Southern California Regional NMR Facility, support by National Science Foundation Grant No. CHE-7916324, is also gratefully acknowledged. We thank Professors Dennis Dougherty, Robert Bergman, and Dr. Chris Roe for helpful discussions during the course of this work, and Professor Jack Halpern for a preprint of ref 8c.

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Supplementary Material Available: An appendix containing a description of the physical basis for the magnetization trans transfer experiment, the FORTRAN program used for nonlinear least-squares analysis of the magnetication equation for chemical exchange, and the ^1H NMR data for the alkyl derivatives, $Cp^*_2Nb(CH_2CH_2R)(CO)$ (**8b-e**, **9**) and $Cp^*_2Nb(CH_2CH_2R)(CNMe)$ (**10b,d-g**) (15 pages). Ordering information is given on any current masthead page.

A Molecular Orbital Evaluation of Possible Factors Affecting the Homolytic Activation of Coenzyme B_{12}

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Abstract: Utilizing the approximate ab initio method of partial retention of diatomic differential overlap (PRDDO), we have investigated the overlap population of the Co–C bond in a model system of coenzyme B_{12} after applying a variety of electronic perturbations. The results of the calculations show that electronically, the organocobalt linkage is particularly susceptible to angular distortion or steric crowding. However, the weakening of this linkage is not significantly advantaged by equatorial ligand "pucker" or a trans-electronic effect. It is therefore likely that steric interaction, probably causing the angular distortion of the Co–C bond, is primarily responsible for the weakening of the Co–C bond and its ultimate homolysis in actual B_{12} holoenzymes.

Coenzyme B_{12} is unique among biological molecules in that it contains a stable cobalt–carbon bond.[1] Furthermore, it is generally agreed that organometallic homolysis heralds the catalytic mechanism in enzymatic reactions dependent on the coenzyme.[2,3] However, the mode of activation of this dissociation under the relatively mild conditions of an enzymatic process remains a mystery, since the scission is only accomplished under nonphysiological conditions readily by photolysis. This activation could arise from steric crowding, electronic perturbations, or a combination of both effects induced upon the binding of coenzyme to apoenzyme or the binding of substrate to holoenzyme.

The observation that the corrinoid skeleton of coenzyme B_{12} is relatively flexible[4] has led to the suggestion that steric effects arising from its distortion are catalytically important. Such effects are demonstrably significant in the Co–C homolysis of model compounds. Halpern[5,6] has rationalized a relatively weak Co–C bond in coenzyme B_{12} on the basis of kinetic and thermodynamic studies on model compounds and also observed that steric interaction between the alkyl and equatorial ligands significantly decreases the dissociation energy. Indeed, Halpern and colleagues have recently determined the Co–C dissociation energy of the coenzyme itself to be 26 ± 2 kcal/mol and proposed that steric interaction between the 5′-deoxyadenosyl group and the corrinoid macrocycle are likely responsible for the bond-weakening effects.[7] Additionally, sterically crowded alkylcobalamines display an inherent instability likely arising from corrinoid distortion.[8] Studies of the coenzyme itself with modified peripheral groups indicate that these groups interact with the enzyme to facilitate the catalysis,[9] further suggesting that a conformational change in the corrinoid is catalytically significant. Such a conformational change could sterically induce a linear and/or angular distortion of the Co–C bond, resulting in its activation. Alternatively, such a conformational change could be catalytically significant in light of its perturbation of the stereoelectronic environment about the central cobalt ion. The ionic radius[10] of Co^{3+} is 0.63 Å, whereas that of Co^{2+} is 0.74 Å. During the course of homolysis, therefore, the corrinoid must be able to accommodate an increase in diameter of the cobalt ion of more than 0.2 Å. The corrinoid could distort to accommodate the larger ion; conversely, upon corrinoid distortion, perhaps accompanying the binding of coenzyme to apoenzyme, the $Co^{3+} \rightleftharpoons Co^{2+}$ transition might be advantaged through stereoelectronic effects of the ligands.

The role of the trans ligand to organometallic bonds in model compounds has received considerable speculation and study; the

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role of the benzimidazole ligand trans to the deoxyadenosyl ligand in the coenzyme itself has generally been considered in light of its possible steric interaction with the corrinoid ring, which in turn can interact with the deoxyadenosyl ligand. Such a steric transmission has been designated as the trans-steric effect.[11] However, it has recently been shown that alkyl–cobalt dissociation energies are influenced by the basicity of trans-4-substituted pyridines in model compounds.[12] Co–C dissociation energy systematically increases with increasing basicity of the trans ligand, consistent with the concomitant decrease in the cobalt oxidation state from +3 to +2 which accompanies homolysis: more basic ligands favor the higher oxidation state and thus stabilize the organometallic complex. The implications of this observed trans-electronic effect for the coenzyme are obvious: the longer the Co–N(benzimidazole) bond trans to the deoxyadenosyl ligand, the poorer the electron donation to the metal center, and the weaker the alkyl–cobalt bond. Steric interaction of the trans ligand with the corrinoid could force the benzimidazole ligand away from the metal center in an enzymic system. Indeed, recent crystallographic studies on model compounds depict such interactions,[11,13] of which the primary features are very long Co–N bonds trans to alkyl–cobalt linkages.

Calculations

It was the purpose of this molecular orbital study to compare the relative efficiency of different factors affecting the strength of the Co–C bond (i.e., its net bonding electronic population), but without invoking its actual scission. Hence, no calculations were performed upon a model B_{12r} intermediate, since we were only interested in bond-weakening effects reflected in the Co^{3+} model system. Ab initio calculations have been performed on model systems of coenzyme B_{12}, but these studies primarily concerned the detailed electronic structure of the Co^{3+} system,[14,15] interpretations of the optical spectrum of the corrinoid,[16-19] or full mechanistic analysis of substrate–product conversion.[20] The bond-weakening effects considered in this study consist of linear and angular distortion of the Co–C bond, a model of steric crowding at the organocobalt linkage, and an evaluation of the trans-electronic effect in both native and slightly puckered models of coenzyme B_{12}. The method employed, partial retention of diatomic differential overlap (PRDDO), utilizes minimum basis sets (MBS) of Slater atomic orbitals to perform approximate ab initio closed-shell Hartree–Fock self-consistent-field calculations, and it closely reproduces MBS ab initio results.[21-23] Although the limitations of MBS calculations are well-known, the method serves rather well here since we are interested in the qualitative evaluation of trends, rather than the exact quantitative measurement, of SCF energies and electronic populations. Coordinates for the cobalt ion and ligand atoms were obtained from the refined structure of coenzyme B_{12} reported by Lenhert.[24] In the model system, ammonia (NH_3) molecules were substituted as cobalt ligands for the three equatorial pyrroline and axial benzimidazole two-electron donors. An amide (NH_2) moiety was placed at the coordination site of the one-electron equatorial pyrroline donor, and the axial 5′-deoxyadenosyl one-electron donor ligand was replaced by a methyl group. In their experimental analyses of Co^{3+} trans-electronic effects, Heeg and Elder concluded that equatorial ligands of ammonia or cobaloxime to Co^{3+} did not significantly alter axial Co^{3+}–NH_3 bond lengths.[25] It would appear that the effects of such equatorial ligand substitutions on the chemical nature of the central Co^{3+} ion were negligible. Thus, the ligand simplifications made in our model system did not compromise the actual stereoelectronic environment of the Co^{3+}–corrinoid system of the coenzyme itself. An illustration of this model system appears in Figure 1.

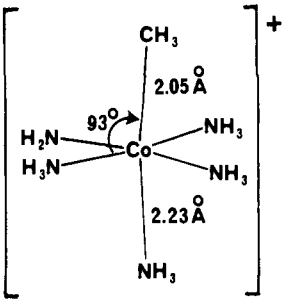

Figure 1. Model system of coenzyme B_{12} utilized in these calculations (pertinent coordinates are indicated).

Calculations were first performed on the model system with native ligand coordinates. In one trial, a linear variation was allowed in the Co–C bond distance in order to evaluate the electronic implications of its direct distortion. Then, with the Co–C distance held constant, one N_{eq}–Co–C angle was varied from its corresponding crystal structure value of 93° (see Figure 1). To model a system of steric crowding at the site of the organometallic linkage (an effect likely to bring about a direct Co–C distortion), a methane molecule was introduced to the system at a 120° angle to the cobalt-bound methyl group. This angle was selected so that the interaction of the methane with equatorial ligands would be minimized. The distance of this methane molecule was allowed to vary, and electronic effects were analyzed for this primarily steric effect. Subsequent trials involved the variation of the Co–N_{trans} distance in order to evaluate the influence of a trans-electronic effect on the Co–C bond. Presumably, a change in the net overlap population between the cobalt center and the methyl carbon would be observed as the system accommodated the electronic perturbations brought about by the trans ligand. Similar calculations were also performed on a model system in which a ligand distortion was induced such that trans-equatorial ligands were bent tetrahedrally about 5° above and below the mean coordination plane. This model was considered representative of a possible ligand distortion encountered by the corrinoid upon its binding to the apoenzyme. In all trials the Co^{3+} ion *remained* in the coordination plane of the corrinoid macrocycle; the consideration of its movement out of the plane was left for a future study.

It must be stressed that the gas-phase model utilized in these calculations was not regarded as catalytically active in any way, nor as such could it serve as grounds for investigating the conformational energetics of the actual holoenzyme. It did, however, serve as a foundation upon which an evaluation of purely stereoelectronic effects of the cobalt–ligand environment could be made with their implications for the catalytic mechanism. In the discussion to follow, the relative Co–C bond strength is correlated with the Co–C reduced overlap population (ROP). The ROP is calculated by generating the sum of individual Mulliken overlap populations[26,27] over Slater atomic orbitals for each atom in the system in order to find a specific value for net interatomic overlap; i.e., the sum of interorbital overlaps is the interatomic overlap, or ROP.

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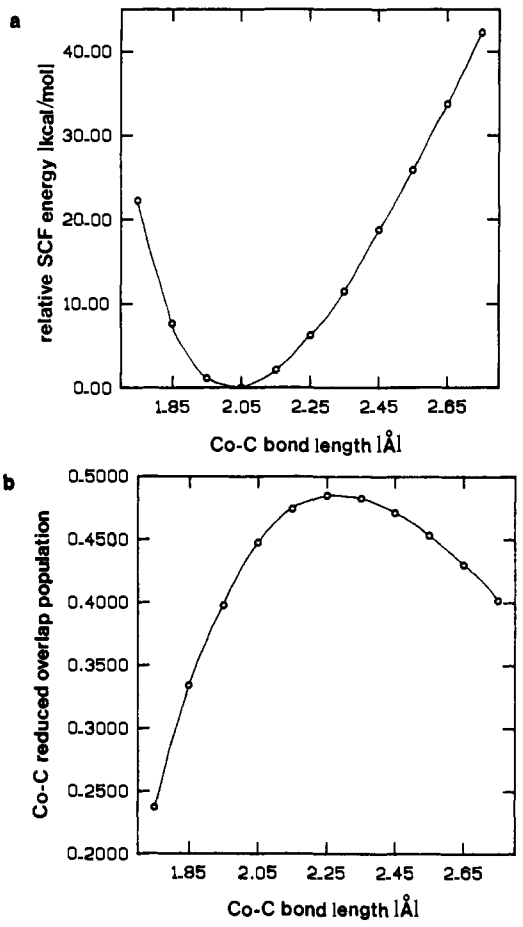

Figure 2. SCF energy (relative to the minimum) and population data for Co–C bond length variation.

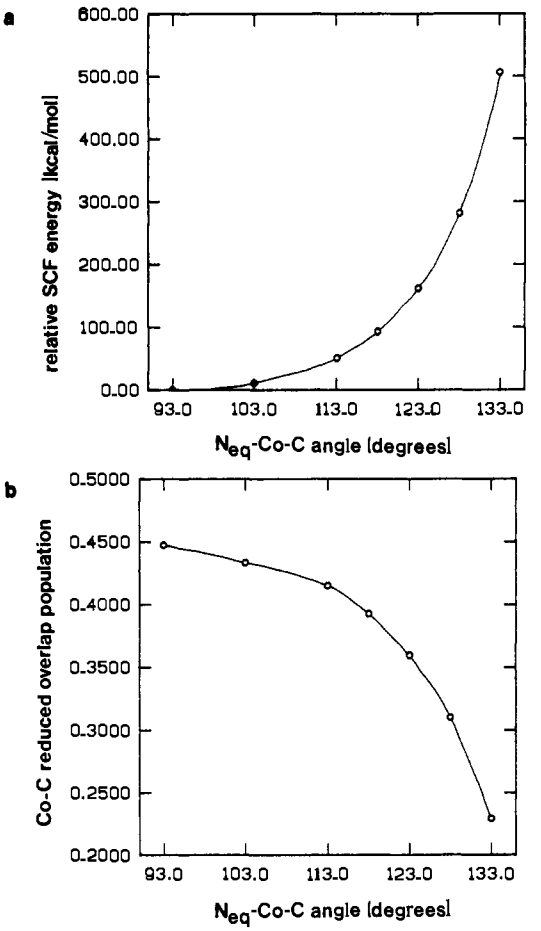

Figure 3. SCF energy (relative to the minimum) and population data for N_{eq}–Co–C angular variation; this angle is indicated in Figure 1.

Results and Discussion

The Co–C distance of 2.05 Å of the coenzyme in the crystal structure lies at the minimum of the potential well calculated for the native model system with variation along this coordinate. It might be noted, however, that a structure of methyl–B_{12} recently reported[28] shows a Co–C distance of about 2.0 Å. This apparent discrepancy can be resolved when the broadness of the caculated potential well is considered. The SCF energy of the model system is only about 0.6 kcal/mol higher at a Co–C distance of 2.00 Å than at 2.05 Å. The comparison of such small energy differences is beyond the scope of the method and of this study. These results suggest that the model system, even with ligand substitutions made to simplify the calculations, serves as an acceptable representation of the coenzyme with regard to the stereoelectronic environment of the organometallic complex. Upon the initial increase of the Co–C bond length from 2.05 to 2.25 Å, an increase of 8.4% in the Co–C ROP is observed, even though this distortion is not energetically favorable in the model system by 6.25 kcal/mol. Upon further extention beyond 2.25 Å, a consistent decrease is observed in the Co–C overlap population. Self-consistent-field (SCF) energies and Co–C overlap populations are graphically presented in Figure 2a,b for linear Co–C distortion. Angular Co–C distortion reflects a sensitive dependence of the Co–C overlap population. For example, given a 20° distortion of the C–Co–N_{eq} angle, a 7.3% decrease in Co–C overlap is observed; for a 40° C–Co–N_{eq} distortion, a 48.8% decrease in Co–C overlap is observed. The energetic expense of such a distortion in this model system is great (about 500 kcal/mol), but this expense could conceivably be offset by conformational considerations and steric interactions brought about in the actual holoenzyme. SCF energies and Co–C overlap data are presented in Figure 3a,b.

The result of steric interaction with the cobalt-bound methyl group by an approaching methane molecule indicates that considerable interaction commences at the $C_{methane}$–$C_{B_{12}}$ distance of 3.0–3.5 Å, and this interaction increases with further approach. Allowing the methane molecule to approach from 3.0 to 2.0 Å incurs an energetic expense of 370.50 kcal/mol (with the B_{12}-bound methyl held stationary). The need to alleviate such an energetic expense could result in an angular distortion of the Co–C bond. Such distortion was shown to be energetically expensive, but this expense could well be offset by steric effects analogous to those approximated in this model. Additionally, steric interaction as set forth in this model affects the Co–C overlap population. In the critical range of 3.0–2.0 Å, a decrease of 18.1% is observed in the Co–C overlap. Hence, steric effects may not serve only to distort or "push" toward a particular coenzyme conformation, but they may actually serve as a net stereoelectronic weakening force as well. The pertinent SCF energy and Co–C overlap data are presented in Figure 4a,b. It is interesting to note the onset of strong C–C antibonding interaction between the methane carbon and the cobalt-bound carbon upon their steric crowding. The Co–C linkage is the only one exhibiting such a significant decrease in ROP; the only decreases observed in C–H linkages of either the approaching methane molecule or cobalt-bound methyl group (in fact, most display slight increases) are on the order of 1–6%. A comparison of C–C, C–H, and Co–C ROP data at various $C_{methane}$–$C_{B_{12}}$ distances is presented in Table I.

In the native model in which attention is accorded to variation in the Co–N_{trans} distance, a correlation of Co–C overlap population is observed with proximity of the trans ligand to the metal center. A trans-electronic effect is reflected consistently in the results of these calculations, although the magnitude of the observed trend is questionable in terms of its catalytic importance. Within a ±0.5 Å range about the distance of 2.23 Å in the crystal structure, the

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Table I. Changes in Reduced Overlap Populations Brought about by Steric Crowding of an Approaching Methane Molecule to the Cobalt-Bound Methyl Group

d-($C_{methane}$–$C_{B_{12}}$), Å	ROP-(Co–C)	ROP-($C_{methane}$–$C_{B_{12}}$)	ROP($C_{B_{12}}$–H)			ROP($C_{methane}$–H)			
			C–H1	C–H2	C–H3	C–H1	C–H2	C–H3	C–H4
2.0	0.362	−0.572	0.847	0.940	0.716	0.794	0.802	0.756	0.755
3.0	0.443	−0.019	0.773	0.799	0.762	0.771	0.770	0.763	0.763
4.0	0.447	0.000	0.769	0.781	0.765	0.762	0.763	0.766	0.766
5.0	0.448	0.000	0.769	0.780	0.765	0.763	0.763	0.765	0.765

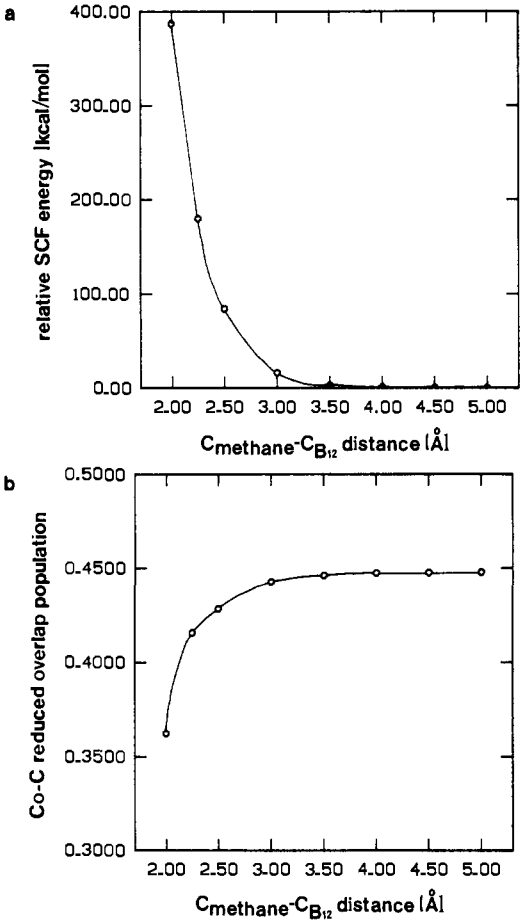

Figure 4. SCF energy (relative to the minimum) and population data for the approach of a methane molecule toward the cobalt-bound methyl group.

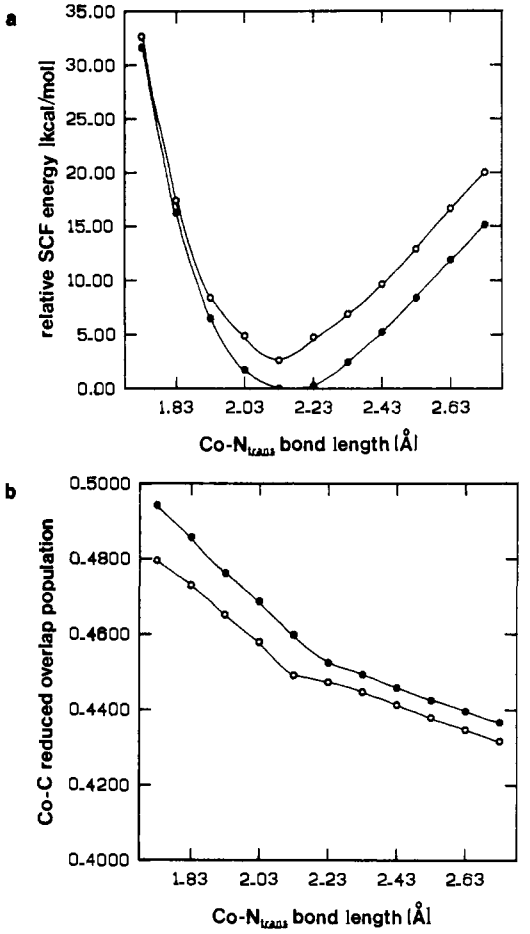

Figure 5. SCF energy (relative to the minimum for the puckered model) and population data for Co–N_{trans} variation in native (open circles) and puckered (filled circles) model systems.

overlap population varies by only 11.1%. It does, however, increase as the N_{trans} ligand approaches the metal center, and it increases more sharply in the 2.13–1.73 Å range. The decrease is only 3.5% as the Co–N_{trans} distance is lengthened from 2.23 to 2.73 Å. The minimum of the calculated potential for variation of the Co–N_{trans} coordinate lies at a relatively long 2.13 Å. The distance in the crystal structure is 2.23 Å. The slight discrepancy of 0.1 Å is probably due to the nature of the model system; the actual coenzyme possesses a distal nucleotide loop connecting the trans-benzimidazole ligand to the corrinoid proper. Steric and conformational considerations which are impossible to account for in the model system are likely responsible for this 0.1 Å difference between the theoretically favored Co–N_{trans} distance and that actually observed experimentally. Again, the relative agreement of theoretical and experimental coordinate values indicates that the model system, particularly the substitution of ammonia molecules for the sp^2-hybridized pyrroline donor nitrogens of the coenzyme, is a good overall approximation of the actual stereoelectronic environment in the coenzyme.

In the puckered model system, the potential well with regard to the Co–N_{trans} coordinate is broadened, and the minimum lies closer to 2.23 Å. Although not involving the steric and conformational effects certainly important in the function of the coenzyme, this system is slightly more stable than the native model system (especially in the Co–N_{trans} range of 2.23–2.73 Å) by about 5 kcal/mol. The slight desymmetrization induced in the already asymmetric pseudooctahedral Co^{3+} environment serves to slightly increase the Co–C overlap population (e.g., at the Co–N_{trans} distance of 2.23 Å the increase is 1.2%). Overall, the same slight trend of a trans-electronic effect is observed as for the native model system. If corrinoid distortion is catalytically important in B_{12}-dependent mechanisms, it is so strictly from steric/conformational rather than electronic considerations. The SCF energies and ROP data for the Co–C bond in both native and puckered model trans-effect analyses are graphically recorded in Figure 5a,b.

In all calculations described, a σ/π analysis of individual overlap populations over atomic orbitals reveals that the Co–C bond consistently displays 2–4% π character. The only cases in which deviations occur are those of variations in the Co–C linear and N_{eq}–Co–C angular coordinates. These deviations consist of minor decreases in the already small π component to the Co–C bond. Upon shortening the Co–C bond to 1.75 Å, a very slight π-antibonding interaction is observed (less than 1% that of the total σ-bonding interaction). Also, upon angular distortion of the indicated N_{eq}–Co–C angle to 133°, a slight π-antibonding interaction is observed (1.4% that of the total σ component).

Conclusions

The catalytic importance of the trans-electronic effect in coenzyme B_{12} dependent mechanisms is questionable in light of the magnitude of the calculated effect on the Co–C reduced overlap population observed in the present model. Additionally, the slight Co–C weakening brought about by $Co–N_{trans}$ lengthening could be virtually offset by the electronic effects resulting from any slight corrinoid pucker (conceivably brought about through the binding of coenzyme to apoenzyme) analogous to that modeled herein. In view of the observed activity of cobinamide coenzyme (coenzyme B_{12} less the distal nucleotide loop),[29] the theoretical and experimental importance of the trans-electronic effect, as well as the trans-steric effect, in the holoenzyme appears to diminish. Likewise, since these results suggest that simple corrinoid distortion about the central metal ion does not serve to weaken the organocobalt linkage on purely stereoelectronic grounds, any possible catalytically important corrinoid distortion likely involves Co–C activation brought about through straightforward steric interactions rather than underlying electronic effects. Indeed, recent experiments[30] demonstrate that in model compounds possessing phosphine ligands trans to the Co–C bond, organometallic dissociation is by far more dependent on steric bulk of the trans ligand rather than its basicity; the steric effect, albeit a trans-steric effect, nearly masks the electronic effect. Additionally, Halpern and colleagues propose a cis steric interaction between the 5′-deoxyadenosyl group and the corrinoid macrocycle to be responsible for the relatively low dissociation energy of the coenzyme.[7]

The importance of steric effects in coenzyme B_{12} and model systems is obvious from the results of these calculations as well as the experimental data. The Co–C overlap population, and hence the Co–C bond strength, reflect a sensitive dependence to the $C–Co–N_{eq}$ angle. Also important is the approach of a steric "push", which not only could serve as the initial means for the angular distortion of the Co–C bond but also could serve in and of itself as an electronic effector, decreasing the Co–C overlap population by means of associated electronic effects. Steric interaction as calculated here serves to bring about significant antibonding interaction between the cobalt-bound carbon and the offending atom(s); in turn, the Co–C bonding population decreases, and in the model system it is only this linkage which is weakened by such an effect.

It appears that the Co–C linkage is electronically susceptible to the onset of steric crowding directed at the cobalt-bound carbon. It is therefore likely that steric interactions, very possibly inducing the angular distortion of the Co–C bond, and the accompanying electronic phenomena herein described are primarily responsible for the initial homolytic activation in enzymatic mechanisms dependent on coenzyme B_{12}.

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Ab Initio MO Study of the Coordination Modes and Bonding Nature of $Rh^I–N_2$ Complexes

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Abstract: An ab initio MO study of $RhCl(PH_3)_2L$ (L = η^1-end-on N_2, η^2-side-on N_2, C_2H_4, CO, HCN, HNC, and NH_3) is presented. Two coordination modes of N_2, η^1-end-on and η^2-side-on, are compared. Though both coordination modes have the similar degree of back-donative ($Rh \rightarrow N_2$) interaction, the η^1-end-on mode receives much larger electrostatic stabilization and slightly larger donative ($N_2 \rightarrow Rh$) stabilization, and as a result, the η^1-end-on mode is more stable than the η^2-side-on mode. The bonding nature and electronic structure of the η^1-end-on N_2 complex are also examined: The π-back-donative interaction contributes to the N_2 coordination more strongly than the σ-donation, and the relative importance of the π-back-donation to the σ-donation is larger in the N_2 coordination than in the coordination of similar ligands, such as CO, HCN, and HNC. The coordinate bond of Rh(I) complexes is compared with that of Ni(0) complex, and $RhCl(PH_3)_2$ is suggested to possess versatile ability to form coordinate bond with various ligands.

Since the first synthesis of $[Ru(NH_3)_5(N_2)]X_2$ (X = Cl, Br, or I),[2] many transition-metal dinitrogen complexes have been synthesized and investigated actively.[3] Interests found in the chemistry of dinitrogen complexes are summarized as follows: (1) How does the inert N_2 molecule coordinate to transition metal? (2) Why is the η^1-end-on N_2 coordination usually found but the η^2-side-on coordination not common? (3) How can the N_2 ligand be reduced to N_2H_4 (or further to NH_3) under mild condition?

Recently, several MO studies of N_2 complexes have been carried out. Veillard[4] and Hori et al.[5] reported that the η^1-end-on N_2 complex was more stable than the η^2-side-on N_2 complex, and Lauher and Hoffmann[6] discussed the condition allowing the η^2-side-on N_2 coordination. For η^1-end-on N_2 complexes, Murrell et al.[7a] showed that the electron distribution was very sensitive

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