From Homogeneous to Heterogeneous Catalysis: Novel Anchoring of Polypyrazolylborate Copper(I) Complexes on Silica Gel through Classical and Nonclassical Hydrogen Bonds. Use as Catalysts of the Olefin Cyclopropanation Reaction

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The fixation of the preformed polypyrazolylborate copper(I) complexes BpCu (**1**), Tp*Cu (**2**), and [B(pz)$_4$]Cu (**3**) (Bp = dihydrobispyrazolylborate, $H_2B(pz)_2$; Tp* = hydrotris(3,5-dimethyl)pyrazolylborate, HB(pz*)$_3$; B(pz)$_4$ = tetrakispyrazolylborate) on silica gel and their use, under heterogeneous conditions, as catalysts for the olefin cyclopropanation reaction are reported. The catalytic activity is very similar to that observed under homogeneous conditions, as a consequence, according to the studies presented herein, of a ligand-to-support interaction that would involve the hydroxyl groups of the silica surface and the borohydride B−H group and/or the pyrazolyl nitrogen atoms. The strength of such interactions allows the recovery and recycling of the supported catalysts for a number of cycles.

Introduction

Heterogeneous catalysis is widely preferred in industry due to the well-known advantages of easier products−catalyst separation and recovery of the catalyst processes and, very often, the resistance of the catalyst to drastic operation conditions.[1] But in terms of selectivity, homogeneous catalysis usually provides better results.[2] Obviously, the fixation of known homogeneous catalysts on solid supports is the ideal combination in order to achieve the advantages of both heterogeneous and homogeneous catalysis.[3] But problems arise when doing so. The main strategy for years has consisted in the anchoring of ligands to the support and the subsequent addition of the metal to those already-fixed ligands.[4] This method is not perfect since other ligand exchange processes would favor some metal leaching. An alternative method is the so-called "tethering" of transition metal complexes, in which the metal compound is added and fixed to the support.[5,6] But in order to achieve the desired homogeneous−heterogeneous activities parallelism, the metal center environment, at least during catalysis, should be similar in both cases. This would require the anchoring of the metal complex through the ligands in such a way that no metal−support interaction could take place. Based on these premises, we herein report the fixation of preformed polypyrazolylborate copper(I) complexes on silica gel and their use, under heterogeneous conditions, as catalysts for the olefin cyclopropanation reaction. Their catalytic activities are very similar to those observed under homogeneous conditions, as a consequence, according to the studies that we present, of a ligand-to-support interaction that might involve the hydroxyl groups of the silica surface and the borohydride B−H group and/or the pyrazolyl nitrogen atoms.

Results and Discussion

Immobilization of the Copper Complexes. Previous work from this laboratory[7] has shown the catalytic activity of polypyrazolylborate[8] copper(I) complexes in the reaction of olefins and diazocompounds to give cyclopropanes (eq 1). The complexes BpCu (Bp = dihydrobispyrazolylborate, $H_2B(pz)_2$), **1**, and Tp*Cu(C_2H_4) (Tp* = hydrotris(3,5-dimethyl)pyrazolylborate, HB(pz*)$_3$), **2**, are good catalysts for such transformations under homogeneous conditions.[9] Those results have also

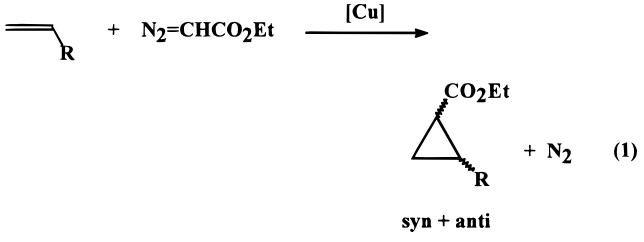

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Table 1. Adsorption[a] of the Complexes 1−3 in Silica Gel

catalyst	[Cu] (M, initial solution)	[Cu] (M, final solution)	mg Cu/g SiO_2	% Cu adsorbed
$(H_2Bpz_2)Cu$ (**1**)	8.4×10^{-4}	4.8×10^{-4}	0.58	43
$(HBpz^*_3)Cu(C_2H_4)$ (**2**)	7.3×10^{-4}	5.8×10^{-5}	1.07	92
$(Bpz_4)Cu$ (**3**)	9.5×10^{-4}	1.6×10^{-5}	1.48	98

[a] A mother solution was prepared, and two identical portions of 25 mL were taken. One portion was treated with 1 g of silica gel. After 12 h of stirring, the filtrate and the blank were investigated by AAS.

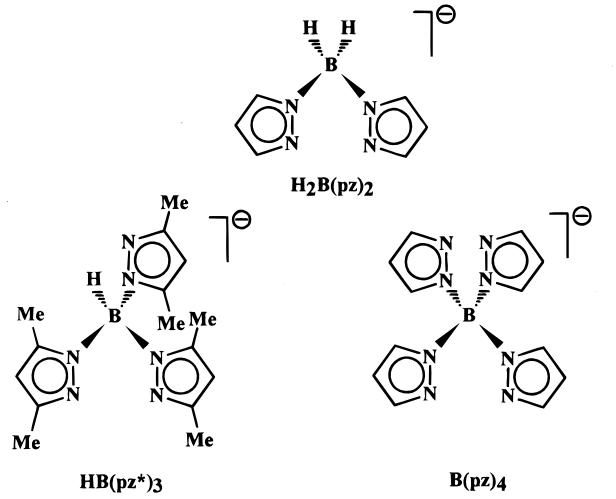
Table 2. Amount of Copper[a] Removed by Washing with Several Solvents[b]

catalyst	petroleum ether	$ClCH_2CH_2Cl$	CH_2Cl_2	THF	acetone
$(H_2Bpz_2)Cu$ (**1**)	2	15.6	16.3	33.6	37.6
$(HBpz^*_3)Cu(C_2H_4)$ (**2**)	1	5.6	9.7	90.6	68.4
$(Bpz_4)Cu$ (**3**)	1	1.2	1.3	56	66.3

[a] Determined by AAS. [b] Percentage of leaching over the Cu adsorbed on the silica gel upon stirring with 15 mL of the corresponding solvent for 5 min.

shown the catalytic activity of **1** when supported on silica gel. We have now studied these two complexes as well as the tetrakispyrazolylborate derivative, $(B(pz)_4)$-Cu (**3**), under heterogeneous conditions, to investigate the nature of the complex−support linkage.

When dichloromethane solutions of complexes **1**−**3** of similar concentrations were treated with 1 g of silica gel, no change in color was observed neither in the solution nor in the solid support. However, upon filtration, washing with dichloromethane, and drying (see Experimental Section), an air-unstable solid was obtained: its exposure to air induced the appearance of the typical greenish color of Cu(II). A set of experiments to determine the amount of Cu adsorbed were carried out as described in the Experimental Section. The



results are displayed in Table 1. Complex **3** was adsorbed almost twice as much as complex **1**, whereas **2** was adsorbed to a similar extent as **3**. These data provided some information about the linkage: (i) the lower the number of B−H bonds per molecule, the higher the amount of complex adsorbed, and (ii) the amount of complex adsorbed increased with the number of pyrazolyl rings in the molecule. Washing of the supported complexes with different solvents was also carried out, and the results are shown in Table 2. The use of chlorinated (CH_2Cl_2, $ClCH_2CH_2Cl$) solvents induced minor leaching, whereas acetone or THF substantially removed the corresponding complex. Successive washing with CH_2Cl_2 led to a small amount of leaching after each cycle (Table 3). When petroleum ether was employed, the leaching was reduced to a minimum, making this solvent the most appropriate to run the catalytic reactions under rigorous heterogeneous conditions. Now, the observed trend is somewhat different from that derived from the adsorption process. The chlorinated solvents seem to induce a similar, small effect in all cases, but with acetone or THF there are significant distinctions: the complex with two B−H bonds was retained more than those with one or no B−H units.

Table 3. Consecutive Extractions of Supported 2 with CH_2Cl_2

	wash no.[a]			
	1	2	3	4
% Cu leached[b,c]	9.7	2.8	2.4	2.4

[a] The solid (see Table 1) was stirred with 15 mL of CH_2Cl_2 for 5 min. [b] Determined by AAS. [c] Percentage of copper in the filtrate relative to the remaining Cu in the solid.

Catalytic Experiments. We have tested the catalytic activity of the supported complexes **1**−**3** employing methylene chloride or petroleum ether as the solvent. Although the use of the former supposes the existence of small, but also catalytic, amounts of the copper complex in solution, as inferred from data in Table 3, that amount is negligible compared to that adsorbed on the silica gel. Table 4 displays the results of these catalytic experiments as well as the comparison with the corresponding homogeneous systems, in terms of yields and selectivities. It is clear that the homogeneous catalyst does not seem to be significantly altered after heterogenization. In addition, the catalyst appears to be robust enough for a recycling process since the yield and selectivity values are very similar under heterogeneous conditions when methylene chloride or petroleum ether was employed as the solvent, despite the fact that the complexes **1**−**3** are very soluble in the former and present a very poor solubility in the latter.

Tests of catalyst recovery and recycling have also been performed for three different olefins. Figure 1 shows the

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(9) Complex Tp*Cu can be employed instead of $Tp^*Cu(C_2H_4)$ with no differences observed. See: Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711−718.

Table 4. Comparison of the Catalytic Activity[a] of Complexes 1−3 under Homogeneous and Heterogeneous Conditions

	homogeneous[b] (CH_2Cl_2)		heterogeneous[c] (CH_2Cl_2)		heterogeneous[c] (petroleum ether)	
catalyst	yield[d]	anti:syn[d]	yield[d]	anti:syn[d]	yield[d]	anti:syn[d]
(H_2Bpz_2)Cu (**1**)	76	75:25	90	60:40	90	54:46
(HBpz*$_3$)Cu(C_2H_4) (**2**)[e]	80	43:57	81	47:53	80	46:54
(Bpz_4)Cu (**3**)	74	78:22	75	63:37	80	64:36

[a] Reactions performed with a 1:5 EDA:styrene ratio. [b] 0.05 mmol of [Cu] employed, 4% with respect to EDA. [c] 1% of [Cu] with respect to EDA. [d] Determined by GC after total consumption of EDA. [e] The use of Tp*Cu provides the same results.

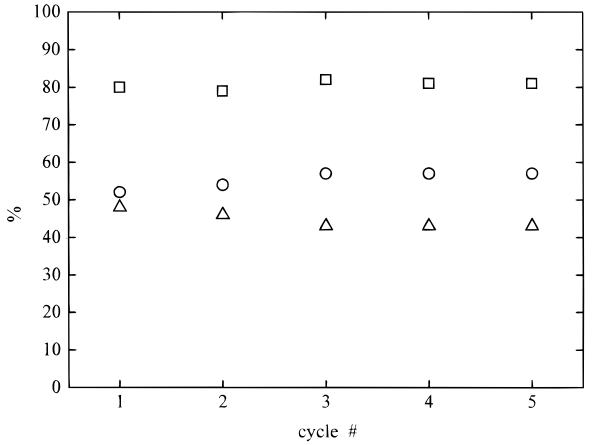

Figure 1. Styrene cyclopropanation using silica gel-adsorbed complex **2** recovering and reusing the supported catalyst: (□) yield of cyclopropanes (syn + anti); (○) percentage of the anti isomer in the mixture of cyclopropanes; (△) percentage of the syn isomer in the mixture of cyclopropanes.

values of cyclopropane yields and the amounts of the syn and anti isomers obtained during five catalytic cycles, accounting for a total of 5000 equiv of EDA, relative to copper, converted ([Cu]:[EDA]:[styrene] ratio = 1:1000:5000, each cycle). The yield and selectivity values remained constant from each cycle to another. Moreover, since dichloromethane was employed as the solvent, the metal leaching displayed in Table 3, after successive washings, does not affect the overall process in terms of yields and selectivities. In any case, the use of petroleum ether would reduce to a minimum the mentioned leaching. Similar experiments have been carried out with *cis*-cyclooctene and 1-hexene, as shown in Figures 2 and 3. The number of cycles has been increased to 10, and again the same conclusion is reached: the catalysts can be reused with no significant loss in the catalytic activity.

The role of the copper center in the adsorption process has been studied by means of catalytic competition experiments with para-substituted styrenes. For example, when complex **2** was employed as the catalyst precursor, very similar values of ρ were obtained for homogeneous (CH_2Cl_2, −0.83)[7b] and heterogeneous (−0.81 and −0.84, for CH_2Cl_2 and petroleum ether as solvents, respectively) conditions (Figure 4). We interpret this analogy as the result of the similarity of the metal center environment in both cases, meaning that, at least during the catalytic cycle, there is no interaction between the metal center and the support surface.

Nature of the Extracted Materials. The experiments in Tables 2 and 3 have shown the possibility of removal of copper from the support. In addition to the

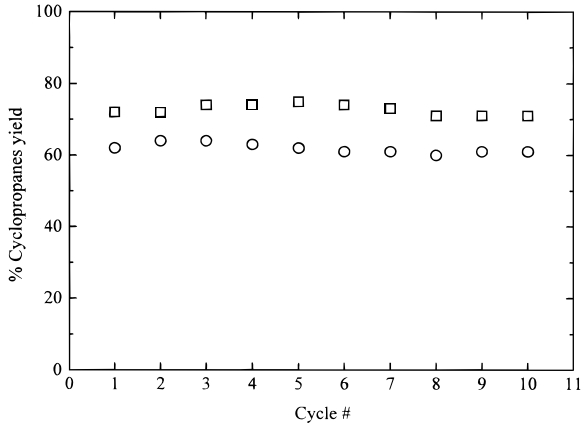

Figure 2. Yield of cyclopropanes (syn + anti) using silica gel-adsorbed complex **2** during 10 cycles upon recovering and reusing the supported catalyst: (□) *cis*-cyclooctene; (○) 1-hexene.

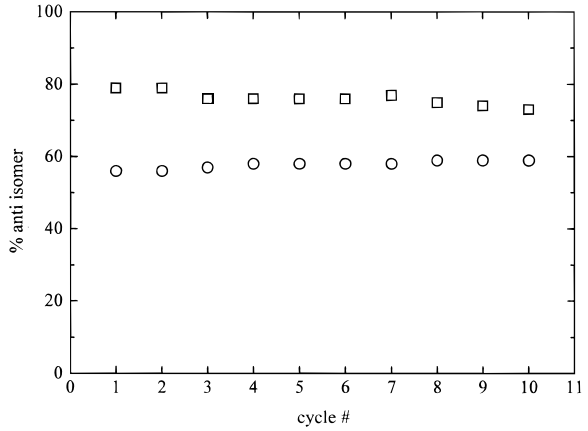

Figure 3. Percentage of the anti isomer in the mixture of cyclopropanes using silica gel-adsorbed complex **2** during 10 cycles upon recovering and reusing the supported catalyst: (□) *cis*-cyclooctene; (○) 1-hexene.

quantitative analysis, we have also investigated the nature of the extracted material. Thus, IR studies have shown that when supported, complex **2** does not present the typical absorption in the 2550−2500 cm^{-1} region attributable to the B−H bond (Figure 5). However, NMR studies carried out with recovered samples of **1** or **2** after successive washing with methylene chloride (as in Table 3) clearly assesses the recovery of these complexes with their B−H groups unaltered. On the other hand, when acetone or THF is employed in the washing process, a yet unknown reaction takes place, no B−H absorptions being observed in the IR spectrum of the recovered materials (no direct reaction of these complexes with neat acetone was observed). Complex **3** can be recovered in high yield from the silica gel using acetone, the NMR

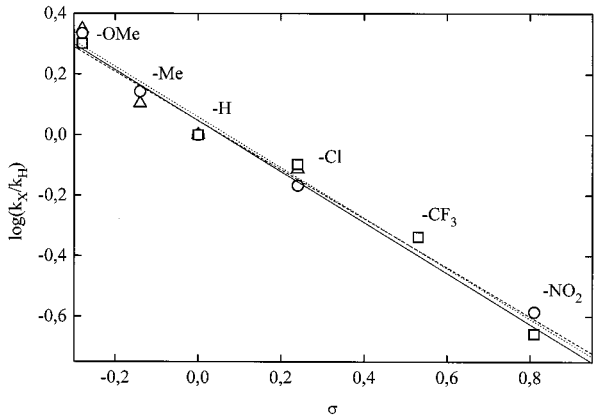

Figure 4. Hammett plot for the competition experiments with para-substituted styrenes using **2** as the catalyst: (—, ○) heterogeneous conditions, petroleum ether as solvent; (---, △) heterogeneous conditions, methylene chloride as solvent; (···, □) homogeneous conditions, methylene chloride as solvent.

spectra of the recovered material being identical to those of a fresh sample of **3**.

Complex−Support Interaction: Formation of Classical Hydrogen Bonds and Nonclassical Dihydrogen Bonds. The experiments described above have allowed the proposition of a complex-to-support linkage through the polypyrazolyl ligands and not through the metal center. It is worth mentioning at this stage that XPS as well as solid-state NMR studies have failed to provide more information on this adsorption process, mainly due to the small proportion of copper adsorbed and to the interferences of impurities in the silica gel employed. We believe that the formation of the adsorbate−adsorbent pair can be explained in terms of hydrogen bonds. Since only the B−H bonds are available to interact with the silica surface in complex **1**, we propose the existence of one (or eventually, two) O−H···H−B dihydrogen bond (DHB in Figure 6a) similar to that recently found by Klooster, Koetzle, and Crabtree in the molecules of BH_3NH_3.[10] As proposed by Crabtree et al., this class of bonds must be interpreted as the interaction of the NH proton and the BH bond as a whole. In our case, hydroxyl groups of the surface would interact with the borohydride group, an interaction that would be in accord with the loss of the BH band in the IR spectrum of adsorbed **2** (Figure 5).

The opposite case is that of supported **3**. A recent contribution from this laboratory has demonstrated that the active copper species for cyclopropanation reaction is that of a 14-e geometry, independently of the ligands attached to the metal center.[11] This means that in the case of **3** the tetrakispyrazolylborate ligand would bind the metal in an η^2 fashion, the other two pyrazolyl rings being free to interact with the silica surface. The formation of a classical hydrogen bond (CHB in Figure 6c) between the hydroxyl groups of the silica and the nitrogen atom of one (or two) of the non-copper-bound pyrazolyl rings would explain the adsorption of **3**. This case would be similar to Drago's report[12] about the adsorption of pyridine on HZSM-5, a thermodynamically favored process based on classical hydrogen bonding. The formation of such bonding between the surface hydroxyl groups and electronegative atoms has also been proposed by Bianchini et al.[13] for the tethering of sulfonated polyphosphine rhodium catalysts. In the case of **2**, in which a B−H bond and a non-metal-bound pyrazolyl group coexist (assuming again the need of a 14-e center), both types of hydrogen bonds (CHB and DHB) might occur (Figure 6b).

The observed fixation of polypyrazolylborate copper(I) complexes on silica gel constitutes a starting point in the fixation of the relatively high number of polypyrazolylborate derivatives of many elements. Work to expand this new fixation route in silica gel and other supports is currently under way in our laboratory.

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents employed were degassed before use. Potassium tetrakis(pyrazolyl)borate[8] and the complexes BpCu,[7a] Tp*Cu,[9] and Tp*Cu(C_2H_4)[7c] were prepared according to literature methods. The olefins, ethyl diazoacetate, and CuI as well as the para-susbtituted styrenes were purchased from Aldrich and employed without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer, chemical shifts being referred to TMS. GC data were collected with a Varian GC-3350, and AA data were collected with a Varian model AAS-110 instrument.

Synthesis of B(pz)$_4$Cu (3). To a solution of CuI (0.095 g, 0.5 mmol) in acetonitrile (30 mL) was added K[B(pz)$_4$] (1 equiv). The mixture was stirred for 3 h, and the solvent was evaporated. The complex was extracted with CH_2Cl_2, and volatiles were removed under vacuum to give **3** as a white solid with analytical purity. Yield: 85%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298): δ 7.13, 6.97, 6.24 (br s, 4H each). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ 141.5, 135.3, 105.6 (4C each).

Heterogeneization of Catalysts. The anchoring of polypyrazolylborate copper(I) complexes on silica gel was carried out following the same procedure: 0.05 mmol of the complex was dissolved in 30 mL of CH_2Cl_2, and 1 g of silica gel was added to the solution. The mixture was stirred for 12 h at room temperature, and the solid was separated by filtration. Upon washing with CH_2Cl_2 (15 mL), the solid was dried under vacuum. The filtrates were collected and analyzed as described below.

Amount of Copper Determined by AAS. To determine the amount of Cu supported on silica gel, a set of experiments was carried out: The solid obtained as described above was placed in a PTFE vessel, and a mixture of 10 mL of 48% m/v HF, 5 mL of 60% m/v $HClO_4$, and 10 mL of *aqua regia* was added. The mixture was heated to dryness at 90 °C in a sand bath. The residue was dissolved with 1 mL of HNO_3, and the solution was transferred into a 25 mL calibrated flask. The copper content was evaluated by AAS. The same procedure was applied to the filtrates; the results are shown in Table 1.

Catalytic Experiments. (A) Olefin Cyclopropanation under Heterogeneous Conditions. The silica gel-supported copper complex was suspended in petroleum ether (30 mL), and 25 equiv of EDA and 150 equiv of olefin were added

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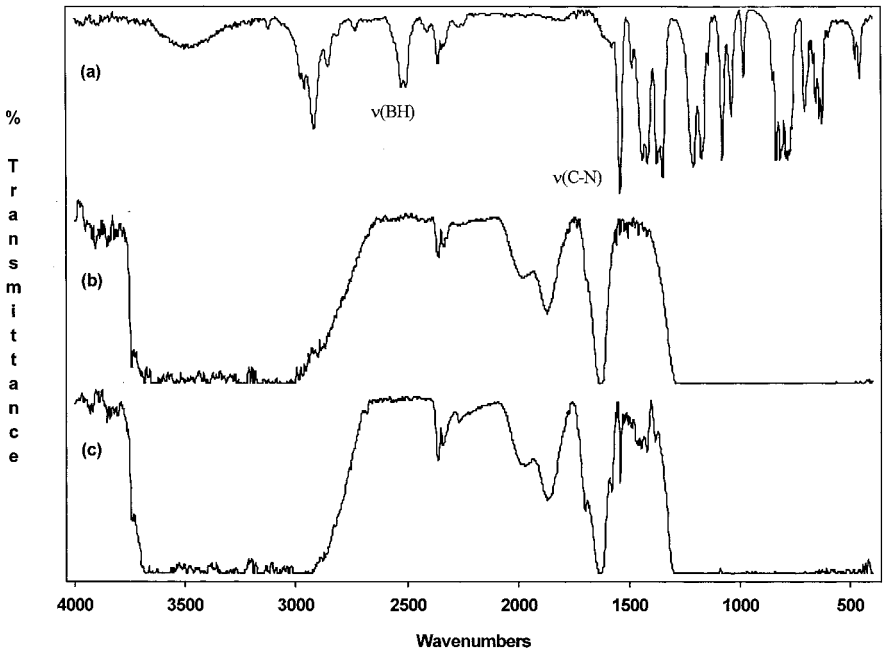

Figure 5. (a) IR spectrum of Tp*Cu(C_2H_4) in KI. (b) IR spectrum of silica gel. (c) IR spectrum of Tp*Cu(C_2H_4) supported on silica gel.

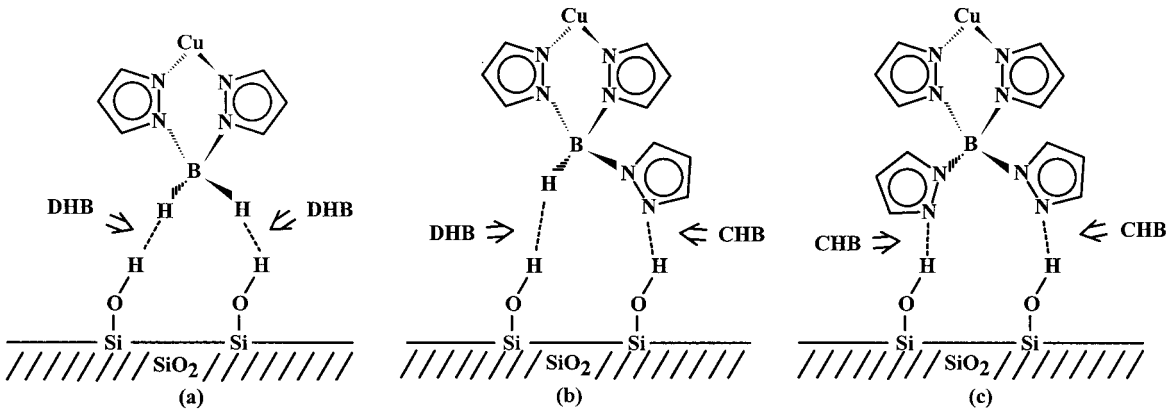

Figure 6. Complex−support interaction: formation of classical hydrogen bonds (CHB) and nonclassical dihydrogen bonds (DHB).

simultaneously. The mixture was stirred until no EDA was detected by GC.

(B) Recovery and Recycling of Catalysts. At the end of the cyclopropanation reaction, i.e., when no EDA was detected by GC, the mixture of excess olefin and products was filtered. The residue of silica gel-containing catalyst was washed with CH_2Cl_2 (2 × 20 mL) to completely remove the remains of products and/or reactants.

(C) Cyclopropanation Competition Experiments with para-Substituted Styrenes. The catalyst precursor **2** (0.05 mmol) was dissolved in 40 mL of 1,2-dichloroethane, and 300 equiv (15 mmol) of an equimolar mixture of styrene and the corresponding para-substituted styrene were added to the stirred solution. Ethyl diazoacetate (0.285 g, 2.5 mmol) was immediately added, in one portion, to the above solution. The ratio of products was determined by GC after total consumption of the ethyl diazoacetate. The cyclopropanation competition experiments with copper-supported precatalysts were carried out following the same procedure employing CH_2Cl_2 or petroleum ether as the reaction solvent. The ratio of products was determined by GC after total consumption of the ethyl diazoacetate.

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