

triblock copolymer. Triblock copolymer films were obtained by evaporating a concentrated toluene solution of the copolymer and a hPS standard ($\bar{M}_w = 2500 \text{ g mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.09$) in a mass ratio of 1.00/0.40 over 3 d. The films were then annealed at 120 °C for one week. To incorporate Fe_2O_3 , an excess of FeCl_2 was equilibrated with the nanotubes with PAA-lined cores in deoxygenated THF. The excess FeCl_2 was removed after precipitation of the Fe^{2+} -impregnated tubes into methanol. The trapped Fe^{2+} was then treated with NaOH in THF containing 2 % water to form iron(II) hydroxide or oxide. Fe_2O_3 was prepared by oxidizing the iron(II) hydroxide or oxide with hydrogen peroxide.

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- [1] F. S. Bates, G. H. Fredrickson, *Phys. Today* **1999**, 51(2), 32.
- [2] G. J. Liu, J. Ding, L. Qiao, A. Guo, J. T. Gleeson, B. Dymov, T. Hashimoto, K. Saijo, *Chem. Eur. J.* **1999**, 5, 2740.
- [3] J. Massey, K. N. Power, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **1998**, 120, 9533.
- [4] K. Ishizu, A. Onen, *J. Polym. Sci. A* **1989**, 27, 3719.
- [5] G. J. Liu, J. Ding, T. Hashimoto, K. Saijo, F. M. Winnik, S. Nigam, *Chem. Mater.* **1999**, 11, 2233.
- [6] J.-S. Lee, A. Hirao, S. Nakahama, *Macromolecules* **1989**, 22, 2602.
- [7] M. Kato, T. Ichijo, K. Ishii, M. Hasegawa, *J. Polym. Sci. A* **1971**, 9, 2109.
- [8] R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russell, D. R. Huffman, *Science* **1992**, 257, 219.
- [9] a) B. H. Sohn, R. E. Cohen, *Chem. Mater.* **1997**, 9, 264; b) B. Z. Tang, Y. H. Geng, J. W. Y. Lam, B. S. Li, X. B. Jing, X. H. Wang, F. S. Wang, A. B. Pakhomov, X. X. Zhang, *Chem. Mater.* **1999**, 11, 1581.
- [10] L. Neel, *Rev. Mod. Phys.* **1953**, 25, 293.
- [11] T. M. Whitney, J. S. Jiang, P. C. Searson, C. L. Chien, *Science* **1993**, 261, 1316.
- [12] A. Urbas, R. Sharp, Y. Fink, E. L. Thomas, M. Xenidou, L. J. Fetters, *Adv. Mater.* **2000**, 12, 812.
- [13] a) K. Yamaguchi, T. Sato, Y. Kato, M. Inoue, T. Fujii, *Mater. Sci. Forum* **1998**, 287–288, 483; b) O. Jarjayes, P. H. Fries, G. Bidan, *J. Magn. Magn. Mater.* **1994**, 137, 205.
- [14] E. Kroll, F. M. Winnik, R. F. Ziolo, *Chem. Mater.* **1996**, 8, 1594.
- [15] J. A. Lopez-Perez, M. A. Lopez-Quintela, J. Mira, J. Rivas, S. W. Charles, *Phys. Chem. B* **1997**, 101, 8045.
- [16] a) S. Mann, J. Skarnulis, R. J. P. William, *J. Chem. Soc. Chem. Commun.* **1979**, 1030; b) I. I. Yaaco, A. C. Nunes, A. Bose, *J. Colloid Interface Sci.* **1995**, 171, 73.
- [17] R. M. Metzger, V. V. Konovalov, M. Sun, T. Xu, G. Zangari, B. Xu, M. Benakli, W. D. Doyle, *IEEE Trans. Magn.* **2000**, 36, 30.
- [18] H. Cao, Z. Xu, H. Sang, D. Sheng, C. Tie, *Adv. Mater.* **2001**, 13, 121.

Thermally Stable Homogeneous Catalysts for Alkane Dehydrogenation**

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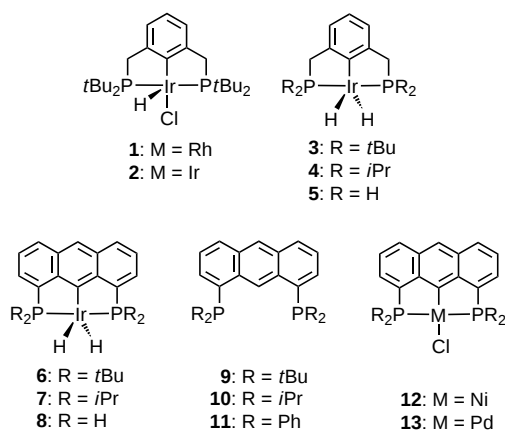
Dedicated to Professor Heinz A. Staab on the occasion of his 75th birthday

Thermostable homogeneous catalysts have three major advantages: the first is that less reactive substrates, for which the kinetics require high temperatures, can be transformed to products; second, they expand the field of homogeneous catalysis to include more endothermic processes, for which the thermodynamics require high temperatures; the third benefit is facile catalyst separation by distillation of educts and products. A process where such catalysts would definitely show great promise is the C–H activation of alkanes in homogeneous solution with dehydrogenation to alkenes and hydrogen.^[1] However, thermostable homogeneous catalysts for endothermic processes are almost nonexistent^[2] and the synthesis of suitable organometallic coordination compounds seemed destined to be abandoned because of complex instability at high temperatures.^[3] This trend was reversed with the introduction of tridentate coordination compounds^[4] in the form of PCP pincer complexes $[\text{MCl}(\text{H})\{\text{C}_6\text{H}_3(\text{CH}_2\text{PrBu})_2-2,6\}]$ (**1**, **2**)^[5] and their subsequent conversion into $[\text{M}(\text{H})_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{PrBu})_2-2,6\}]$ and $[\text{M}(\text{H})_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PrBu})_2-2,6\}]$ ($\text{M} = \text{Rh}, \text{Ir}$).^[6, 7] The transition metal dihydrides, especially the iridium compounds **3** and **4**, are thermally stable up to 200 °C and are reactive to aliphatic and cycloaliphatic C–H bonds.^[7]

An even higher thermostability can be expected for “anthraphos” complexes **6** and **7** which are obtained by replacing the benzylic PCP pincer ligands with anthracene-

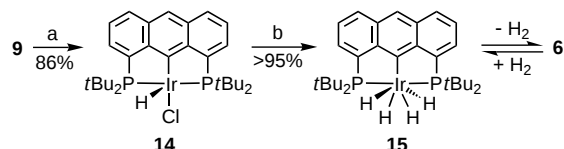
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1,8-diphosphanes **9** and **10**.^[8] The rigidity and chemical inertness of the polycyclic aromatic ligand backbone resulted in remarkably stable cyclometallated complexes **12** and **13** formed from anthraphos **11**.^[9] This observation prompted us to synthesize **6** and to investigate its application as a thermostable homogeneous catalyst for alkane dehydrogenation.

Anthraphos **9** was prepared similarly to **11**^[9b] by direct nucleophilic substitution of 1,8-difluoroanthracene with two equivalents of potassium di-*tert*-butylphosphide (*t*Bu₂PK, dioxane/THF 5/1, reflux, 1 h, 80% yield).^[10, 11] In analogy to the preparation of **2**^[5a] the reaction of **9** and IrCl₃·3H₂O in 2-propanol/water gave **14** (red crystal powder, m.p. 196°C (differential scanning calorimetry; DSC), dec. 308°C (DSC), 86%, Scheme 1). Reduction of **14** under an atmosphere of



Scheme 1. a) IrCl₃·3H₂O, 2-propanol/water (15/2), reflux 24 h; b) NaH, THF, sonication, 12 h.

hydrogen gave mixtures of the yellow iridium tetrahydride **15** and the red iridium dihydride **6**. By saturating solutions of such mixtures with hydrogen the equilibrium was shifted towards **15** and by evaporating the solvent under vacuum the red solid of pure **6** was obtained in >95%.

The structures of the anthraphos complexes **14**, **15**, and **6** are unambiguously revealed by their NMR spectroscopic data and by comparison with the data of the corresponding PCP pincer complexes **2** and **3**.^[5a, 6b,c] In accordance with the structure of **14**, in which the chloride is situated in the anthracene plane and the hydride perpendicular to that plane, the ¹H and ¹³C NMR spectra show two sets of signals for each of the two different types of *tert*-butyl groups (apparent C_s symmetry). On the other hand, all four *tert*-butyl groups are equivalent for **15** and **6** showing apparent C_{2v} symmetry. In ³¹P NMR spectra with {¹H}offset (proton decoupling with exception of the hydride region) the number of hydrogen atoms bound to iridium is indicated by the signal splitting (**14**: δ =

66.8 (d, ²J_{H,P} = 10.0 Hz), **15**: δ = 76.4 (quint, ²J_{H,P} = 9.5 Hz), **6**: δ = 92.3 (t, ²J_{H,P} = 9.5 Hz)).

Whereas the pincer iridium dihydrides **3** and **4** are instantaneously decomposed above 200°C,^[7] the anthraphos compound **6** in alkane solution was found to be stable at 250°C and to catalyze the dehydrogenation of, for example, cyclododecane to *cis/trans*-cyclododecene (1/2.4) and hydrogen at this temperature (Figure 1).^[12] To our knowledge this

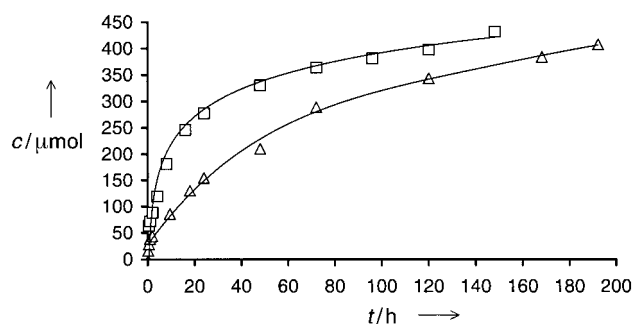


Figure 1. Formation of cyclododecene (total, *cis/trans* 1/2.4, μmol) in the dehydrogenation of cyclododecane catalyzed by **6** (3.3 μmol) at 230°C (Δ) and 250°C (□). Experiments were performed under argon in glass vessels which allowed release of hydrogen. For gas chromatography (GC) analysis, catalyst-free samples were prepared by vacuum transfer and recondensation.

represents the highest thermostability yet reported for an organometallic homogeneous catalyst. At 250°C the initial turn over frequency (TOF) was 40 h⁻¹ and the turn over number (TON) of 136 was reached after 148 h. At 230°C an initial TOF of 30 h⁻¹ and a TON of 126 after 192 h was observed. With increasing olefin formation the rate decreases, but apparently because of the high temperature the dehydrogenation does not come to a complete standstill as was observed with pincer complexes **3** and **4** at 200°C.^[13] However, if the initial TOF for dehydrogenation of cyclooctane at 150°C is compared, the reactivity of **6** at this low temperature is found to be about one order lower than for **3** and about two orders lower than for **4**.

The reaction mechanism of catalytic alkane dehydrogenation requires that the alkane makes contact with the metal center of the catalyst. A conformationally flexible catalyst molecule should be appropriate to simulate the rate-determining step for reactions at high temperatures. In addition, the relative accessibility of the metal center, which can be determined by calculating the accessible molecular surface (*ams*),^[14, 15] is a very simple approach for rationalizing the relative activities of catalysts. During the two-step procedure the conformational flexibility of the catalyst molecule is introduced by generating a “super molecule”, which is a superposition of all relevant conformers within a certain energy range (*E* < 3 kcal mol⁻¹). In the second step, Connolly’s method^[16] is applied to this super molecule. The resulting *ams* can be regarded as a measure of the minimal accessible surface at the center considered. Figure 2 shows this surface for catalysts **3**, **4**, **6**, and **7**. The lower reactivity of the anthraphos catalyst **6** compared to the pincer catalysts **3** and **4** is reflected in its distinctly smaller *ams* value (legend to

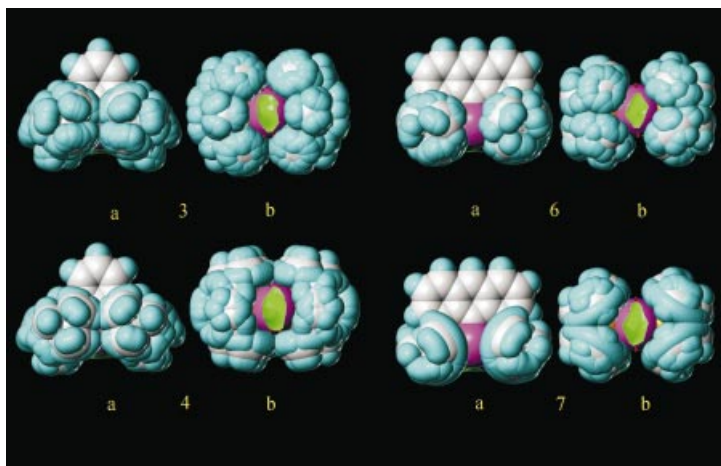


Figure 2. Accessible molecular surface (*ams*) at the Ir (purple) center. The “super-molecular” fragments (no hydride atoms) of **3**, **4**, **6**, and **7** are shown in top (a) and front view (b) with the *ams* in green. Size of the *ams* at the Ir center: *ams* (**3**) = 5.6 Å² (1258 conformers superimposed); *ams* (**4**) = 5.7 Å² (2234 conformers), *ams* (**6**) = 3.5 Å² (50 conformers), *ams* (**7**) = 5.1 Å² (1428 conformers). Size of the *ams* at the Ir center for the most stable conformation (not shown): *ams*_{stable}(**3**) = 8.9 Å², *ams*_{stable}(**4**) = 11.8 Å², *ams*_{stable}(**6**) = 5.9 Å², *ams*_{stable}(**7**) = 6.5 Å².

Figure 2). The models of **3** and **4** take into account the two equilibrating enantiomeric conformers as pictured in Figure 3. On the other hand, anthrapphos catalyst **7** is expected to possess a reactivity similar to **3** and **4**. At low to moderate temperatures the equilibrium structure of the catalyst molecule should gain more importance and in this case the relative catalyst reactivities might better correlate to the corresponding accessibility (*ams*_{stable}). These values show greater differ-

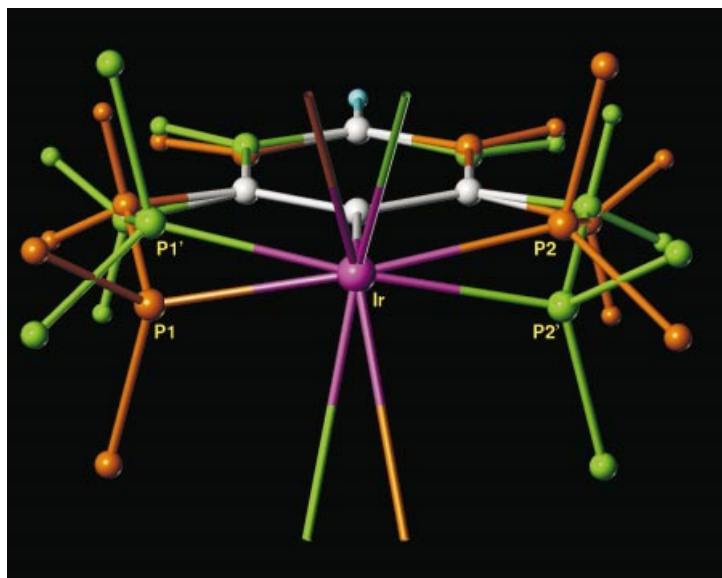
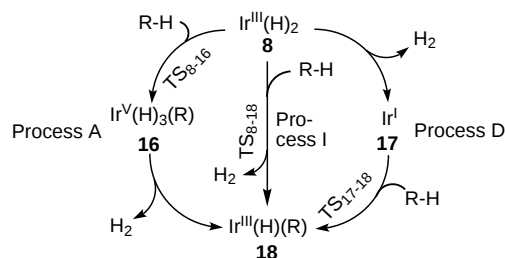


Figure 3. Superposition of the two enantiomers of a pincer IrP₂ fragment. One enantiomer is drawn in brown with P1 and P2 and the other in green with P1' and P2'. The best fit was obtained by superposition of Ir, the metallated carbon atom, and the two *ortho*-C atoms. The endpoints of the sticks at the Ir atom mark for each enantiomer the free coordination sites D which complement the trigonal-bipyramidal coordination geometry at the metal center (distance Ir...D: 2.5 Å). This also allows for a description of their positions relative to that of the corresponding *ams* in Figure 2.

ences between **3** and **4** (**6** and **7**) as well as between **3** and **6** (**4** and **7**) than the *ams* used for the reaction at high temperatures.

The transition states (TS) of the catalytic alkane dehydrogenation were investigated by density functional theory (DFT) techniques by using ethane and the anthrapphos iridium dihydride **8** (phosphorous substituents R = H) as models for the reaction.^[17–24] Although the B3LYP method generally produces excellent results, calculations by higher level ab initio methods, such as coupled cluster with single and double excitations (CCSD) suggest that B3LYP underestimates the stability of the higher oxidation states.^[25] Calibration of CCSD and DFT methods for Ir^V and Ir^{III} suggests that the BP86 functional produces energy differences closer to the more accurate CCSD methods.^[25] The final energies reported here are BP86 energies with zero point and thermal correction from the B3LYP frequency calculations.

Based on experimental and theoretical work^[6, 7, 13, 26] on the related pincer iridium dihydrides **3–5**, it is well established that the Ir^{III}(H)₂ complex exchanges the alkane (RH) and dihydrogen (H₂) to form an Ir^{III}(R)(H) complex, then transfers a β H to form the olefin complex Ir^{III}(R')(H)₂, and lastly releases the olefin (R') to reform the starting complex. However, the details of the formation of Ir^{III}(R)(H) from Ir^{III}(H)₂ and alkane (RH) are not completely clear. Scheme 2 shows three routes for this reaction: an associative process (A) through an Ir^V intermediate, an interchange process (I) through an (RH)/(H₂) exchange transition state, and a dissociative process (D) through an Ir^I intermediate.



Scheme 2. Alternative pathways investigated by DFT calculations for the model reaction of anthrapphos Ir(H)₂ **8** and ethane (RH): A: associative; I: interchange; D: dissociative.

For both model catalysts, the anthrapphos Ir(H)₂ **8** studied here and the previously investigated pincer Ir(H)₂ **5**, the route with the lowest internal energy (lowest barriers and most stable intermediates) passes through the associative path (A). However, an alternative dissociative path (D) would be favored at high temperatures because of its more favorable entropy.^[27]

As we began our investigation of the anthrapphos model catalyst **8** and examined the relative energies of the A and D paths, we discovered an unexpected TS for an interchange mechanism (I). The structure of this TS is shown in Figure 4. The most difficult step, highest ΔG[‡], on the alternative paths (A and D) involves oxidative addition of the alkane (RH) to Ir^{III}(H)₂ and Ir^I respectively. Between room temperature (298 K) and 523 K, the TS for the I path has a lower free

- [6] a) C. M. Jensen, S. Nemeh, W. C. Kaska, presented at the 1980 Biennial Inorganic Chemistry Symposium, (Guelph, Ontario, Canada), **1980**; b) S. Nemeh, C. Jensen, E. Binamira-Soriaga, W. C. Kaska, *Organometallics* **1983**, *2*, 1442–1447; c) M. Gupta, C. Hagen, W. C. Kaska, R. E. Cramer, C. M. Jensen, *J. Am. Chem. Soc.* **1997**, *119*, 840–841.
- [7] C. M. Jensen, *Chem. Commun.* **1999**, 2443–2449, and refs. therein.
- [8] “Anthraphos” has previously been used to refer to the chiral ligand *trans*-11,12-bis(diphenylphosphino)-9,10-dihydro-9,10-ethanoanthracene: a) T. Y. Fu, Z. Liu, J. R. Scheffer, J. Trotter, *Tetrahedron Lett.* **1994**, *35*, 7593–7596; b) T. Y. Fu, Z. Liu, S. T. Rettig, J. R. Scheffer, J. Trotter, *Acta Crystallogr. Sect. C* **1997**, *53*, 1577–1579. We thank Prof. J. R. Scheffer for the permission to reuse this name.
- [9] a) M. W. Haenel, D. Jakubik, C. Krüger, P. Betz, *Chem. Ber.* **1991**, *124*, 333–336; b) M. W. Haenel, S. Oevers, J. Bruckmann, J. Kuhnigk, C. Krüger, *Synlett* **1998**, 301–303.
- [10] *t*Bu₂PSiMe₃^[11] with *t*BuOK in analogy to: F. Uhlig, R. Hummelt, *J. Organomet. Chem.* **1993**, *452*, C9–C10.
- [11] *t*Bu₂PSiMe₃: H. Schumann, L. Rösch, *Chem. Ber.* **1974**, *107*, 854–868. Alternatively it was prepared from *t*Bu₂PH in THF by consecutive addition of *n*BuLi in hexane and Me₃SiCl.
- [12] In cyclododecane (b.p. 250 °C) the ring strain of 2.4 kcal mol^{−1} is much lower than in cyclodecane (12.0 kcal mol^{−1}) or cyclooctane (10.0 kcal mol^{−1}) which frequently are used as test substrate for catalytic dehydrogenations. The enthalpy of about 33 kcal mol^{−1} necessary to dehydrogenate alkanes to alkenes and hydrogen is reduced by relief of ring strain.
- [13] a) W.-W. Xu, G. P. Rosini, M. Gupta, C. M. Jensen, W. C. Kaska, K. Krogh-Jespersen, A. S. Goldman, *Chem. Commun.* **1997**, 2273–2274; b) F. Liu, A. S. Goldman, *Chem. Commun.* **1999**, 655–656.
- [14] M. T. Reetz, G. Haderlein, K. Angermund, *J. Am. Chem. Soc.* **2000**, *122*, 996–997.
- [15] Computations were carried out using a Silicon Graphics Octane workstation and the modeling software SYBYL 6.7 (Tripos Assoc., St. Louis, USA, **2001**). Important parameters for the *ams* calculation: geometries of the catalyst fragments without the phosphorus and iridium substituents are based on X-ray structures of **3**^[6c] and of the IrCl₃ complex of **9** (C. W. Lehmann, M.-A. Schneider, S. Oevers, W. C. Kaska, M. W. Haenel, unpublished results). Systematic search about the P–C_{alkyl} bonds with 5° and the C_{alkyl}–C_{methyl} bonds with 30° (**3**, **6**) or 60° (**4**, **7**) torsion angle increments. All conformations with *E* < 3 kcal mol^{−1} (force field: TAFF, no charges) higher than the energy minimum are superimposed according to Figure 2, forming a “super-molecular” fragment. The *ams* was determined using Connolly’s method^[16] analogous to the previously published procedure^[14] by “rolling” a sphere of 1.8 Å diameter over the Ir part of the molecular surface of these super-molecular fragments.
- [16] M. L. Connolly, *Science* **1983**, *221*, 709–713.
- [17] Computational Details: All of the calculations were carried out by using DFT^[18] with either B3LYP or BP86^[19, 20, 21] as implemented in Gaussian 98.^[22] TS are confirmed by separated frequency calculations. The Ir basis set was a modified LANL2DZ basis.^[23] For the P atoms, the LANL2DZ basis set was augmented by a d-type polarization function.^[23b, 24] The carbon and hydrogen atoms bonded to Ir and those in ethane, ethene, and dihydrogen were described by the Dunning–Huzinaga double-zeta basis sets with polarization functions (D95*), while STO-3G was used for the uncoordinated carbon and hydrogen atoms in the ligand of **8**.
- [18] R. G. Parr, W. Yang, *Density-functional theory of atoms and molecules*, Oxford University Press, Oxford, **1989**.
- [19] a) A. D. Becke, *Phys. Rev.* **1988**, *A38*, 3098–3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [20] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785–789.
- [21] J. P. Perdew, *Phys. Rev.* **1986**, *B33*, 8822–8824.
- [22] Gaussian 98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [23] a) LANL2DZ basis set is Dunning D95 basis sets on the first row, Los Alamos ECP plus double-zeta basis sets on Na–Bi; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310; c) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284–298; d) M. Couty, M. B. Hall, *J. Comput. Chem.* **1996**, *17*, 1359–1370.
- [24] A. Hollwarth, M. Bohme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 237–240.
- [25] H.-J. Fan, E. Webster, M. B. Hall, unpublished results.
- [26] a) S. Niu, M. B. Hall, *J. Am. Chem. Soc.* **1999**, *121*, 3992–3999; b) S. Li, M. B. Hall, *Organometallics* **2001**, *20*, 2153–2160; c) S. Li, M. B. Hall, *Organometallics* **2001**, *20*, 3210; d) M. Kanzelberger, B. Singh, M. Czerw, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2000**, *122*, 11017–11018.
- [27] K. Krogh-Jespersen, M. Czerw, M. Kanzelberger, A. S. Goldman, *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 56–63.

Nickel-Catalyzed Homoallylation of Aldehydes in the Presence of Water and Alcohols**

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By virtue of their high polarity, a wide variety of allylic metal and metalloid (e.g., B, Si, Sn) complexes can serve as nucleophilic reagents toward carbonyl compounds;^[1] some allylations can be successfully performed even in the presence of water under Barbier conditions.^[2] On the other hand, because of their low polarity, the homoallylic metals that are capable of undergoing a nucleophilic addition reaction are likely to be limited to some electropositive main group metals (e.g., Li, Mg).^[3] Accordingly, reactions with these homoallylic metals should be performed with care under strictly water-free conditions and could be applied effectively to those compounds that do not possess an acidic hydrogen.

Here, we disclose that even in the presence of water and alcohols, nickel complexes serve as a catalyst to promote homoallylation of aldehydes with 1,3-dienes. The reaction proceeds under essentially the same conditions as those reported recently from these laboratories for a nickel-catalyzed homoallylation of carbonyl compounds with dienes in the presence of a stoichiometric amount of Et₃B.^[4–6] These two reactions, that is, in the presence and in the absence of water, provide bishomoallyl alcohols in comparable yields

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