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A Molecular Mechanics Model of Ligand Effects. 4. Binding of Amines to $Cr(CO)_5$: E_R Values for Amines

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Molecular mechanics methods have been applied to compute the energy-minimized structures of a series of 27 alkylamines and their complexes with $Cr(CO)_5$. The MMP2 force field was employed, using the comprehensive computational program BIOGRAF. The computed structures of $Cr(CO)_5(L)$ (L = piperidine or quinuclidine) are in good agreement with the structural parameters determined by X-ray diffraction studies. In general, substantial changes in the lowest energy conformations are observed in the complexes as compared with the free ligands. The energy-minimized structures are employed to calculate a new measure of ligand steric effect, the ligand repulsive energy, E_R, obtained by computing the van der Waals repulsive force acting between the ligand and $Cr(CO)_5$ fragments along the Cr–N axis, at the equilibrium Cr–N distance, r_e. The repulsive force is scaled by r_e to obtain E_R: $E_R = r_e[dE_{vdw}(\text{repulsive})/dr(\text{Cr–N})]$. The amine E_R values correlate well with cone angle for amines ($r_{corr} = 0.94$). The amine E_R values are compared with those of phosphines. The advantages of E_R as a measure of ligand steric effect are also described.

The steric and electronic properties of ligands have important consequences for the reactivities of inorganic and organometallic compounds.[2] In assessing these properties, researchers have used many different approaches. Electronic properties have been correlated with enthalpies of protonation in nonaqueous media,[3] gas-phase proton affinities,[4] pK_a or half-neutralization potentials in polar aprotic media,[5] or the A_1 symmetry carbonyl stretching frequencies[6] or ^{13}C NMR chemical shift of CO in $Ni(CO)_3(PR_3)$ complexes.[7] However, approaches to assessing the steric properties of ligands have been few. The cone angle θ, developed by Tolman, is the most commonly-employed measure of the steric requirements of trivalent phosphorus and related ligands.[8] Tolman's cone angle concept has the advantage of simplicity and generality, but the approach has several limitations, as noted earlier.[9] As a result of these limitation, modifications of the cone angle concept have been developed; these include modified space-filling molecular models,[10] mathematical models,[11] modifications using X-ray structural data,[12] and semiempirical molecular orbital calculations.[13]

Table I. Added Parameters for MMP2 Force Field Calculations

A. Force Constants for Bond Stretching

bond type	k_s,[a] mdyn $Å^{-1}$	r_0, Å
Cr–N	1.50	2.14
Cr–C(sp) radial	2.10	1.88
Cr–C(sp) axial	2.10	1.85
C(sp)–O(sp) radial	17.04	1.12
C(sp)–O(sp) axial	17.04	1.15
O(sp)–LP[b]	4.60	0.60

B. Force Constants for Bond Angle Deformation

bond angle type	k_b, mdyn Å rad^{-2}	θ, deg
C_{rad}–Cr–N	0.50	90
C_{ax}–Cr–N	0.00	180
Cr–N–C(sp^3)	0.21	115
Cr–N–H	0.21	105

[a] Multiply by 143.88 to convert from mdyn $Å^{-1}$ to kcal mol^{-1} $Å^2$. [b] LP = lone pair.

Molecular mechanics models of phosphite[14] and phosphine[15] ligands and their complexes with a prototypical metal binding site, $Cr(CO)_5$, have been described in previous publications. A new measure of ligand steric effect, the ligand repulsive energy,[9] E_R, based on molecular mechanics calculations has been evaluated for a large number of phosphorus and arsenic ligands. As a continuation of our efforts to develop a versatile, realistic, and readily-employed measure of ligand steric effects, the ligand interactions of amine ligands with the prototypical metal center, $Cr(CO)_5$, have been investigated by molecular mechanics, and E_R values for these ligands have been computed.

Amines are important ligands in transition-metal chemistry and are industrially important compounds. They are frequently found coordinated to metal centers in organometallic compounds,

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Table II. Calculated Molecular Mechanics Energies (kcal mol^{-1}) of the Free Amines and Corresponding $Cr(CO)_5(NR_3)$ Complexes in Their Minimum-Energy Configuration

	free amine					$Cr(CO)_5(NR_3)$				
ligand	E_T	E_b	E_θ	E_ϕ	E_{vdw}	E_T	E_b	E_θ	E_ϕ	E_{vdw}
NH_3	0.67	0.00	0.67	0.00	0.00	−2.97	0.00	0.16	0.00	−3.13
NH_2Me	0.59	0.01	0.18	0.00	0.40	−2.92	0.07	0.54	0.02	−3.55
NH_2Et	1.19	0.06	0.28	−0.15	1.00	−2.10	0.12	0.80	−0.04	−2.97
$NH_2(n\text{-}Pr)$	1.85	0.13	0.40	−0.15	1.48	−1.53	0.18	0.86	−0.044	2.53
$NH_2(i\text{-}Pr)$	1.64	0.15	0.40	−0.31	1.39	−1.02	0.22	1.87	−0.09	−3.01
$NH_2(i\text{-}Bu)$	2.99	0.27	0.57	0.35	1.80	−0.04	0.34	1.33	0.58	−2.30
NH_2(neo)[a]	4.34	0.54	0.88	0.89	2.03	1.47	0.63	2.01	1.05	−2.22
$NH_2(s\text{-}Bu)$	3.27	0.26	0.81	0.13	2.07	0.31	0.33	2.10	0.37	−2.49
NH_2Cy	6.63	0.40	0.62	1.86	3.75	3.73	0.46	2.03	2.14	−0.90
$NHMe_2$	2.16	0.09	0.57	0.00	1.50	−1.51	0.41	1.10	0.01	−3.03
NHMeEt	2.77	0.16	0.59	−0.14	2.16	0.79	0.59	1.91	0.43	−2.14
piperidine	6.82	0.31	0.75	2.00	3.75	3.81	0.63	1.78	2.24	−0.84
$NH_2(t\text{-}Bu)$	2.05	0.35	0.46	−0.34	1.59	0.65	0.42	3.99	−0.27	−3.49
$NHEt_2$	4.58	0.25	1.28	0.31	2.71	3.24	0.81	3.69	0.69	−1.95
NH_2(ada)[b]	17.02	1.07	0.64	8.25	7.06	15.35	1.14	4.27	8.32	1.63
$NH(n\text{-}Pr)_2$	4.60	0.38	0.86	−0.29	3.65	5.04	1.33	2.93	1.21	−0.43
NMe_3	5.04	0.33	1.17	0.03	3.51	2.05	1.91	1.17	0.05	−1.08
quinuclidine	22.37	0.90	1.23	11.49	8.76	20.69	3.13	2.65	11.44	3.47
NMe_2Et	7.03	0.51	1.73	0.37	4.42	4.91	4.65	2.13	0.47	−2.35
$NHCy_2$	16.55	1.12	3.03	4.47	7.93	22.25	6.01	7.30	4.77	4.17
$NH(i\text{-}Pr)_2$	6.75	0.57	2.30	0.27	3.61	12.44	5.28	6.35	0.91	−0.09
$NH(i\text{-}Bu)_2$	6.56	0.66	1.19	0.74	3.97	10.04	5.03	3.03	3.52	−1.53
$NMeEt_2$	9.23	0.69	2.38	0.69	5.46	8.70	4.87	4.20	1.05	−1.42
NEt_3	11.70	0.94	3.22	0.95	6.60	13.87	5.37	6.55	1.61	0.35
$NH(s\text{-}Bu)_2$	9.74	0.83	2.93	1.32	4.66	15.62	5.09	7.28	4.32	−1.07
$N(n\text{-}Pr)_3$	13.66	1.12	4.21	1.27	7.07	14.21	5.65	6.83	1.19	0.54
$N(i\text{-}Pr)_3$	26.06	2.21	8.27	6.47	9.10	43.33	8.83	20.10	5.72	8.68

[a] neo = neopentyl. [b] ada = adamantyl.

Table III. Calculated Molecular Mechanics Energy (kcal mol^{-1}) Differences upon Complex Formation (ΔE in Eq 1) and the Ligand Repulsive Energy, E_R

ligand	ΔE_T	ΔE_b	ΔE_θ	ΔE_ϕ	ΔE_{vdw}	E_R	θ	r_e, Å
NH_3	−1.46	0.00	−0.51	0.00	−0.95	10	94	2.145
NH_2Me	−1.33	0.06	0.37	0.02	−1.78	30	106	2.163
NH_2Et	−1.10	0.06	0.52	0.11	−1.19	31	106	2.163
$NH_2(n\text{-}Pr)$	−1.20	0.05	0.46	0.11	−1.84	31	106	2.162
$NH_2(i\text{-}Pr)$	−0.47	0.07	1.47	0.22	−2.23	41	106	2.167
$NH_2(i\text{-}Bu)$	−0.85	0.08	0.76	0.23	−1.91	33	106	2.163
NH_2(neo)[a]	−0.69	0.10	1.13	0.16	−2.07	35	106	2.163
$NH_2(s\text{-}Bu)$	−0.78	0.08	1.29	0.24	−2.38	43	113	2.169
NH_2Cy	−0.72	0.06	1.41	0.28	−2.47	41	115	2.167
$NHMe_2$	−1.49	0.32	0.53	0.01	−2.34	64	119	2.196
NHMeEt	0.21	0.43	1.32	0.57	−2.12	62	119	2.205
piperidine	−0.83	0.32	1.03	0.24	−2.42	61	121	2.199
$NH_2(t\text{-}Bu)$	0.78	0.07	3.54	0.08	−2.90	53	123	2.178
$NHEt_2$	0.87	0.57	2.41	0.38	−2.48	73	125	2.214
NH_2(ada)[b]	0.51	0.06	3.63	0.07	−3.25	53	127	2.178
$NH(n\text{-}Pr)_2$	2.63	0.95	2.07	1.50	−1.89	81	127	2.235
NMe_3	−0.81	1.58	−0.01	0.02	−2.41	93	132	2.279
quinuclidine	0.50	2.23	1.42	−0.05	−3.10	104	132	2.330
NMe_2Et	0.06	4.14	0.40	0.10	−4.58	81	132	2.519
$NHCy_2$	7.88	4.90	4.27	0.30	−1.58	113	133	2.541
$NH(i\text{-}Pr)_2$	7.88	4.72	4.04	0.64	−1.53	105	137	2.537
$NH(i\text{-}Bu)_2$	5.67	4.39	1.84	2.78	−3.31	85	138	2.521
$NMeEt_2$	1.65	4.17	1.82	0.35	−4.70	93	145	2.527
NEt_3	4.35	4.43	3.33	0.67	−4.08	109	150	2.539
$NH(s\text{-}Bu)_2$	8.06	4.26	4.35	3.00	−3.55	88	158	2.523
$N(n\text{-}Pr)_3$	2.73	4.53	2.61	−0.08	−4.35	112	160	2.538
$N(i\text{-}Pr)_3$	19.45	6.62	11.83	−0.76	1.94	179	220	2.583

[a] neo = neopentyl. [b] ada = adamantyl.

classical coordination complexes, and bioinorganic systems. The steric and electronic properties of amines in metal complexes are important in understanding reactivity and selectivity of catalytic processes, such as hydrodenitrification,[16] reductive amination of alcohols,[17] reduction of nitriles,[18] and hydrocyanation.[19] Although

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quantitative information regarding the steric properties of amines would be of value, most work related to amine ligand reactivity has focused on electronic effects based on pK_a trends,[20] metal–ligand bond enthalpies,[21] or strain energies in the formation Lewis acid–base adducts.[22] Recently, the cone angle concept has been applied to amines.[23] However, the cone angle as a measure of amine steric requirements has the limitations alluded to above. We have, therefore developed the mechanics model for these ligands. In this paper, we present E_R values for amines and compare them to cone angle values for amines and E_R values for the analogous phosphine ligands.

Molecular Mechanics Methods

All molecular mechanics calculations were carried out on a Stardent Titan computer, using BIOGRAF (version 2.2), a comprehensive package of molecular modeling programs developed by Molecular Simulation, Inc., Sunnyvale, CA. The force field model employed is MMP2. The components of the energy terms in the calculations are described in detail elsewhere.[14,24] Table I lists added or modified parameters, where these differ from the standard MMP2 set or those listed in previous papers.[14,15]

The strain-free Cr–N distance was set at 2.14 Å. From the crystal structure data for $Cr(CO)_5$(piperidine) (2.204 Å),[25] $Cr(CO)_5$(pyridine) (2.165, 2.148 Å),[26] and $Cr(CO)_5$(quinuclidine) (2.249 Å),[27] the average Cr–N distance in the X-ray structures is estimated to be 2.19 Å. In general, the Cr–N distance for ammonia is about 0.08 Å shorter than that of tertiary amines.[28] Use of 2.14 Å as the assumed strain-free Cr–N distance in the molecular mechanics calculation yields a computed equilibrium Cr–N distances of 2.199 and 2.330 Å for $Cr(CO)_5$(piperidine) and $Cr(CO)_5$(quinuclidine), respectively. Because the calculations were carried out for a large number of ligands involving primary, secondary, and tertiary amines, in the interest of simplicity, the strain-free Cr–N distance has been assumed to equal 2.14 Å in all cases. The Cr–N force constant (1.5 mdyn/Å) was chosen to be smaller (75% of Cr–P, 2.0 mdyn/Å) than that for Cr–P based on the general observation that amine ligands are bound less strongly than phosphines. All dihedral angle torsional barriers involving Cr were set equal to zero, as described previously.[14,15]

The energy-minimization computations for a series of 27 alkylamines and their $Cr(CO)_5$ complexes were carried out using conjugate-gradient methods and similar procedures as described previously.[14] In general, a molecular mechanics program computes the potential energy of a molecule at a local minimum and not the global minimum over the space of all possible conformations of the ligand or complex. A Monte Carlo search procedure was used to find the global minimum when the conformational space was large. Typically 300–400 conformations were generated by random variations in any of a set of key dihedral angles; each was then partially minimized. From the results of this initial minimization, the 10–15 lowest energy structures were selected and fully minimized. In addition, molecular mechanics calculations were also performed on conformations which seemed intuitively to be promising to represent the global minimum. The lowest energy structure of the fully-minimized set was then assumed to represent the global energy minimum.

The procedure for calculating E_R values of the $Cr(CO)_5$(amine) complexes was similar to that employed previously.[9] In brief, the procedure is as follows:

(1) Obtain the energy-minimized structure for $Cr(CO)_5$(amine) as described.

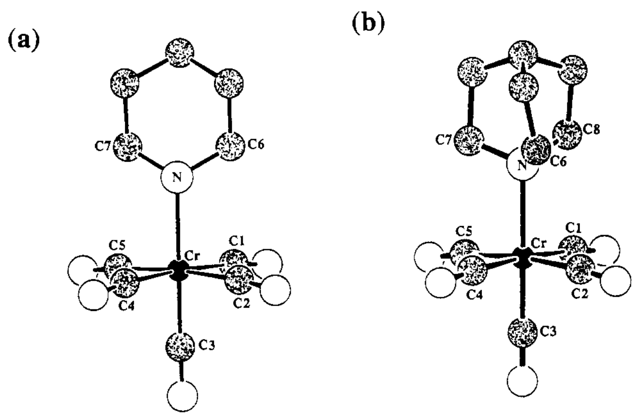


Figure 1. X-ray structure drawings of (a) $Cr(CO)_5$(piperidine) and (b) $Cr(CO)_5$(quinuclidine).

(2) Change the parameter set for the van der Waals potential to a purely repulsive form:

$$E_{vdw}(\text{repulsive}) = \sum D_0 \exp[\gamma[(r_0 - r)/r_0]] \quad (1)$$

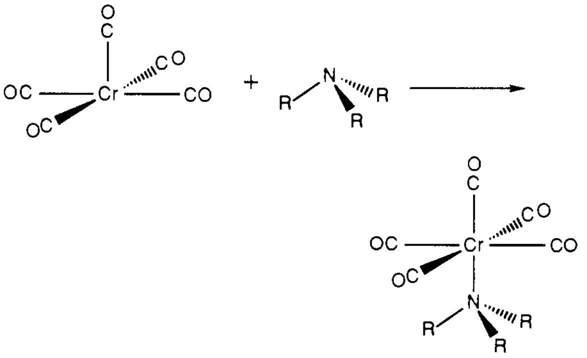
Here D_0 represents the potential well depth in the full exponential-6 expression, γ is typically 12.5, r is the interaction distance, and r_0 is the sum of the two scaled van der Waals radii for the interacting atoms.

(3) With all internal coordinates except the Cr–N bond distance frozen, compute the van der Waals repulsive energy for the energy-minimized structure with respect to the Cr–N distance, in the region about the equilibrium Cr–N distance, r_e. In practice, the computed energy varies linearly with respect to the Cr–N distance over about 0.08 Å on each side of r_e. The computed gradient is then multiplied by r_e to give the *ligand repulsive energy*, E_R:

$$E_R = r_e[dE_{vdw}(\text{repulsive})/dr(\text{Cr–N})] \quad (2)$$

Results

Molecular mechanics calculations were carried out for a series of amine ligands and their $Cr(CO)_5$ complexes. Table II lists the calculated total molecular mechanics energies, E_T, of free amines 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 corresponding to complex formation (eq 3) are summarized in Table III. The molecular mechanics energy change in this process (eq 4) is obtained by computing the energy-minimized structures for $Cr(CO)_5$, the free amine ligand, and the complex $Cr(CO)_5L$, where E_{Cr-N}, E_N, and E_{Cr} correspond to the total energy or one of the components of the total energy for $Cr(CO)_5(NR_3)$, NR_3, and $Cr(CO)_5$, respectively. The energy terms corresponding to the energy-minimized structure for $Cr(CO)_5$ are $E_T = E_{vdw} = -2.18$ kcal/mol with all other energy terms zero.



(3)

$$\Delta E = E_{Cr-N} - E_N - E_{Cr} \quad (4)$$

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Table IV. Comparison of the Key Bond Distances (Å) and Angles (deg) for the X-ray Crystal Structures of $Cr(CO)_5$(piperidine) and $Cr(CO)_5$(quinuclidine) with Those of Their Structures Computed Using MMP2

bond distance or angle	$Cr(CO)_5$(piperidine)		$Cr(CO)_5$(quinuclidine)	
	X-ray[a]	calc	X-ray[b]	calc
Cr–N	2.204(3)	2.199	2.249(5)	2.330
Cr–C1	1.896(6)	1.881	1.887(5)	1.881
Cr–C2	1.906(6)	1.881	1.898(6)	1.881
Cr–C3	1.824(5)	1.849	1.824(9)	1.850
Cr–C4	1.909(5)	1.881	1.898(6)	1.881
Cr–C5	1.894(5)	1.881	1.887(5)	1.881
N–C6	1.483(5)	1.513	1.48(3), 1.45(2)[c]	1.520
N–C7	1.478(5)	1.513	1.50(3), 1.47(2)[c]	1.520
N–C8			1.54(3), 1.54(2)[c]	1.520
N–Cr–C1	92.9(2)	93.0	93.2(2)	90.8
N–Cr–C2	91.5(2)	89.7	92.3(2)	92.7
N–Cr–C3	179.6(2)	177.8	180.0	178.7
N–Cr–C4	91.7(2)	89.9	92.3(2)	93.4
N–Cr–C5	93.9(2)	92.9	93.2(2)	92.6
Cr–N–C6	115.3(3)	114.2	109(1), 113(1)[c]	109.5
Cr–N–C7	115.6(3)	114.2	112(1), 112(1)[c]	109.4
Cr–N–C8			110(2), 110(1)[c]	110.1

[a] Reference 25. [b] Reference 27. [c] Two values are reported because of disordering.

The E_R values of the $Cr(CO)_5(NR_3)$ complexes are also presented in Table III. Table IV lists the computed and X-ray structural values for key bond distances and angles in $Cr(CO)_5$(piperidine) and $Cr(CO)_5$(quinuclidine).

Discussion

Structure Comparisons. The X-ray crystallographically-determined structures have been reported for $Cr(CO)_5$(piperidine)[25] and $Cr(CO)_5$(quinuclidine).[27] The fairly good agreement between observed X-ray and computed structures shows that the values chosen for MMP2 parameters are appropriate. We could have readily achieved a close agreement between the calculated and observed Cr–N distance in the quinuclidine complex by assessing a smaller value for the strain-free Cr–N distance. However, we chose in the interest of simplicity and uniformity to assume a single value for this parameter for all ligands. Further, as discussed below, the computed distance is probably not reliable in this special case.

In the $Cr(CO)_5$(amine) complexes, the lowest energy conformations of the ligands may differ significantly from those of the free amine. The computed energy-minimized structure of NEt_3 has 3-fold axial symmetry; the methyl groups are oriented toward the lone pair of nitrogen. This structure differs from Brown's[29] proposed NEt_3 structure, in which two of the three ethyl groups are oriented away from the lone pair. There is an energy difference of 3.2 kcal mol^{-1} between the lowest-energy conformer (11.7 kcal) and Brown's structure (14.9 kcal) in the molecular mechanics calculation. This result could arise from the fact that molecular mechanics places too much importance on the attractive component of the van der Waals interactions between the lone pair and methyl groups.

The computed conformation of NEt_3 changes substantially on complex formation, as shown in Figure 2. In the complex, two of the ethyl groups are in approximately the orientation seen in free NEt_3, but the third ethyl group is rotated about 90° around the Cr–N–C–C dihedral angle, to relieve the steric repulsion with the $Cr(CO)_5$ fragment. However, alkyl group conformations in the longer chain amine $N(n\text{-}Pr)_3$ do not change significantly between free amine and complex. In both free and complexed $N(n\text{-}Pr)_3$, two of the propyl groups are oriented similarly to free NEt_3, but the third propyl group is oriented similarly to one of the ethyl groups in $Cr(CO)_5(NEt_3)$. In contrast to the case of NEt_3, the C_3 symmetry configuration for free $N(n\text{-}Pr)_3$ is unfavorable because of steric congestion. Therefore, $N(n\text{-}Pr)_3$ has a configuration of C_s symmetry both as the free ligand and in the $Cr(CO)_5$ complex. The orientation of the ethyl groups of NEt_3 observed in the X-ray structure of $[Pd(dmpe)(Me)(NEt_3)][BPh_4]$[23] is similar to that computed for $Cr(CO)_5(NEt_3)$.

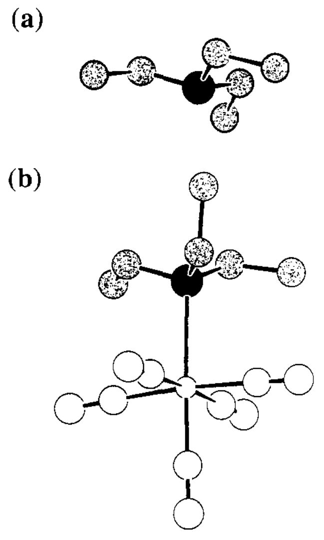

Figure 2. Energy-minimized structures for (a) NEt_3 and (b) $Cr(CO)_5(NEt_3)$.

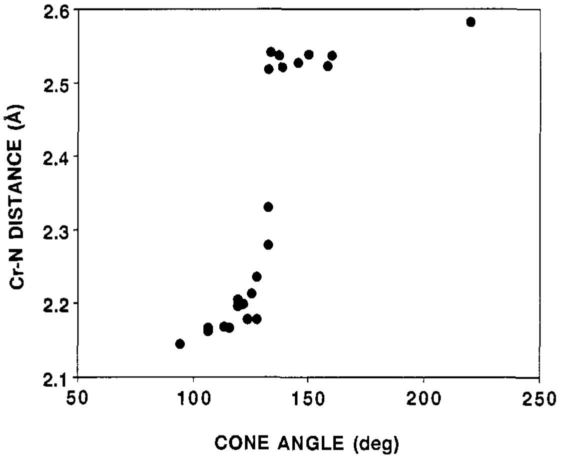

Figure 3. Variations in Cr–N distance with ligand cone angle for alkylamine complexes of $Cr(CO)_5$.

As the size of groups bound to the nitrogen increase in the $Cr(CO)_5$ complexes, the steric repulsions increase, resulting in an increase in the N–C bond distance, from 1.505 Å for the smallest ligand to 1.554 Å for the largest. Additional evidence for increasing steric repulsion between the ligand and the metal carbonyl complex is seen in a decrease in C_{ax}–Cr–C_{rad} angles and increasing Cr–N distance with increasing ligand steric requirement. These changes are due entirely to the effects of repulsive interactions on bond distances and angles as the system seeks a minimum-energy configuration; the assumed strain-free values of the parameters are the same throughout the series.

There is a small but steady increase in Cr–N distance with increasing ligand cone angle (Figure 3) from 2.145 Å for $Cr(CO)_5(NH_3)$ to 2.330 Å for $Cr(CO)_5$(quinuclidine). For the bulkier amine complexes of larger steric requirement (cone angle larger than 130°), the equilibrium Cr–N distance is much larger (2.5 Å). The discontinuous increase in Cr–N distances indicates that the repulsive interactions between the ligand and the metal complex are too large to permit formation of a normal Cr–N bond. The particular range of Cr–N distances at which the ligand–metal interaction is established in these cases is an artifact of the cubic form assumed for the stretching potential, eq 5, which is designed to take account of anharmonicity in the stretching

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(29) Brown, H. C.; Sujishi, S. *J. Am. Chem. Soc.* **1948**, *70*, 2878.

$$E_b = (k_b/2)(r - r_0)^2[1 + d(r - r_0)] \qquad (5)$$

vibration at large displacements from equilibrium. Typically, $d = -2$. To prevent dE_b/dr from becoming negative, the sign of dE_b/dr is reversed in BIOGRAF for $r - r_0$ values larger than $-^2/_3d$. For $d = -2$, the inflection point occurs at $r - r_0 = 0.33$ Å. The computed values of Cr–N distances for the bulkier amine complexes correspond to $r - r_0$ values of 0.38–0.44 Å. They are clearly not comparable with the values for the other amine ligands. The discontinuity in Cr–P distance occurs at a larger cone angle value (>175°) in the series of $Cr(CO)_5$(phosphine) complexes.[15] The steric repulsive effect of the amine for a given cone angle should be larger than that of the phosphine because of the smaller covalent bond radius of nitrogen as compared with phosphorus.[30] The prediction of a threshold steric bulkiness for forming complexes with $Cr(CO)_5$ is an interesting byproduct of the molecular mechanics calculations. It is noteworthy that the computed Cr–N distance for $Cr(CO)_5$(quinuclidine) is in the region of the discontinuity in Figure 3. Even a slight change of parameters can cause the computed Cr–N distance to increase to a much larger value, in the vicinity of 2.5 Å. The fact that even the smaller computed value of 2.33 Å for the Cr–N distance is 0.08 Å larger than the observed value may be due in part to the fact that the anharmonic connection, eq 5, is not accurate at the extension involved.

The quinuclidine ring is twisted and disordered in the X-ray structure, but in the computed structure, it is symmetric. It is possible that crystal packing forces cause distortion of the quinuclidine ring in the solid state. Although the pK_a's of quinuclidine (10.95)[31] and triethylamine (10.61)[32] in H_2O are similar, the binding ability of quinuclidine is 360-fold greater than that of triethylamine in $[Pd(dmpe)Me]^+$.[23] The cyclic amine may form a stronger N–Cr bond than cyclic amines. However, in the absence of firm data to the contrary, the Cr–N stretching force constant is assumed to be constant in the series of calculations.

Energy Changes. The variations in the total energy changes and components of the energy change for complex formation as a function of the ligand cone angle value are plotted in Figure 4. Note that the energy scale is the same for each component. The total energy change is more or less independent of cone angle at values below about 125°, and then the variation is rather irregular, though there is an upward trend for ligands of large cone angle. In the phosphine case, the secular total energy changes begins at 145°.[15] The principal components of the overall energy change in the amines are bond strength and bond bend.

The torsional component of the energy change on complex formation is significantly different for $NH(i\text{-}Bu)_2$ and $NH(s\text{-}Bu)_2$ from those for the other ligands. In these ligands, it is possible for the free ligand to adopt a conformation that does not result in internal repulsive interactions that give rise to torsional distortions. However, in the complex the constraints imposed on Cr–N–C–C dihedral angles by repulsive interactions with $Cr(CO)_5$ result in unavoidable internal repulsions. Similar anomalous behavior has been observed in the $Cr(CO)_5(P(i\text{-}Bu)_3)$ molecular mechanics calculation.[15] This type of energy term was first recognized by Brown and co-workers and referred to as "backstrain".[33] The present examples illustrate the existence of contributions to the total energy change on complex formation that are not adequately reflected in the cone angle.

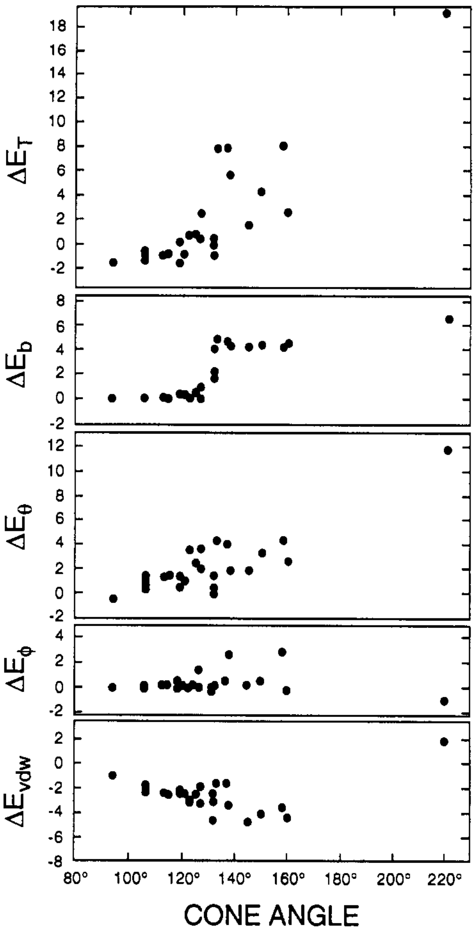

Figure 4. Total molecular mechanics energy change upon complex formation, ΔE_T, and the components of ΔE as a function of increasing cone angle of the ligand, for alkylamine complexes of $Cr(CO)_5$.

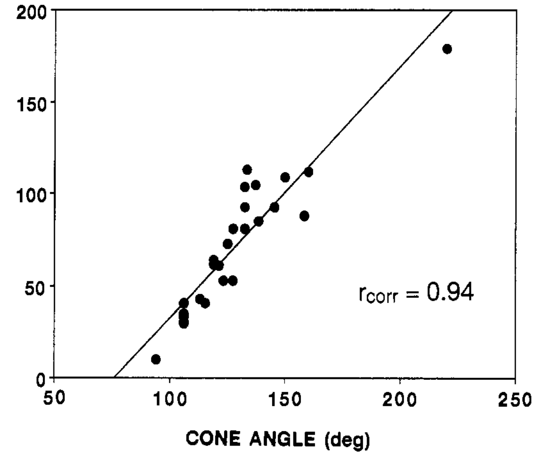

Figure 5. E_R vs cone angle for alkylamine complexes of $Cr(CO)_5$.

As discussed previously,[9] the ΔE_{vdw} term contains contributions from both repulsive and attractive van der Waals terms. As the groups attached to the amine grow more highly branched, their repulsive interactions with one another and with CO groups of the $Cr(CO)_5$ fragment increase. At the same time, the longer-range attractive interactions increase. Therefore, there is an irregular relationship with cone angle because the two terms tend to cancel. In the molecular mechanics model, the sum of new attractive energy terms occasioned by complex formation is larger than the corresponding sum of new repulsive energy terms, except for the very bulky $N(i\text{-}Pr)_3$. Thus, ΔE_{vdw} is generally negative.

The Ligand Repulsive Energy, E_R. As shown in Figure 4, ΔE_T and θ are not well-correlated, for the reasons discussed. On the other hand, the E_R values correlate rather well with the cone

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(30) It is noteworthy that, in measuring cone angle values for amines, Trogler employed a metal–nitrogen distance only 0.08 Å shorter than the value assumed by Tolman for an M–P distance in calculating cone angles for phosphorus ligands.[7] Thus, differences in cone angles between amine and nitrogen ligands owe little of their origin to the assumed difference in metal–ligand bond lengths.

(31) Alder, R. W. *Chem. Rev.* **1989**, *89*, 1215.

(32) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

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

angle, considering the wide range of ligands involved. The plot of E_R vs θ for the amines is shown in Figure 5.

The E_R values obtained for the bulky amines (cone angle larger than 130°) require comment, because the molecular mechanics calculations for the $Cr(CO)_5$ complexes of these ligands lead to exceptionally large equilibrium Cr–N distances, in excess of 2.5 Å (Figure 3). These large values indicate that it is not possible to form a normal Cr–N bond of force constant in the range of 1.5 mdyn/Å, because of excessive steric repulsion between the ligand and the metal complex. As noted above, the computed values of Cr–N distances in these cases are an artifact of the assumed bond stretching potential at large departures from the equilibrium bond distances. Nevertheless, while the Cr–N distances are not quantitatively on the same basis as the values for the other ligands, the larger values appropriately reflect the larger ligand steric requirements. The E_R values computed from these ligands using the energy-minimized structures seem reasonable in comparison with those for the other amine ligands.

The E_R values have several limitations as described previously;[9] at the same time, they offer several advantages over the cone angle as a measure of ligand steric requirement. First, E_R values are computed for each ligand in a conformation appropriate to its binding to a metal center based on the molecular mechanics energy minimization. This conformation often differs significantly from that for the free ligand. This difference is not accounted for in the CPK model for which cone angle values are measured. For example, the cone angle values for NH_2Me, NH_2Et, NH_2(*n*-Pr), NH_2(*i*-Bu), and NH_2(neopentyl) are all the same (106°),[23] but one can intutively see that the steric requirement should be different. In contrast to the cone angle values, the computed E_R values for those ligands vary (Table III). Second, E_R values can be computed for unsymmetric ligands without the need to result to an averaging approximation, as in estimating the the cone angle. Third, the E_R concept can be extended to ligands of nearly any kind and to a metal center other than $Cr(CO)_5$.

Steric Threshold. It is noteworthy that in the correlation between E_R and θ (Figure 5) E_R approaches zero at $\theta = 76°$. This intercept in the phosphine ligand series was defined previously as the absolute steric threshold.[9] For a given series of ligands, the value of the absolute steric threshold is determined by the degree of crowding of the metal center, as determined by the other groups bound to the metal. In comparing the absolute steric thresholds for amines and phosphines, we might expect that the value would be smaller for the amines because of smaller covalent radius of N. The absolute steric threshold value for amines is lower than for a series of analogous phosphorus ligands in $Cr(CO)_5$ complexes, 76° vs 95°. The absolute steric threshold should be distinguished from an apparent steric threshold, which is reflected in the variation in total energy change, ΔE_T, for the $Cr(CO)_5$–ligand interaction as a function of ligand size. In the amine case, ΔE_T is virtually independent of θ up to a ligand cone angle of about 125° and then increases as the cone angle increases. The variation in ΔE_T with ligand size results from a counterbalancing of repulsive energies by a corresponding dispersion energy term up to a certain range of ligand size. The apparent steric threshold for phosphines is about 145°.

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