the different donor atoms. Therefore for chp, there will be two values for Y, while for $PhPO_3^{2-}$ there will be three values of Y. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence O before N. See: R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *Dalton Trans.* **2000**, 2349–2356.

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Remote Communication between Charge Centers and Hydrogen-Bonding Sites: Possibility for a Signal Transducer?**

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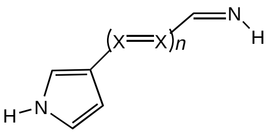
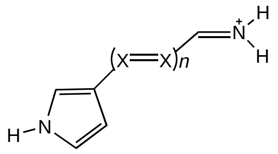
Hydrogen bonding and charge interactions are both essential for molecular recognition and the self-assembly of biological macromolecules. They are also employed heavily in the design of new systems for fundamental, biological, and materials research. The influence of a charge-bearing functional group on pK_a values[1] and chemical reactivity[2] has been well documented in the form of Hammett-type substituent constants in physical organic studies. Changes in the hydrogen-bonding behavior of ligands upon complexation with cationic transition metal centers have been indicated by theoretical calculations.[3] Such calculations also indicated that anions could induce a large cooperative effect in the hydrogen-bonding network of peptides.[4] Enhancement was observed experimentally in urea · carboxylate binding when the carbonyl group of the urea molecule was coordinated to a Lewis acid.[5] The optical property of $[Ru(bpy)_3]^{2+}$ (bpy = bipyridine) in a phosphodiester sensor was changed when the hydrogen-bonding sites were bound.[6] Although both hydrogen-bonding and charge-bearing sites are important in molecular recognition, interestingly, it is not common to find examples in supramolecular chemistry in which hydrogen-bonding sites are designed to be controlled by a covalently bound charge-bearing substituent. Charge-assisted C–H ··· X hydrogen bonds have been recognized in recent years[7] and metallocene complexes have been used to achieve redox-switched binding.[8] Nevertheless, the binding sites are basically adjacent to the charged centers, and we felt that charge centers can have a more far-reaching influence on a binding site.



1a: X = CH, $n = 1$
1b: X = CH, $n = 2$
1c: X = CH, $n = 3$
1d: X = CH, $n = 4$

3a: X = N, $n = 1$
3b: X = N, $n = 2$
3c: X = N, $n = 3$
3d: X = N, $n = 4$



2a: X = CH, $n = 1$
2b: X = CH, $n = 2$
2c: X = CH, $n = 3$
2d: X = CH, $n = 4$

4a: X = N, $n = 1$
4b: X = N, $n = 2$
4c: X = N, $n = 3$
4d: X = N, $n = 4$

If a charged group and a binding site can communicate with each other, one can use a three-component system (a charged group, a linker, and a binding site) as a signal transducer. The charge-bearing group can be viewed as a reaction site, whose charge state can be altered by reactions such as protonation, metalation, oxidation, reduction, or chemical transformation of a functional group. On the basis of this concept we designed test compounds **1a–d** and **2a–d**, and calculated the energies of formation of a hydrogen bond (binding energies) to find out how efficiently the reaction and binding centers can communicate with each other. In these compounds the reaction center is an imine group and the binding center is pyrrole; compounds **1a–d** are neutral imines and **2a–d** are cationic iminium compounds. Ammonia was chosen as the hydrogen-bonding partner of the N–H group of pyrrole for the sake of geometric simplicity, since it only has one lone pair of electrons. The ammonia binding energy of **2a** ($-13.17\ \text{kcal mol}^{-1}$) at the HF/6-31G* level is double that of cationic **1a** ($-6.84\ \text{kcal mol}^{-1}$) (Table 1).[9] While the binding energies of neutral systems (**1a–d**) remain fairly constant as the linker gets longer, the binding energies of cationic systems

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[**] This work was supported by the National Science Council and Academia Sinica of Taiwan (ROC). The granting of computer time by the National Center for High-Performance Computing and the Computing Center of Academia Sinica is acknowledged. We also thank Ning Juan for her assistance in preparing the manuscript.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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Table 1. Binding energies (kcal mol^{-1}) of the three-component systems (**1**–**4**) with NH_3 calculated at the HF/6-31G* level.

	1	**2**	**3**	**4**
a	− 6.84	− 13.17	− 7.39	− 15.50
b	− 6.73	− 12.04	− 7.66	− 16.45
c	− 6.64	− 11.18	− 7.84	− 17.99
d	− 6.57	− 10.47	− 7.95	− 19.07

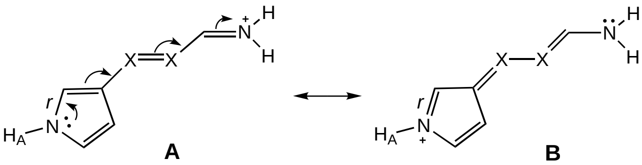
(**2a**–**d**) decrease gradually, as one would expect. Nevertheless, even when the $N\cdots N$ distance is as far as 14 Å in **2d**, the binding energy is − 10.47 kcal mol^{-1}, which is still significantly stronger than the neutral systems.

In our search for new types of linkers we replaced the carbon linkers with nitrogen linkers (**3a**–**d**, **4a**–**d**). The binding energy of cationic **4a** (− 15.50 kcal mol^{-1}) with ammonia was also roughly double that of **3a** (− 7.39 kcal mol^{-1}). To our surprise, the binding energies of **4a**–**d** got larger as the linker got longer (Table 1). If we think of our molecules as signal transducers, the increase in binding energy means that the signal sent by the reaction center dose not die out as the wire becomes longer, instead, the wire acts as an amplifier to enhance the signal. Results at higher levels of theory for the cationic $N{=}N$ series **4a**–**d** (Table 2) are in line with the HF/6-31G* results, even though the extent of energy increase varies. These results are in direct contrast with the concept that through-bond or through-space effects of a functional group should diminish with increasing distance.

Table 2. Binding energies (kcal mol^{-1}) of **4a**–**d** with NH_3 calculated with ab initio and DFT methods.

	4a	**4b**	**4c**	**4d**
HF/6-31G*	− 15.50	− 16.45	− 17.99	− 19.07
HF/6-31 + G**	− 13.41	− 14.29	− 15.77	− 16.78
HF/6-31 + G(2d,2p)	− 12.94	− 13.90	− 15.36	− 16.33
B3LYP/6-31G*	− 19.19	− 19.37	− 19.57	− 19.79
B3LYP/6-31 + G**	− 16.06	− 16.26	–	–
MP2/6-31G*	− 18.72	− 19.27	− 20.08	− 21.43
MP4(SDQ)/6-31G*	− 17.75	− 19.04	–	–
MP4(SDQ)/6-31G*//B3LYP/6-31G*	− 17.42	− 18.30	–	–

Examination of calculated structures of uncomplexed **2a**–**d** and **4a**–**d** reveals that the importance of resonance form **B** in Scheme 1 increases in **4a**–**d** as the linker gets longer, but decreases in **2a**–**d**. For example, the C−N bond (labeled *r* in Scheme 1) in the pyrrole ring was shorter in **4d** (1.281 Å) than in **4a** (1.305 Å). In series **2**, *r* is shorter in **2a** (1.325 Å) than in **2d** (1.340 Å).[10] The Mulliken charge of H_A (Scheme 1) in **4a**–**d** increases from 0.448 to 0.467 at the HF/6-31G* level of theory as the importance of resonance form **B** increases.[11] This observation is in good agreement with the increase in binding ability as the length of the N linker increases. The shift in the $N{=}N \leftrightarrow N{-}N$ resonance is not without precedence. The importance of the N−N resonance form was invoked in a recent study of negative solvatochromism of azo dyes to rationalize a polar ground state.[12] The larger driving force for favoring form **B** in **4a**–**d** than in **2a**–**d** can be understood by the weaker bond strength of $N{=}N$ relative to the $C{=}N$ and $C{=}C$ bonds;[13] some of the weaker $N{=}N$ bonds in form **A** become $C{=}N$ bonds in form **B** (Scheme 1). The increasing binding ability of pyrrole in series **4** probably reflects the larger electron-withdrawing power of longer N linkers. From a more practical standpoint, it is difficult to synthesize consecutive $N{=}N$ bonds. We have, therefore, tested the same type of cationic compounds with $-((CH{=}CH)_n{-}N{=}N)_x-$ linkers. Their binding energies are shown in Table 3. It is found that the signal-amplifying phenomenon persists as *x* varies from 1 to 2. The ability of the linkers in Table 3 to maintain the influence of a charge center is significantly better than the pure C linkers (**2a**–**d**), although the degree of increase in the binding energy is smaller than that of pure N linkers (**4a**–**d**).



Scheme 1. Charge delocalization of the protonated system.

Table 3. Ammonia binding energies (kcal mol^{-1}) of the protonated three-component system with different linkers at the HF/6-31G* level.

	$x = 1$	$x = 2$
$-(CH{=}CH{-}N{=}N)_x-$	− 14.63	− 15.62
$-((CH{=}CH)_2{-}N{=}N)_x-$	− 13.90	− 14.49
$-((CH{=}CH)_3{-}N{=}N)_x-$	− 13.19	− 13.64
$-((CH{=}CH)_4{-}N{=}N)_x-$	− 12.61	− 12.98

It is known that the medium has a profound influence on the binding geometry of DNA base pairs[14] and on the structure and electronic properties of organic materials with conjugated π systems.[15] Therefore, we are currently examining the effects of counterions and solvent molecules on our three-component system. Preliminary studies showed that the existence of a counterion indeed reduces the binding energy of a cationic system, but the binding energy is still significantly higher than that of the neutral system. Whether the effect of a counterion could be reduced by using different types of counterions or by using anion-binding hosts is under investigation.

In conclusion, we have explored the possibility of using a reaction center to modulate the binding behavior of a remote hydrogen-bonding site. This concept of “remote control” mechanism can be incorporated into the design of new types of chemical sensors and be used to tune the structure and properties of supramolecular assemblies. The contrasting behavior of pure C and pure N linkers demonstrates that linkers with different chemical compositions may have a very different effect on the communication between reaction and binding centers.

Received: January 11, 2001
Revised: April 23, 2001 [Z16407]

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[10] The structures were calculated at the HF/6-31G* level. See the Supporting Information for more structural details.

[11] The charge of H_A in **2a–d** decreased from 0.435 to 0.418.

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nido ↔ *closo* Interconversion of Six-Vertex Metallacarboranes: Access to CoC_2B_3 and CoC_2B_4 Clusters with Nonadjacent Carbon Atoms[**]

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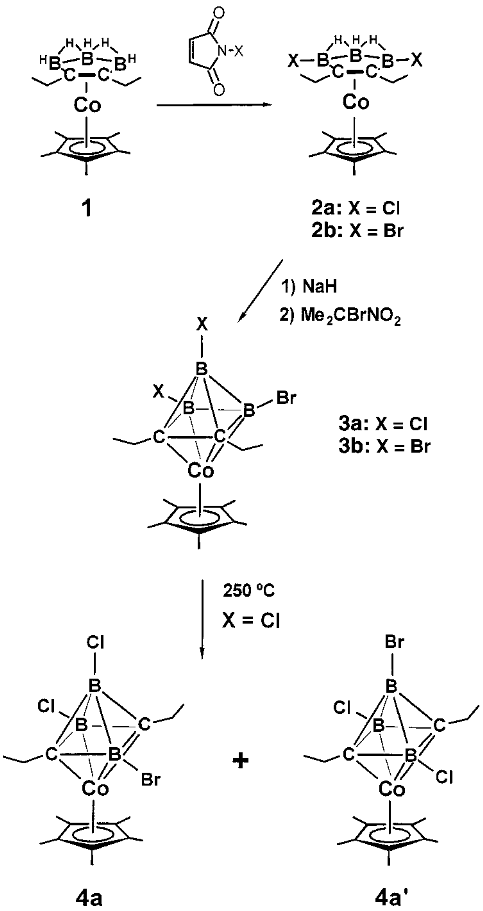
Russell N. Grimes[*]

Metallacarborane chemistry has been well developed for 12-vertex (icosahedral) and 7-vertex (pentagonal bipyramidal) clusters and, to a lesser extent, for other systems having 8 to 14 vertices.[1] In contrast, little is known of the smallest members of the metallacarborane family, for example, 6-vertex *closo*-MC_2B_3 polyhedra. The first such species were prepared in the 1970s[2,3] by thermal insertion of metal reagents into *closo*-1,5-$C_2B_3H_5$, a relatively inaccessible small carborane. To date, fewer than half a dozen 6-vertex *closo*-metallacarboranes have been reported,[2–4] and just one crystal structure of a *closo*-MC_2B_3 system is available.[3] In principle, such clusters should be accessible by the oxidation of *nido*-$LMC_2B_3H_5^{2-}$ open-cage dianions having 16 skeletal electrons, generating neutral 14-electron *closo*-$LMC_2B_3H_5$ species as predicted from simple electron-counting arguments (Wade's rules).[5] However, no such conversion has been reported experimentally, and earlier attempts to do this in our laboratory were unsuccessful; our experience has been that oxidants sufficiently strong to remove two electrons tend to degrade the cage structure.

It seemed possible that this problem might be circumvented by modifying the cluster to make it easier to oxidize. Here we report an application of this approach, in which a tribrominated *nido*-1,2,3-MC_2B_3 cage with adjacent carbon atoms undergoes oxidative closure to form the desired *closo* system. This product in turn can be converted into 7-vertex *closo*- and 6-vertex *nido*-metallacarboranes having nonadjacent carbon atoms, families that have heretofore been difficult to access.

Deprotonation of the 4,6-dichloro- or dibromo-*nido*-cobaltacarboranes[6] **2a** or **2b** (Scheme 1) with sodium hydride in THF, followed by addition of 2-bromo-2-nitropropane and



Scheme 1. Synthesis of **3a** and **3b** as well as the thermal rearrangement of **3a** to form a mixture of isomers **4a** and **4a'**.

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[**] Organotransition-Metal Metallacarboranes, part 57. This work was supported in part by the National Science Foundation (grant CHE 9980708) and the Alexander von Humboldt Foundation (Feodor Lynen postdoctoral fellowship to H.-J. Schanz). Part 56: M. Bluhm, H. Pritzkow, W. Siebert, R. N. Grimes, *Angew. Chem.* **2000**, *112*, 4736; *Angew. Chem. Int. Ed.* **2000**, *39*, 4562.