear throughout the whole range of angles. Although this may not be surprising there are several possible reasons for this and for the large values of  $\Delta E_{\text{vdw}}(\text{mod})$  observed. The fixed geometry constraints may prevent the molecule from minimizing to the lowest energy conformations. Also, for very large cone angles many of the complexes do not exist and modeling



**Figure 5.** Change in van der Waals energy,  $\Delta E_{\text{vdw}}(\text{mod})$  as a function of the Tolman cone angle for (a)  $\text{Pd}(\text{PR}_3)_2 + \text{PR}_3 \Rightarrow \text{Pd}(\text{PR}_3)_3$  and (b)  $\text{Pd}(\text{PR}_3)_3 + \text{PR}_3 \Rightarrow \text{Pd}(\text{PR}_3)_4$ .

them may result in exaggerated van der Waals energies. That is, a linear relationship between the Tolman cone angle and the change in  $\Delta E_{\text{vdw}}(\text{mod})$  might only be valid for modest van der Waals energies. There is, however, a linear relationship between  $\Delta E_{\text{vdw}}(\text{mod})$  of  $\text{Pd}(\text{PR}_3)_4$  and  $\theta$  to  $>130^\circ$  where the tricoordinated species becomes prevalent (Figure 5b). Similarly,  $\Delta E_{\text{vdw}}(\text{mod})$  of  $\text{Pd}(\text{PR}_3)_3$  is reasonably proportional to  $\theta$  in the range  $130^\circ < \theta < 155^\circ$  where tricoordination is prevalent (Figure 5a). The large values of  $\Delta E_{\text{vdw}}(\text{mod})$  for the  $\text{PdL}_n$  systems near 150 kcal/mol are particularly impressive when compared to the rather modest values (less than 15 kcal/mol) observed for the  $\text{Cr}(\text{CO})_5\text{L}$  complexes. Since  $\Delta E_{\text{vdw}}(\text{mod})$  is defined to give a reasonable estimation of the real strain energy, this reflects the fact that the

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**Figure 6.** Change in total molecular mechanics energy,  $\Delta E_{\text{vdw}}(\text{mod})$  as a function of the Tolman cone angle for (a)  $\text{Pd}(\text{PR}_3)_2 + \text{PR}_3 \rightarrow \text{Pd}(\text{PR}_3)_3$  and (b)  $\text{Pd}(\text{PR}_3)_3 + \text{PR}_3 \rightarrow \text{Pd}(\text{PR}_3)_4$ .

$\text{PdL}_n$  complexes are significantly more sterically strained than the  $\text{Cr}(\text{CO})_5\text{L}$  complexes.

The change in coordination number of the  $\text{Pd}(\text{PR}_3)_n$  systems from  $n = 4$  to  $n = 3$  is known experimentally<sup>8d</sup> to take place at  $\theta \sim 130^\circ$  with  $\text{PR}_3 = \text{PET}_3$ . This point represents the threshold at which steric demands,  $\Delta E_{\text{steric}}$ , outweigh the electronic complexation energy,  $\Delta E_{\text{elec}}$  (eq 2). The term  $\Delta E_T$  is in our opinion closely related to  $\Delta E_{\text{steric}}$  of the total bond energy,  $D(\text{A}-\text{B})$ , eq 2. When the electronic and steric contributions of a bond in absolute terms are discussed, the total molecular mechanics energy should be used for the steric component,  $\Delta E_{\text{steric}}$ , since the steric interactions of the bond formation are not only manifested in the van der Waals interactions but also in the bond stretches, bends, and torsions. Although it contains  $\text{Pd}-\text{PX}_3$  bond terms, the total molecular mechanics energy lacks the electronic stabilization energy due to the formation of the  $\text{Pd}-\text{PX}_3$  bond. Thus,  $\Delta E_{\text{elec}}$  and  $\Delta E_T \cong \Delta E_{\text{steric}}$  would have to be combined according to eq 2 in order to obtain the total bond energy,  $D(\text{Cr}-\text{PX}_3)$ . We calculate  $\Delta E_T(3-4)$  for  $\text{PET}_3$  to be 21.5 kcal/mol in the MMP2 parametrization with the van der Waals energy represented by  $\Delta E_{\text{vdw}}(\text{mod})$ , Table 7.

The corresponding change from  $\text{Pd}(\text{PR}_3)_3$  to  $\text{Pd}(\text{PR}_3)_2$  takes place at  $\theta \sim 160^\circ$  with  $\text{PR}_3 = \text{P}(i\text{-Pr})_3$ .<sup>8a</sup> We calculate  $\Delta E_T(2-3)$  of  $\text{P}(i\text{-Pr})_3$  to be 20.80 kcal/mol, Table 6. Thus, the MMP2 parametrization provides quite similar steric threshold energies for the two dissociation processes in eqs 15a and 15b. The related changes in the van der Waals energies are also comparable with  $\Delta E_{\text{vdw}}(\text{mod}) = 12$  kcal/mol for  $\text{PET}_3$ , Table 7, and  $\Delta E_{\text{vdw}}(\text{mod}) = 14.6$  kcal/mol for  $\text{P}(i\text{-Pr})_3$ , Table 6.

Lack of experimental  $D(\text{Pd}-\text{PX}_3)$  bond energies makes it difficult to estimate  $\Delta E_{\text{elec}}$  and judge whether the calculated steric threshold energies of  $\sim 21$  kcal/mol are reasonable. We have previously calculated<sup>12</sup> the average  $D(\text{Pd}-\text{PF}_3)$  bond energy in  $\text{Pd}(\text{PF}_3)_4$  as 23 kcal/mol. Despite the crudeness of these molecular mechanics calculations,  $\Delta E_{\text{tot}}$  is in good agreement with this value and it is felt that steric threshold energies of around 20 kcal/mol are realistic.

Entropy effects might make the ligand dissociation more facile by contributing with as much as  $-10$  kcal/mol to the free energy

of dissociation in the related  $\text{Ni}(\text{PR}_3)_4$  systems.<sup>13</sup> However, the arguments presented above are still valid if the entropic contribution to the free energy of dissociation is the same for the two processes in eq 15.

A calorimetric study of Tolman and co-workers,<sup>13b</sup> showed that the number of phosphorus ligands able to bind with nickel in competition with 1,5-cyclooctadiene is dependent on the steric size of the ligand. The strain energies for a number of  $\text{NiL}_4$  complexes with  $\text{Ni}(\text{P}(\text{OMe})_3)_3$  ( $\theta = 107^\circ$ ) taken as the strain-free reference were determined. The average slope the  $\text{NiL}_4$  strain energy with respect to the cone angle was about 6 kcal/mol for every  $10^\circ$  increase in cone angle in the range of  $107-145^\circ$ . This is not too different from the slope over the same range in Figure 5b which was found also to be about 6 kcal/mol for every  $10^\circ$  increase in  $\theta$ .

The present MMP2 force field with some modifications to the van der Waals potential is able to give good relative steric indexes and shows potential in determining absolute steric energies. Work is now in progress to develop accurate MM ligand force fields from quantitative theoretical calculations based on density functional theory.<sup>14</sup> DFT-based methods have been shown to provide accurate harmonic force fields<sup>15</sup> even for transition-metal systems.<sup>14d</sup> Gauges of steric bulk in both relative and absolute terms, based on more accurate force fields should provide better results and hopefully be able to reproduce trends in  $D(\text{L}_n\text{M}-\text{L}')$  energies for a series of similar ligands  $\text{L}'$ .

## VII. Conclusion

The original MMP2 van der Waals energy expression with a repulsive/attractive exponential-6 potential,  $E_{\text{vdw}}(\text{rep/att})$ , has been modified to an all repulsive potential,  $E_{\text{vdw}}(\text{mod})$ . The new energy expression,  $E_{\text{vdw}}(\text{mod})$ , has been applied to calculations on van der Waals energy changes,  $\Delta E_{\text{vdw}}(\text{mod})$ , associated with the formation of  $(\text{CO})_5\text{CrPX}_3$  from  $(\text{CO})_5\text{Cr}$  and  $\text{PX}_3$  for a series of trialkyl phosphites and trialkylphosphines. It has been demonstrated that  $\Delta E_{\text{vdw}}(\text{mod})$  correlates well with the Tolman cone angle in contrast to  $\Delta E_{\text{vdw}}(\text{rep/att})$  from the original MMP2 van der Waals potential.

Studies have also been carried out on the dissociation equilibria  $\text{Pd}(\text{PX}_3)_n \rightarrow \text{Pd}(\text{PX}_3)_{n-1} + \text{PX}_3$  and  $n = 4$  and  $n = 3$ . A good correlation was obtained between the Tolman cone angle,  $\theta$ , and  $\Delta E_{\text{vdw}}(\text{mod})$  for the range of  $\text{PX}_3$  ligands where  $\text{Pd}(\text{PX}_3)_n$  still is observable. The dominant coordination is known to change from tetracoordination to tricoordination at a cone angle of approximately  $130^\circ$  with  $\text{PR}_3 = \text{PET}_3$  and from tricoordination to dicoordination at a cone angle of about  $160^\circ$  with  $\text{PR}_3 = \text{P}(i\text{-Pr})_3$ . The calculated steric energies of complexation for these two processes are in good agreement with one another and a reported calculated  $D(\text{Pd}-\text{PF}_3)$  bond energy of 23 kcal/mol.

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