Articles

anti-Spin-Delocalization Effect in Co−C Bond Dissociation Enthalpies

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The homolytic Co−C bond dissociation enthalpy (BDE) is central to the understanding of organocobalt-mediated reactions in the areas of both bioinorganic chemistry and transition-metal catalysis. However, the determination of the Co−C BDEs still remains a difficult task using either an experimental or theoretical approach. Here we investigate how to use the density functional theory method to accurately calculate the Co−C BDEs by testing a number of functionals. It is found that the recently developed TPSS/LANL2DZ+p method can reproduce 28 experimental Co−C BDEs within a precision of ca. 2.2 kcal/mol. Equipped with this useful tool, we next examined the effects of the in-plane ligands on the Co−C BDEs in a systematic fashion for the first time. It is found that the in-plane ligands can vary the Co−C BDEs by ca. 10 kcal/mol. Across different in-plane ligands the Co−C BDEs are found to exhibit a strong, *negative* correlation with the spin densities at the cobalt atoms after the homolysis. This observation is not consistent with the conventional chemical intuition that delocalization of the spin of a free radical through the hyperconjugation interactions should stabilize the radical and, thereby, weaken the chemical bond that undergoes homolysis. We name this unexpected finding the *anti*-spin-delocalization effect. Further analyses of the molecular orbitals and atomic charges indicate that (1) the in-plane ligands can reduce the Co spin density through hyperconjugation with their empty antibonding π^* orbitals and (2) the in-plane ligands can also stabilize the Co−C starting material through ionic interactions by attracting electrons from Co. Both the stabilization effects are determined by the electronegativity of the in-plane ligands. Thus the origin for the *anti*-spin-delocalization effect is proposed to be that the stabilization effect of the in-plane ligands is larger for the starting material than for the radical.

1. Introduction

The formation and homolysis of cobalt−carbon bonds in the organocobalt complexes are interesting and useful chemical processes that find importance in the areas of both bioinorganic chemistry (e.g., the biological function of the B12 coenzyme[1]) and transition-metal catalysis (e.g., cobalt-mediated free radical polymerization[2] and atom-transfer radical polymerization[3]). Accordingly, in the past few decades extensive investigations have been carried out on both biologically active cobalamins and synthetic organocobalts to determine the strength of the various types of cobalt−carbon bonds and analyze the factors that influence such bond dissociation.[4] For instance, the groups of Halpern,[5] Finke,[6] and others[7] developed kinetic methods to measure the Co−C bond dissociation enthalpies (BDEs) of the B12 coenzyme and related model compounds using appropriate

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Table 1. Theoretical BDE Values of the Cobalt−Carbon Bonds Calculated by Different DFT Methods (unit: kcal/mol)

complex	exptl	B3LYP	B3P86	BP86	G96LYP	PBE	BB95	TPSS
(imidazole)Co(DH)$_2$-CHMePh	20.8	6.3	12.4	18.8	6.3	23.0	24.3	18.6
(benzimidazole)(salen)Co-CH$_3$	32.5 ± 2	19.1	19.7	31.6	33.5	33.8	37.2	29.0
(H$_2$O)(salen)Co*n*-C$_4$H$_9$	27.7 ± 2	17.3	21.0	31.1	22.7	34.0	36.7	29.2
(py)(saloph)Co-CH(CH$_3$)$_2$,	20	9.6	13.9	21.7	11.6	25.3	28.2	20.8
(py)(saloph)Co-CH$_2$C(CH$_3$)$_3$	18 ± 2	8.7	12.8	21.1	10.9	24.6	27.0	18.9
correlation coefficient		0.9306	0.8989	0.9207	0.9105	0.9174	0.9067	0.9331
mean deviation (md)		−11.6	−7.8	+1.1	−6.8	+4.3	+6.9	−0.5
root of mean square error (rmse)		11.8	8.3	2.4	8.4	4.8	7.3	2.0

radical traps. Halpern and co-workers also utilized an equilibrium thermodynamic method to determine the Co−C BDEs of alkylcobaloximes.[8] Toscano et al. reported the calorimetric titration measurement of Co−C BDEs for organocobalts in conjunction with thermochemical cycles.[9] More recently, the groups of Grabowski[10] and Chen[11] determined the Co−C BDEs for coenzyme B12 and methylcobalamins by using the modern photoacoustic calorimetry technique.

The above studies quantitatively gave rise to Co−C BDEs for a number of organocobalt complexes. From these studies it was found that the Co−C BDE values generally fall within the range 20−40 kcal/mol, and these values are strongly affected by the axial and equatorial ligands in the organocobalts. Notwithstanding this, it is important to develop theoretical methods that can rapidly and accurately predict the Co−C BDE of any arbitrarily selected organocobalt even before the complex is synthesized. Such theoretical methods would not only allow for the design and production of novel organocobalts with desired properties but also enable us to improve understanding of the relationship between the Co−C bond and structure. Ideally the theoretical methods should be derived from the first principles without empiricism. However, due to the size and complexity of the organocobalt compounds, first-principle quantum chemical calculations on the Co−C BDEs of organocobalts have been reported only recently.[12–14] It was found that some popular density functional theory methods such as B3LYP seriously underestimated the Co−C BDEs by ca. 10 kcal/mol![12]

The poor accuracy of the B3LYP calculations was proposed to arise from the fact that B3LYP was a hybrid functional in combination with an exact Hartree−Fock (HF) exchange. This hypothesis was validated by a very recent report that the nonhybrid BP86 functional with *no* HF exchange produced much more consistent results than B3LYP in comparison to experimental data.[15] Note that the experimental BDEs for three cobalamins were cited in that particular study,[16] and it remains unclear whether we can reliably calculate the Co−C BDE of any arbitrary organocobalt. To solve this problem we recently have conducted systematic calculations on the Co−C BDEs of various organocobalts to compare against bulk experimental data. Through the study the superiority of using nonhybrid functionals (e.g., BP86) in handling Co−C BDEs is confirmed. It is also found that a newly developed nonhybrid functional, namely, TPSS,[17] can provide even more accurate predictions in the study of organocobalts.

With an array of reliable Co−C BDEs in hand we next ask, for the first time, the question of whether or not there exists a correlation between the Co−C bond strength and the stability of the cobalt-centered radicals. The same question has been asked repeatedly for carbon-centered radicals over the past few decades,[18] and the so-called spin-delocalization effect has been well established as a well-known concept to explain the relationship between carbon radical stability and bond strength.[19] At the present time it is generally believed that the strength of a carbon−carbon (or carbon−hydrogen) bond should decrease if the resulting carbon radical becomes more stable.[20,21] However, to our surprise it is found here that the strength of the Co−C bonds actually increases when the stability of the resulting cobalt radical improves!

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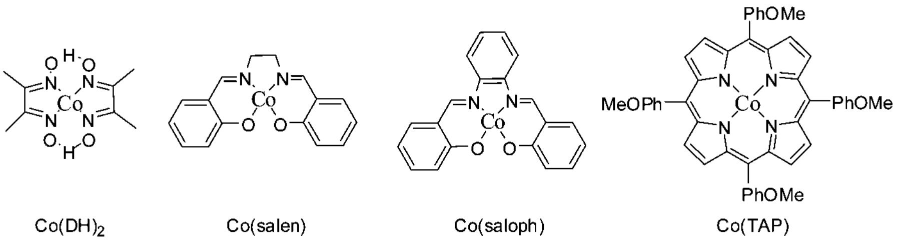

Figure 1. Representative organocobalt complexes.

2. Method Development

Most organocobalt complexes contain more than 15 non-hydrogen atoms, which precludes the utilization of any high-level (e.g., CCSD(T) or QCISD(T)) theoretical method to handle these compounds at the present time. To compromise the quality and cost of the calculation, we focus on the density functional theory methods that include electron correlation per definition. Because it was shown previously that the hybrid DFT methods could not reliably handle the Co complexes,[16] we decide to examine several nonhybrid DFT methods including BP86 (Becke−Perdew 1986 with no HF exchange),[22] G96LYP (Gill−Lee−Yang−Parr 1996 with no HF exchange),[23] PBE (Perdew−Burke−Ernzerhof 1996 with no HF exchange),[24] BB95 (Becke−Becke with no HF exchange),[25] and TPSS (Tao−Perdew−Staroverov−Scuseria 2003 with no HF exchange).[17] Most of these nonhybrid DFT methods have been shown to be applicable to the study of transition-metal complexes.[26,27] Note that the LANL2DZ+p basis set is used for both geometry optimization and energy calculation, where an f-polarization shell is added for cobalt.

To test the applicability of the above DFT methods to the calculation of Co−C BDEs, we selected five representative organocobalt complexes (Table 1). The general structures of these organocobalt complexes are shown in Figure 1. It is found that the popular B3LYP and B3P86 methods underestimate the Co−C BDEs by 11.6 and 7.8 kcal/mol, respectively. These results confirm the previous finding that the hybrid DFT methods are not reliable for the Co complexes.[16] By contrast, the BP86 method only slightly overestimates the Co−C BDEs by 1.1 kcal/mol. The root-mean-square-error (rmse) of the BP86 method is as low as 2.4 kcal/mol. Further calculations show that some more recent nonhybrid DFT methods including G96LYP, PBE, and BB95 cannot reliably predict the Co−C BDEs either, because they exhibit large mean deviations (md) and large rmse values. Finally, it is found that the TPSS method developed in 2003 by Perdew and co-workers[17] can accurately predict the Co−C BDEs with a precision of ca. 2.0 kcal/mol (indicated by the rmse value). The md value of the TPSS method is also as low as −0.5 kcal/mol. Considering the fact that the experimental Co−C BDEs mostly have an error bar of ca. ±2 kcal/mol (see Table 1), we conclude that the TPSS/LANL2DZ+p method is optimal and sufficient for the study of Co−C BDEs.

Using the TPSS/LANL2DZ+p method, we next examined its performance in the prediction of various experimentally determined Co−C BDEs (Table 2). It is found that the theoretical predictions are in good agreement for 28 organocobalt complexes (Figure 2). The correlation coefficient between the experimental and theoretical Co−C BDE values is 0.9034, and the mean derivation is as low as −0.9 kcal/mol. The rmse value of the predictions is calculated to be 2.2 kcal/mol, the magnitude of which is close to that of the experimental error bar. Thus it can be concluded again that the TPSS/LANL2DZ+p method can reliably handle the organocobalt complexes. Nonetheless, it is noteworthy that the theoretical Co−C BDEs of two particular cobalt complexes (i.e., $(H_2O)(salen)Co-CH_3$ and (pyr)(salen)Co-*n*-C_4H_9) are found to be significantly lower than the experimental values by ca. 9 kcal/mol. The cause of these disagreements remains to be clarified, but it appears likely that the experimental values are not accurate. For instance, the calculated Co−C BDEs for $(H_2O)(salen)Co-C_2H_5$ and (H_2O)(salen)Co-*i*-C_3H_7 (i.e., 27.7 and 21.7 kcal/mol) are in good agreement with the corresponding experimental values (i.e., 29.9 and 19.4 kcal/mol). It is therefore difficult to understand why the experimental Co−C BDE for $(H_2O)(salen)Co-CH_3$ radically increases to 40.2 kcal/mol, a value about 9 kcal/mol higher than the theoretical prediction (i.e., 31.8 kcal/mol).

3. *anti*-Spin-Delocalization Effect

The above results demonstrate that it is reliable to use the TPSS/LANL2DZ+p method to derive the Co−C BDEs. Equipped with this useful tool, we next wanted to examine the effects of the in-plane ligands on the Co−C BDEs. Note that recently a considerable number of studies have been conducted to elucidate the effects of the axial base ligands on the Co−C bond strength.[28] Some studies have also been performed to investigate the effects of the axial substituents at carbon on the thermodynamics and kinetics of Co−C homolysis.[29] Despite this progress, very little has been known about the effects of the in-plane ligands on the homolytic cleavage of the Co−C bond. A possible reason for the lack of such studies is the difficulty in synthesizing organocobalt complexes carrying systematically varied in-plane ligands. As a result, a theoretical investigation on this subject is highly warranted at the present time.

In this context we fix the axial base ligand to be pyridine. We also fix the alkyl substituent on cobalt to be the methyl

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Table 2. Experimental and Theoretical BDE Values (kcal/mol) of the Co−C Bonds

complex	experimental	TPSS	BP86	ref
(pyr)Co(DH)$_2$-CH$_3$	33.1 ± 1.6	35.9	37.6	9
(pyr)Co(DH)$_2$-CH(CH$_3$)$_2$	21.3 ± 2.4	24.8	25.7	9
(pyr)(DH)$_2$Co-CH$_2$Ph	27.0 ± 2.0	25.4	26.0	9
(pyr)Co(DH)$_2$-CHMePh	19.7	18.1	18.4	4a
(pyr)Co(DH)$_2$-CH(CH$_3$)COOCH$_3$	28.7	26.0	26.4	4b
(pyr)Co(DH)$_2$-CH(CH$_2$COOCH$_3$)COOCH$_3$	33.2	28.2	28.4	4b
(imidazole)Co(DH)$_2$-CHMePh	20.8	18.6	18.8	4a
PhMeCH-(4-Me-py)Co(DH)$_2$	20.1	18.0	17.8	4a
PhMeCH-(4-NH$_2$-py)Co(DH)$_2$	21.2	18.3	18.7	4a
PhMeCH-(2-NH$_2$-py)Co(DH)$_2$	16.6	15.1	16.1	8a
PhMeCH-(4-CN-py)Co(DH)$_2$	17.9	17.6	18.0	4a
CH(CH$_3$)COOCH$_3$-(4-Me-py)Co(DH)$_2$	29.4	26.0	25.9	4b
CH(CH$_3$)COOCH$_3$-(4-CN-py)Co(DH)$_2$	28.2	25.2	25.8	4b
(PMe$_2$Ph)Co(DH)$_2$-CH$_2$Ph	24.0	26.1	25.9	5f
(PPh$_3$)Co(DH)$_2$-CH$_2$Ph	25.8	23.1	22.9	5c
(benzimidazole)(salen)Co-CH$_3$	32.5 ± 2	29.0	31.6	11a
(pyr)(salen)Co-CH$_3$	30.4 ± 2	29.0	31.5	11a
(H$_2$O)(salen)Co-CH$_3$	40.2 ± 2 (?)	31.8	32.8	11a
(H$_2$O)(salen)Co-C$_2$H$_5$	29.9 ± 2	27.7	30.1	11a
(H$_2$O)(salen)Co-*i*-C$_3$H$_7$	19.4 ± 2	21.7	23.9	11a
(H$_2$O)(salen)Co-*n*-C$_4$H$_9$	27.7 ± 2	29.2	31.1	11a
(H$_2$O)(salen)Co-*i*-C$_4$H$_9$	21.5 ± 2	21.8	24.1	11a
(salen)Co-*n*-C$_4$H$_9$	24.5 ± 0.3	25.6	26.9	11a
(pyr)(salen)Co*n*-C$_4$H$_9$	34.6 ± 0.6 (?)	25.9	27.3	4 h
(pyr)(saloph)Co-CH$_2$C$_6$H$_5$	22	18.4	19.6	4a
(pyr)(saloph)Co-CH(CH$_3$)$_2$,	20	20.8	21.7	4a
(pyr)(saloph)Co-CH$_2$C(CH$_3$)$_3$	18	18.9	21.1	4a
(pyr)(saloph)Co-CH$_2$CH$_2$CH$_3$	25	25.8	27.6	4a
(TAP)Co-C(CH$_3$)$_2$CN	17.8 ± 0.6	17.6	12.7	4d
(TAP)Co-CHMePh	19.5 ± 0.6	18.2	13.5	4d
correlation coefficient		0.9034	0.8587	
mean deviation		1.8	2.0	
root of mean square error		2.2	2.5	

group. The only variable in the system is the in-plane ligand, which can be changed in three different ways: (1) the nature of the chelating atoms; (2) the size and chemical structure of the chelating ring; and (3) the electronic and steric properties of the substituents on the chelating ring. By using this approach we obtain 27 different in-plane ligands (Table 3). For each of these in-plane ligands we have used the TPSS/LANL2DZ+p method to calculate its Co−C BDE.

According to Table 3, it can be seen that the calculated Co−C BDEs vary from ca. 22 to 32 kcal/mol. This magnitude of variation (i.e., 10 kcal/mol) can solely be attributed to the change of the in-plane ligand. To understand how the in-plane ligand affects the Co−C BDEs, we next calculated the Co−C bond lengths and Co−C vibration frequencies at the cobalt atoms before the Co−C homolysis (see Table 3). Through correlation analysis (Figure 3a) it is found that the Co−C BDEs have a negative (albeit relatively loose) correlation with the Co−C bond length (correlation coefficient = −0.7139). This finding is consistent with the chemical intuition that a shorter bond tends to be a stronger bond. Moreover, the Co−C BDEs have a positive correlation with the Co−C vibrational frequency (correlation coefficient = +0.7371). This observation can be attributed to the fact that the Co−C bond lengths have a strong, negative correlation with the Co−C vibrational frequencies (Figure 3b).

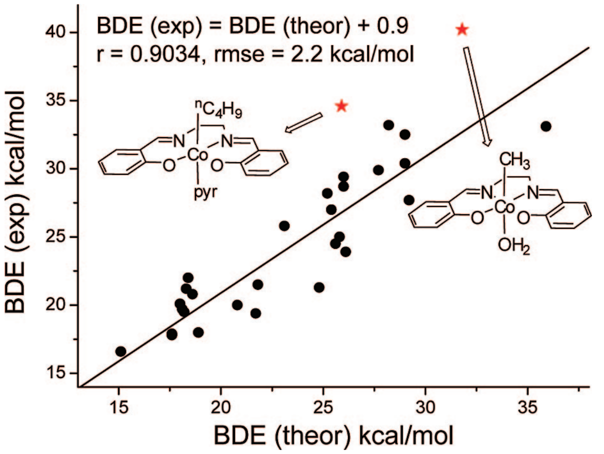

Figure 2. Comparing the theoretical and experimental Co−C BDEs.

It is next found that the Co−C BDEs exhibit a strong, *negative* correlation with the spin densities at the cobalt atoms after the homolysis (Figure 4). The correlation coefficient is as high as −0.9433 for 27 structurally different organocobalts. Note that the correlation between the spin density of the radical center and the bond strength has been observed previously in several types of chemical systems carrying systematically varied substituents, such as substituted toluenes (C−H BDEs),[30] anilines (N−H BDEs),[31] phenols (O−H BDEs),[32] phenylsilanes (Si−H BDEs),[33] and thiophenols (S−H BDEs).[34] However, in all these previous chemical systems the correlation slope is always positive, which can be explained by the classical chemical theory that a more delocalized radical (as reflected

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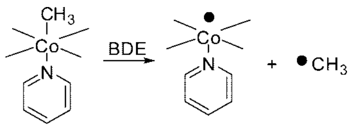
(30) Wu, Y.-D.; Wong, C.-L.; Chan, K. W. K.; Ji, G.-Z.; Jiang, X.-K. *J. Org. Chem.* **1996**, *61*, 746.

(31) (a) Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11085. (b) Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Org. Chem.* **2003**, *68*, 262.

(32) (a) Wu, Y.-D.; Lai, D. K. W. *J. Org. Chem.* **1996**, *61*, 7904. (b) Brinck, T.; Haeberlein, M.; Jonsson, M. *J. Am Chem. Soc.* **1997**, *119*, 4239. (c) Pratt, D. A.; Mills, J. H.; Porter, N. A. *J. Am. Chem. Soc.* **2003**, *125*, 5801.

(33) (a) Wu, Y.-D.; Wong, C.-L. *J. Org. Chem.* **1995**, *60*, 821. (b) Cheng, Y.-H.; Zhao, X.; Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Org. Chem.* **2002**, *67*, 6638.

Table 3. Theoretical Co−C BDEs (kcal/mol), Co−C Bond Lengths (Å), Co−C Vibration Frequencies (cm^{-1}), NBO Charges (*e*), and Spin Densities at the Cobalt Atoms (*e*)



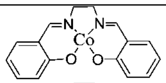
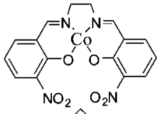
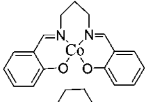
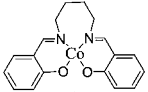
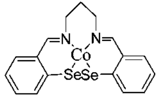
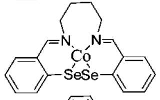
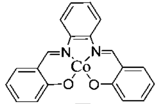
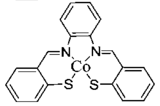
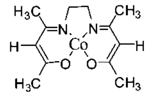
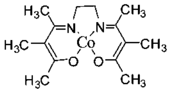
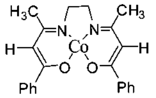
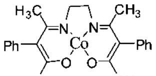
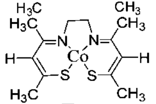
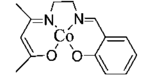
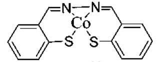
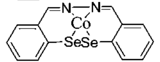
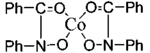
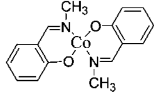
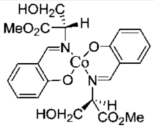
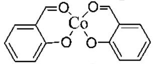
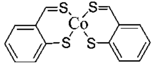
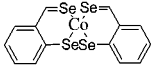
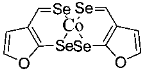
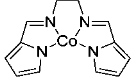
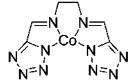
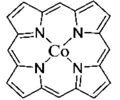
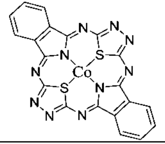
Entry	Organocobalt complex	Co-C BDE	Before homolysis			Spin density at Co after homolysis
			Co-C bond length	ν (Co-C)	NBO charge at Co	
1		29.0	1.97916	537.6	1.43994	0.99322
2		29.0	1.98644	526.2	1.51250	0.98374
3		28.7	1.97820	533.4	1.44384	1.01451
4		27.5	1.98008	531.7	1.45659	1.06571
5		23.8	2.01213	501.4	1.25730	1.13462
6		22.3	2.01466	494.0	1.24503	1.15842
7		29.5	1.97872	538.3	1.42712	0.98460
8		27.3	2.00712	507.4	1.26365	1.02899
9		29.2	1.97739	532.3	1.45537	1.00086
10		29.3	1.97648	533.8	1.44590	1.00044
11		28.9	1.97691	530.5	1.44139	0.99948
12		29.2	1.97704	533.8	1.44690	0.99828
13		26.9	2.00069	514.9	1.28435	1.05311
14		29.0	1.97926	531.8	1.46298	0.99811
15		23.5	2.01148	504.9	1.22731	1.10555
16		22.2	2.01838	497.2	1.17370	1.12863
17		30.8	1.96258	544.3	1.45377	0.98156
18		30.0	1.97757	532.5	1.46149	1.00160

Table 3. Continued

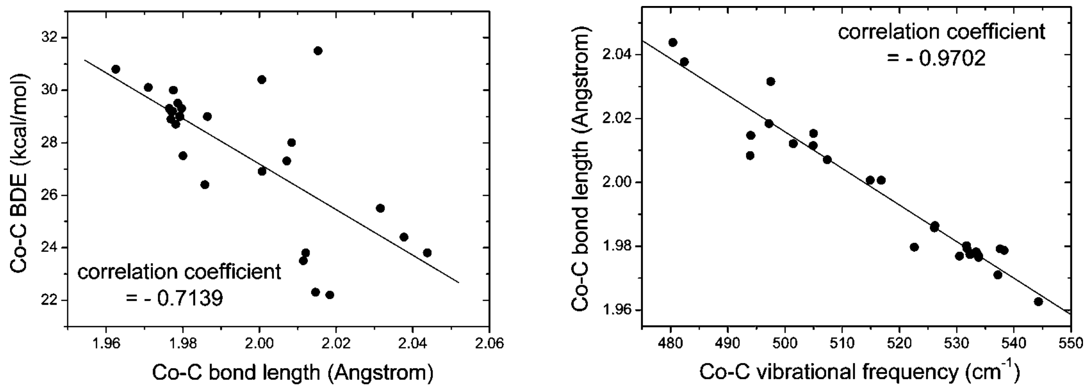
Entry	Organocobalt complex	Co-C BDE	Before homolysis			Spin density at Co after homolysis
			Co-C bond length	ν (Co-C)	NBO charge at Co	
19		29.3	1.97973	522.6	1.45490	1.02220
20		30.1	1.97101	537.2	1.48607	1.00343
21		25.5	2.03159	497.5	1.11390	1.07254
22		23.8	2.04380	480.4	1.05590	1.16898
23		24.4	2.03775	482.4	1.05635	1.14673
24		30.4	2.00064	516.8	1.41746	0.96505
25		31.5	2.01530	505.0	1.42506	0.94875
26		26.4	1.98578	526.1	1.49644	1.01359
27		28.0	2.00841	493.9	1.26923	1.02133

by a lower spin density) is more stable and therefore easier to produce through homolysis (as reflected by a lower BDE).[19]

Contrary to what has been observed in the previous systems,[30–34] the correlation between the Co spin densities and the Co−C BDEs is surprisingly *negative*. This means that a more stable cobalt radical (as reflected by a lower spin density due to spin delocalization) is more difficult to produce from the starting material possessing the Co−C bond (as reflected by a higher Co−C BDE). In other words, spin delocalization of the radical product through hyperconjugation interactions is not connected with the weakening of the chemical bond, as previously observed in many different chemical systems.[19] Instead, spin delocalization of the cobalt radicals is connected with the strengthening of the Co−C bond, an observation that can be named the "*anti*-spin-delocalization effect".

4. Origin of the *anti*-Spin-Delocalization Effect

Conceptually, the cause of the surprising *anti*-spin-delocalization effect is that we tend to overlook the stability of the starting material when considering the bond energy. This practice comes from the tradition of using BDEs as a reference to compare the relative stability of the radicals.[35] However, in a number of recent examples it has been shown that the effect



(a) (b)

Figure 3. Correlation between Co−C BDEs and Co−C bond lengths (a), and correlation between Co−C bond lengths and vibrational frequencies (b).

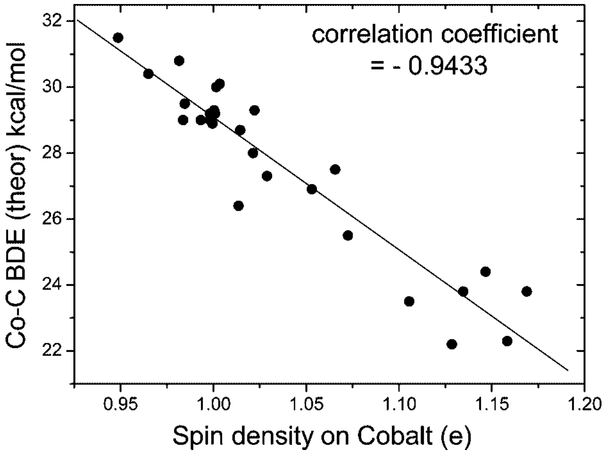


Figure 4. Negative correlation between the Co−C BDEs and the spin densities at Co.

of a substituent on BDE may be attributed not only to the stabilization (or destabilization) of the radical by the substituent but also to the stabilization (or destabilization) of the starting material by the same substituent.[36] Using this argument, we can now explain the negative correlation between the Co spin density and the Co−C BDE as follows: (1) the in-plane ligands can reduce the Co spin density through hyperconjugation interactions and thereby stabilize the Co radicals; (2) the in-plane ligands can also stabilize the organocobalt starting material through ionic interactions; (3) when the stabilization effect of the in-plane ligands is larger for the starting material than for the radical, a more stable Co radical is necessarily associated with a stronger Co−C bond.

The details of the above explanation are given below. First, we elucidate how the in-plane ligands stabilize the Co radical by delocalizing its spin density through hyperconjugation. To do so, we focus on a model cobalt radical as shown in Figure 5, which contains a four-coordinate in-plane ligand and an ammonia as the axial base ligand. It is found that the SOMO (singly occupied molecular orbital) of this model radical is predominantly contributed from three components:[37] (1) the d_{z^2} orbital of cobalt carrying a single electron, (2) the p orbital of the ammonia nitrogen carrying two electrons, and (3) the antibonding π^* orbital of the in-plane ligand carrying zero electrons. Note that the antibonding π^* orbital of the in-plane ligand is *NOT* perpendicular to the equatorial plane, so that it can have a nonzero overlap with the d_{z^2} orbital of cobalt. This leads to the delocalization of the spin of Co to the in-plane ligand, as manifested by the significant spin densities at the N1 and N4 atoms in Figure 5.[38] Additionally, it is the antibonding π^* orbital (but not any π orbital) of the in-plane ligand that participates in the formation of the SOMO. The reason is that the singly occupied d_{z^2} orbital of cobalt (as a metal) is too high lying in energy as compared to the π orbitals of the in-plane ligand (composed of nonmetallic elements).

Second, we explain how the in-plane ligands can stabilize the organocobalt starting material through ionic interactions. To do so, we calculated the NBO (natural bond orbital[39]) charge carried by the Co atom in the starting material before homolysis. As shown in Table 3, the NBO charges of Co vary significantly from ca. $+1.0e$ to $+1.5e$. Comparing these NBO charges to

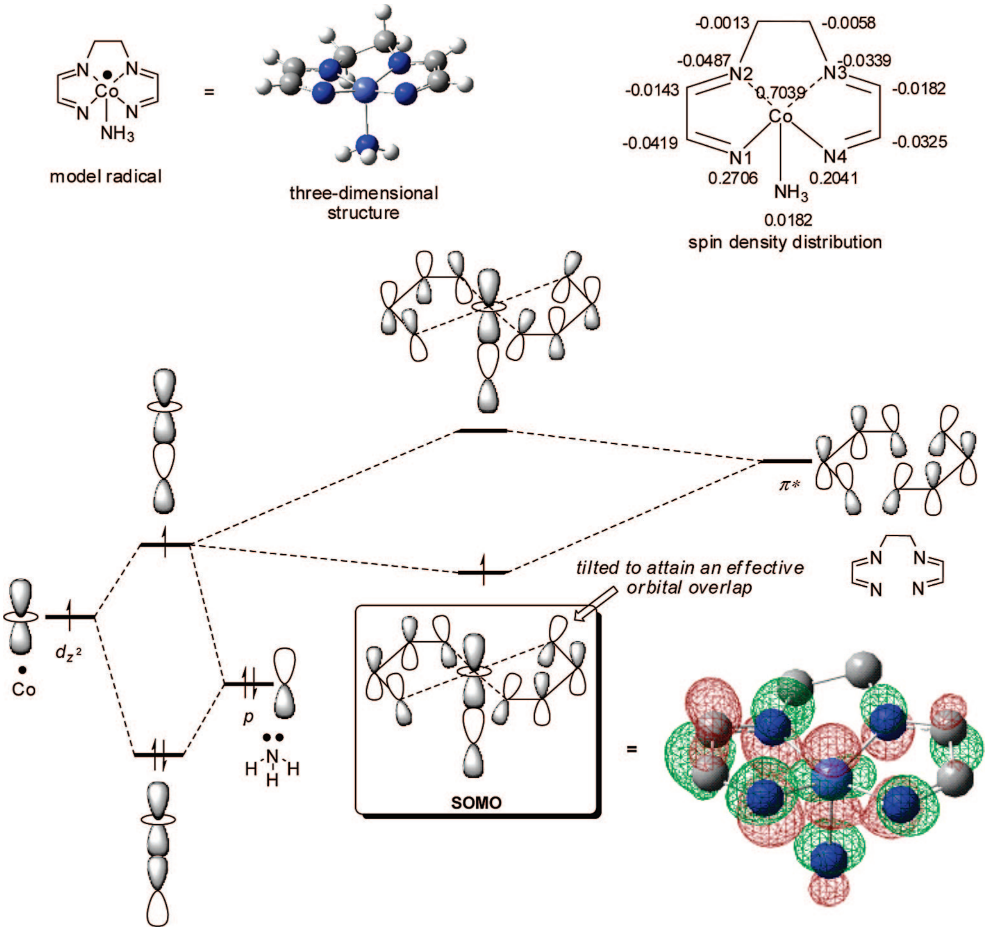
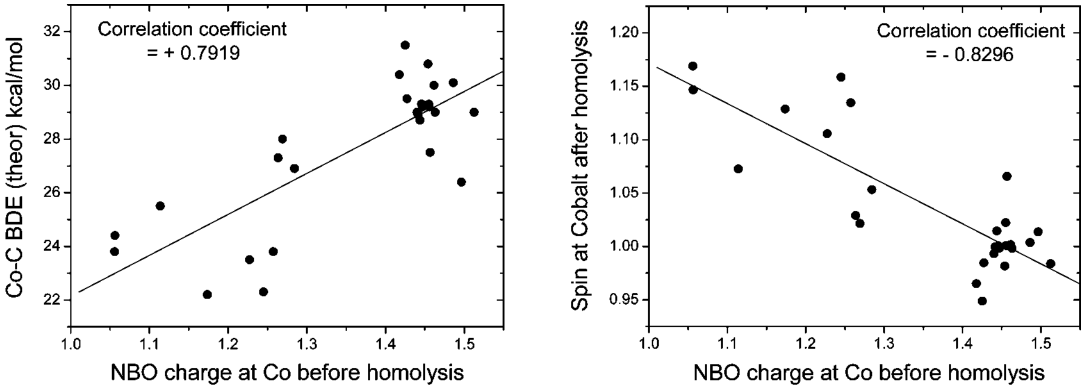


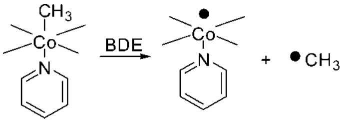
Figure 5. Structure, spin densities, and SOMO of a model cobalt radical.

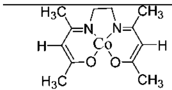
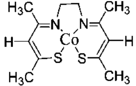
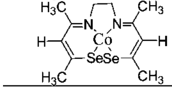
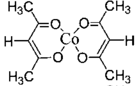
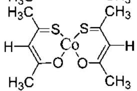
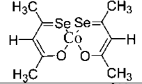
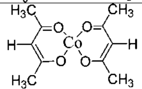
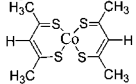
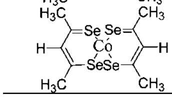


(a) (b)

Figure 6. Correlation of the NBO charges at Co before homolysis with the Co−C BDEs (a) and spin at Co after homolysis (b).

Table 4. Effects of Coordinating Atoms on Co−C BDEs (kcal/mol)



Organocobalt complex	Co-C BDE	NBO charge at Co before homolysis	Spin density at Co after homolysis
	29.2	1.45537	1.000860
	26.9	1.28435	1.053110
	26.0	1.19812	1.110822
	29.4	1.48294	1.016504
	27.7	1.29941	1.086778
	26.7	1.27771	1.137372
	29.4	1.48294	1.016504
	25.5	1.14759	1.114095
	22.9	1.06227	1.183251

the NBO charges at the CH_3 group before homolysis (ca. $-0.3e$), one can see that the Co−C bond has a substantial ionic character. Note that the variation of the Co NBO charge from $+1.0e$ to $+1.5e$ is completely due to the change of the in-plane ligand. Additionally it is noteworthy that the Co−C BDEs exhibit a positive correlation with the NBO charges of Co (Figure 6a), although the correlation coefficient is only modest (i.e., +0.7919). On the basis of the above observations it can be concluded that a stronger polarization of the Co−C bond can lead to a higher Co−C BDE value. This argument reaffirms

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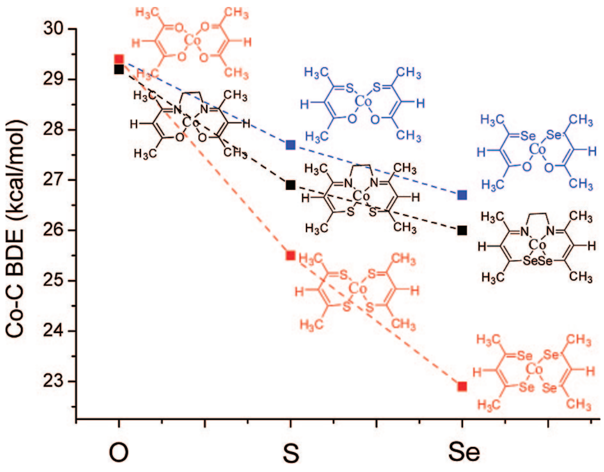


Figure 7. Effects of coordinating atoms on Co−C BDEs.

Zavitsas's conclusions regarding the importance of bond polarity in determining the bond strength, reached on the basis of Pauling's electronegativity equation.[36a,40]

Third, we need to compare the stabilization effect of the in-plane ligands for the starting material with that for the radical. As pointed above, the in-plane ligands can delocalize the spin density of the Co radical through hyperconjugation with their antibonding π^* orbitals. To improve the effectiveness of this hyperconjugation, the antibonding π^* orbital of the in-plane ligand should have a lower energy. At the same time, the in-plane ligands can increase the polarization of the Co−C bond in the starting material by increasing the NBO charge at Co. To enhance the polarization, the in-plane ligand should be more electron-attractive. Evidently a more electron-attractive in-plane ligand is usually associated with a lower antibonding π^* orbital. Thus, the efficiency of spin delocalization is correlated with the effectiveness of the Co−C bond polarization. This argument is supported by the correlation analysis between the NBO charges of Co before homolysis and the spin densities at Co after homolysis (correlation coefficient = −0.8296, Figure 6b). Thus, all the above analyses indicate that the stabilities of the cobalt radical and the Co−C bond are both determined by the electronegativity of the in-plane ligands. The observation that a more stable Co radical is associated with a stronger Co−C bond can be attributed only to the reason that the stabilization effect of the in-plane ligands is larger for the starting material than for the radical product during the homolysis.

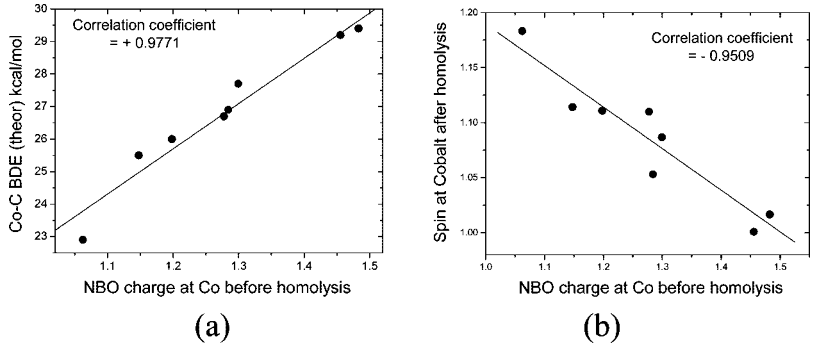
5. Discussion

According to the above analysis, the strength of the Co−C bond has a strong dependence on the electronegativity of the in-plane ligand. Here we want to further show that this electronegativity is determined mainly by the nature of the coordinating atoms directly connected to Co, but not by the remote substituent on the in-plane ligand.

5.1. Effects of Coordinating Atoms on Co−C BDEs. To demonstrate the strong effects of the coordinating atoms, we choose the 1,3-dicarbonyl compound derivatives as the in-plane ligands (Table 4). By changing two oxygen atoms to two sulfur atoms and to two selenium atoms, we observe a decrease of the Co−C BDE by ca. 2 and 3 kcal/mol, respectively (Figure 7). When four oxygen atoms are replaced by four sulfur atoms or by four selenium atoms in the in-plane ligand, we observe a sharp decrease of the Co−C BDE by 3.9 or 6.5 kcal/mol. All these observations can be associated with the fact that oxygen has a higher "electronegativity" than sulfur followed by selenium. Note that "electronegativity" literally describes the power of an atom or a functional group to attract electrons.[41] Therefore, the trends observed in Figure 8 confirm our proposition that the Co−C BDE has a positive correlation with the electronegativity of the in-plane ligand.

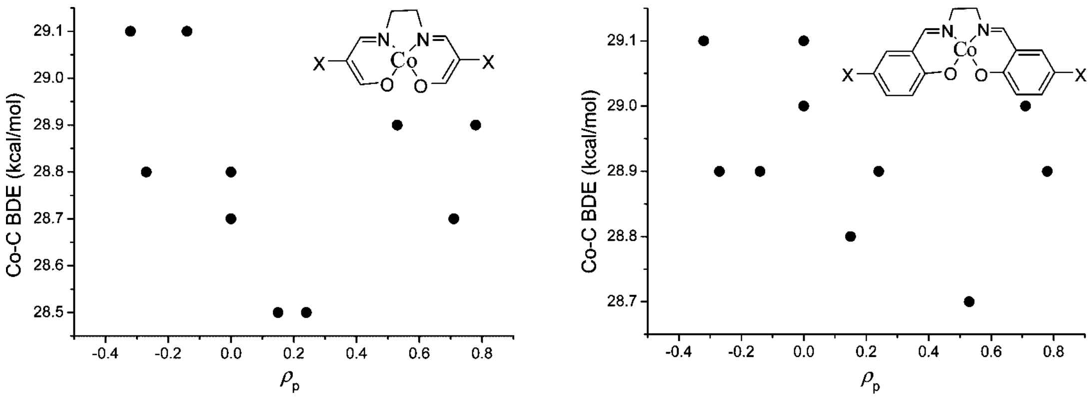
In the discussion on how the electron-attraction power of the in-plane ligands affects both the ionic polarization and spin delocalization, we have used Figure 6, which unfortunately only exhibits modest correlations. Here by focusing on the structurally more related in-plane ligands as listed in Table 4, we can redo the analysis (Figure 8). It is evident from Figure 8a that the Co−C BDEs now exhibit a strong, positive correlation with the NBO charges at Co before the homolysis. This means that the strength of the Co−C bond correlates to the electronegativity of the in-plane ligand. Furthermore, Figure 8b indicates that the NBO charge at Co before the homolysis has a strong, negative correlation with the spin density at Co after the homolysis. This observation means that the electronegativity of the in-plane ligand also connects to the ability of the ligand to delocalize the spin. Thus, the excellent correlations in Figure 8 confirm our explanation for the *anti*-spin-delocalization effect as proposed in Section 4.

5.2. Remote Substituent Effects on Co−C BDEs. In a number of previous studies it has been shown that the remote substituents can exert strong effects on the BDEs in systems such as substituted toluenes,[30] anilines,[31] phenols,[32] and thiophenols.[34] Thus it is an interesting question to ask whether or not the remote substituents in the in-plane ligands can produce some influence on the Co−C BDEs. In this context we have calculated the Co−C BDEs in two representative types of organocobalts that carry systematically varied substituents (Table 5). By plotting the Co−C BDEs against the Hammett ρ_p constants[42] of the substituents (Figure 9), we observe no correlation between the electron demand of the substituents and the strength of the Co−C bonds (Note: Hammett ρ_m constants have also been tried,



(a) (b)

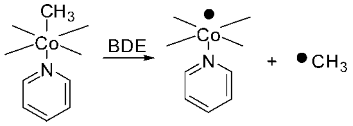
Figure 8. Correlation between the NBO charges and Co−C BDEs (a) and between the NBO charges and spins (b).

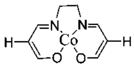
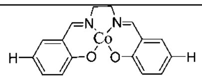
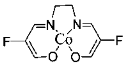
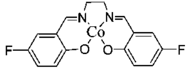
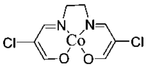
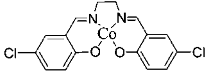
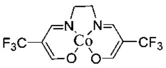
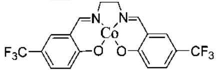
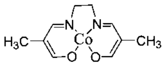
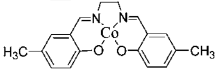
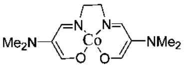
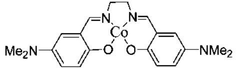
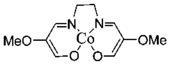
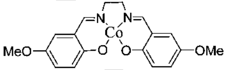
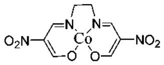
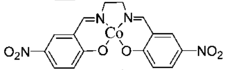
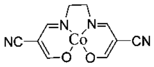
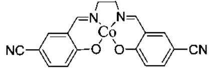
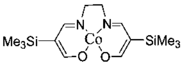
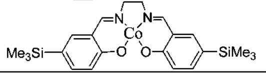


(a) (b)

Figure 9. Correlation between the Co−C BDEs and Hammett substituent constants.

Table 5. Effects of Remote Substituents on Co−C BDEs (kcal/mol)



Organocobalt complex	Co-C BDE	Organocobalt complex	Co-C BDE
	28.7		29.0
	28.5		28.8
	28.5		28.9
	28.9		28.9
	28.7		29.0
	28.9		28.7
	29.1		28.9
	29.1		29.1
	28.8		28.9
	28.8		29.1

but no correlation is found either). This actually is not surprising because it is evident from Figure 9 that across all the different substituents the Co−C BDEs change by less than 0.6 kcal/mol. Thus, it can be concluded that the remote substituents on the in-plane ligands do not exert any significant effects on the Co−C BDEs.

6. Summary

The homolytic Co−C bond dissociation enthalpy is central to the understanding of organocobalt-mediated transformations in the areas of both bioinorganic chemistry and transition-metal catalysis. However, the determination of the Co−C BDEs still remains a difficult task using either an experimental or theoretical approach. In the present study we investigate how to use the density functional theory method to accurately calculate the Co−C BDEs. Among the seven functionals that have been examined (namely, B3LYP, B3P86, BP86, G96LYP, PBE, BB95, and TPSS), it is found that the recently developed TPSS/LANL2DZ+p method can satisfactorily reproduce the experimental Co−C BDEs of 28 structurally unrelated organocobalts within a precision of ca. 2.2 kcal/mol.

Equipped with this useful tool, we next examined the effects of the in-plane ligands on the Co−C BDEs in a systematic fashion for the first time. For the 27 compounds that have been studied, it is found that the in-plane ligands can vary the Co−C BDEs by ca. 10 kcal/mol. Across the 27 different in-plane ligands the Co−C BDEs are found to exhibit a strong, *negative* correlation with the spin densities at the cobalt atoms after homolysis. This observation is not consistent with the conventional chemical intuition that delocalization of the spin of a free radical through hyperconjugation interactions should stabilize the radical and thereby weaken the chemical bond that undergoes homolysis. We name this unexpected finding the *anti*-spin-delocalization effect.

To explain the *anti*-spin-delocalization effect, we next conducted a series of analyses on the SOMO orbital and the NBO charges. On the basis of these analyses we propose that (1) the in-plane ligands can reduce the Co spin density through hyperconjugation interactions with their empty antibonding π^* orbitals and (2) the in-plane ligands can also stabilize the organocobalt starting material through ionic interactions by attracting electrons from Co. Putting these two arguments together, the origin for the *anti*-spin-delocalization effect is that the stabilization effect of the in-plane ligands is larger for the starting material than for the radical. The essence of the theoretical explanation is that the strength of the Co−C bond has a strong dependence on the electronegativity of the in-plane ligand.

7. Computational Methodologies

All the calculations were performed with the Gaussian 03 programs[43] using our HP Superdome Server (32 × 1.5 GHz Itanium 2 Madison CPU). Initial geometry optimization was carried out using the TPSS functional with an effective core potential (LANL2DZ) for the inner electrons and its associated double-ζ basis set for the more external ones. In the case of the Co atom an f-polarization shell was added. Each optimized structure was confirmed by the frequency calculation at the same level of theory to be the real minimum without any imaginary vibration frequency. For compounds that have multiple conformations, efforts were made to find the lowest-energy conformation by comparing the structures optimized from different starting geometries.

Harmonic vibrational frequencies were calculated using the TPSS/LANL2DZ+p method from the optimized geometries. Zero-point vibrational energy (ZPE) corrections were obtained using unscaled frequencies. The gas-phase single-point electronic energies were calculated at the TPSS/LANL2DZ+p level. Subsequently the gas-phase enthalpy changes were obtained by adding the ZPE corrections and thermal corrections (0 → 298 K) to the electronic energies. Note that all the calculated gas-phase enthalpies corresponded to the reference state of 1 atm, 298 K.

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Supporting Information Available: Cartesian coordinates of optimized structures. Detailed thermodynamic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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