DOI: 10.1002/ange.200502905

Tetraphenylborate as a Novel Bridging Ligand in a Zwitterionic Nickel(I) Dimer**

*Yaofeng Chen, Christine Sui-Seng, and Davit Zargarian**

Heterolytic abstraction of anionic ligands such as halides or alkyl substituents can convert coordinatively saturated organometallic complexes into highly electrophilic, usually transient, cationic species that can serve as efficient initiators in various catalytic reactions. This strategy has been used in the development of many catalytic processes based on (quasi) square-planar d^8 metal precursors, including the recently reported systems for olefin polymerization reactions.[1]

In this context, we have shown that abstraction of Cl^- from the complexes [(R-ind)Ni(PPh_3)Cl] (R-ind = indenyl and its substituted derivatives)[2] leads to the generation of a transient species (presumed to be $[(R\text{-ind})Ni(PPh_3)]^+$) that reacts with excess substrate to promote the oligomerization or polymerization of various olefins,[3] $PhC{\equiv}CH$,[4] and $PhSiH_3$,[5] or catalyzes the hydrosilylation of olefins and ketones[6]

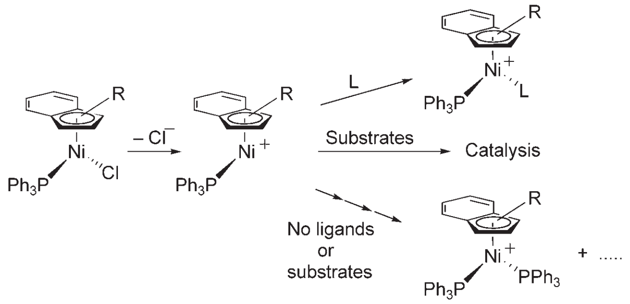
---

[*] Dr. Y. Chen, C. Sui-Seng, Prof. D. Zargarian
Département de Chimie
Université de Montréal
Montréal, PQ H3C3J7 (Canada)
Fax: (+1) 514-343-2468
E-mail: zargarian.davit@umontreal.ca

[**] The authors gratefully acknowledge NSERC of Canada for financial support of this study and Profs. F. Schaper and D. Gusev for many useful discussions.

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

(Scheme 1). We have also shown that abstraction of Cl$^-$ in the presence of suitable ligands L gives [(R-ind)Ni(PPh$_3$)L]$^+$ (L = PR′$_3$; R″CN, *t*BuNC).[3a,4c,5d] If, on the other hand, Cl$^-$ is abstracted in the absence of sufficiently strong coordinating ligands or substrates, we obtain [(R-ind)Ni(PPh$_3$)$_2$]$^+$ in low yields.[3a] Varying amounts of the latter species also form during the above-noted catalytic reactions, thus resulting in lower catalytic activities.



Scheme 1. Reaction pathways following abstraction of Cl$^-$ from the complexes [(R-ind)Ni(PPh$_3$)Cl].

In the search for a strategy to circumvent this built-in deactivation pathway, we set out to determine whether placing sterically bulky substituents on the ind ligands might prevent the formation of [(R-ind)Ni(PPh$_3$)$_2$]$^+$ during catalysis. An initial study showed that the catalytic activities of [(R-ind)Ni(PPh$_3$)Cl] for the hydrosilylation of styrene do increase with more bulky ind ligands (1-Me-ind < 1-SiMe$_3$-ind < 1,3-(SiMe$_3$)$_2$-ind).[7] To answer this question more directly, we have studied the abstraction of Cl$^-$ from [(1-SiMe$_3$-3-R-ind)Ni(PPh$_3$)Cl] (R = H, **1**; SiMe$_3$, **2**) and report our findings herein.

Treatment of **1** with NaBPh$_4$ gave an initial product whose NMR spectra are consistent with the formation of [(1-SiMe$_3$-ind)Ni(PPh$_3$)$_2$][BPh$_4$],[8] although the ready decomposition of this new species prevented its isolation and full characterization. It appears, therefore, that the presence of one SiMe$_3$ substituent on ind destabilizes the bis(phosphane) complex but does not block its formation. In contrast, treatment of **2** with NaBPh$_4$ gave a product that was stable and isolable, but whose spectral features were not those of a bis(phosphane) cation. For instance, the ^{31}P{^{1}H} NMR spectrum of this product displays an A$_2$X system with a doublet at around $\delta = 22$ ppm and a triplet at around $\delta = 126$ ppm ($J_{\mathrm{P,P}} = 35$ Hz), while the ^{1}H and ^{13}C NMR spectra contain many signals in regions typical of phenyl groups (^{1}H: $\delta = 6.5$–7.3 ppm; ^{13}C: $\delta = 122$–138 ppm) in addition to a few peaks farther upfield (^{1}H: $\delta = 5.5$–5.9 ppm; ^{13}C: $\delta = 86$–102 ppm). Significantly, the signals expected for the (SiMe$_3$)$_2$-ind moiety were absent from the latter spectra. In a search for clues regarding the fate of this moiety, we analyzed the reaction mixture by GC-MS and ^{1}H NMR spectroscopy, which enabled the detection of 3-phenyl-1,1-bis(trimethylsilyl)indene.

These spectral analyses did not, however, allow an unambiguous characterization of the main product, but X-ray diffraction analysis of single crystals obtained from repeated recrystallizations allowed us to identify it as **3**, which is a dinuclear zwitterion composed of two (PPh$_3$)Ni$^{\mathrm{I}}$ cations bridged by the anions μ-[PPh$_2$]$^-$ and *syn*,μ-[(η^2:η^2-Ph)BPh$_3$]$^-$ (Figure 1). The main features of this crystal structure are consistent with the solution spectra: the A$_2$X signals observed in the ^{31}P NMR spectrum of **3** can be assigned to a μ-PPh$_2$ and two PPh$_3$ moieties,[9] while the upfield signals in the ^{1}H and ^{13}C NMR spectra can be assigned to the (η^2:η^2-Ph)BPh$_3$ moiety.

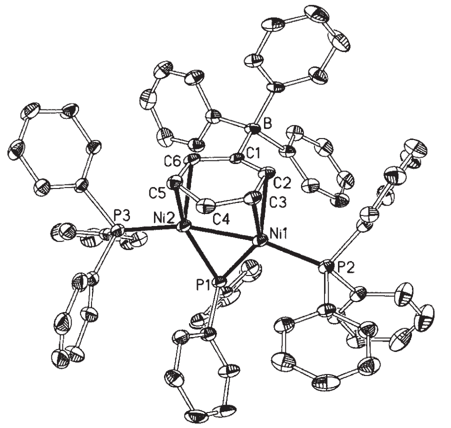
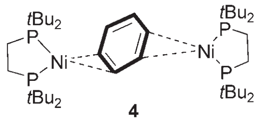


Figure 1. ORTEP view of **3**. Thermal ellipsoids are shown at the 30% probability level. Selected distances [Å] and angles [°]: Ni1-Ni2 2.4471(11), Ni1-P1 2.1397(16), Ni2-P1 2.1395(13), Ni1-P2 2.2055(15), Ni2-P3 2.1841(16), Ni1-C1 2.670(4), Ni1-C2 2.120(4), Ni1-C3 2.094(4), Ni1-C4 2.617(4), Ni2-C1 2.666(5), Ni2-C4 2.522(5), Ni2-C5 2.075(5), Ni2-C6 2.125(5), C1-C2 1.421(6), C2-C3 1.415(6), C3-C4 1.396(6), C4-C5 1.392(6), C5-C6 1.415(6), C6-C1 1.414(6); P1-Ni1-P2 116.27(6), P1-Ni2-P3 110.98(6), P2-Ni1-Ni2 168.82(5), P3-Ni2-Ni1 165.66(5), Ni2-P1-Ni1 69.76(5), P1-Ni1-Ni2 55.12(4), P1-Ni2-Ni1 55.12(4).

The most notable structural feature of **3** is the novel bonding mode of the borate moiety: although there are many precedents for complexes featuring [(η$^{2-6}$-Ph)$_n$BPh$_{4-n}$]$^-$,[10,11] the formation of a complex in which one of the Ph groups bridges two metals is without precedent.[12] Interestingly, the synfacially coordinated μ-PhBPh$_3$ moiety interacts with the two NiL$_2$ moieties through two nonadjacent double bonds from opposite edges of the μ-arene ring, i.e., C2−C3 and C5−C6. We propose that this unusual bonding mode[13] minimizes the steric interactions between the Ph groups on the PPh$_3$ ligands and the borate moiety in **3**.[14]

A more complete picture of the bonding in the Ni$_2$-[μ,η^2,η^2-PhBPh$_3$] moiety emerges from a careful inspection of the individual Ni−C distances, which show that the μ-Ph ring straddles the Ni–Ni axis and is somewhat tilted, giving the following unsymmetrical Ni−C interactions: Ni1−C2 > Ni1−C3; Ni2−C6 > Ni2−C5; Ni(1/2)−C1 > Ni(1/2)−C4. Interestingly, these interactions result in only minor and more or less uniform lengthening of the C−C bond lengths within the μ-Ph ring (1.39–1.42 Å), although the dihedral angle of about 15° between the planes (C1,C2,C3,C4) and (C1,C6,C5,C4) signals a relatively significant butterfly distortion of the ring.[15,16]

It is instructive to compare the unusual Ni–arene interactions found in **3** to those in complex **4**[17], which is a rare

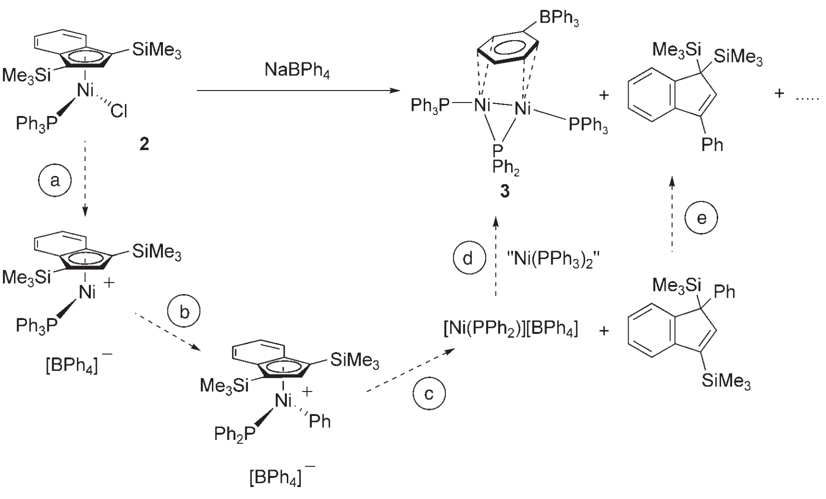


4

Ni_2(μ-arene) species.[18] In contrast to **3**, the $Ni_2(\mu\text{-}C_6H_6)$ interactions in **4** are antifacial and involve two adjacent double bonds, i.e., a 1,3-diene moiety. Furthermore, the Ni–C distances are significantly shorter in **4** (ca. 2.00–2.02 vs. 2.10 Å in **3**), which is presumably due to greater backbonding possible in the Ni^0 complex. It should be noted, however, that the interactions of the Ni centers in **3** with (μ-$PhBPh_3$) are reinforced by the electrostatic attractions within this zwitterionic compound. Accordingly, the arene moiety in **3** cannot be displaced by aromatic solvents, even when heated for extended periods.

The structural parameters discussed above are consistent with a simple bonding picture involving the contribution of two pairs of electrons from $[(\mu,\eta^2,\eta^2\text{-Ph})BPh_3]^-$; when the Ni–Ni bond is taken into consideration,[19] each Ni center ends up with a total of 16 valence electrons. This is in agreement with the conclusions of a theoretical analysis[20] showing that the analogous fragment $[\{(PH_3)Pd\}_2(\mu\text{-Br})]^+$ has only two low-lying vacant orbitals of appropriate symmetry to interact with the two HOMO orbitals of a (μ-C_6H_6) ligand.

The unexpected formation of **3** from **2** raises the question of how this transformation might take place. Although definitive conclusions regarding the reaction mechanism must await further experimental evidence, the sequence of steps shown in Scheme 2 serves to rationalize the conversion of **2** into **3**. The proposed addition of a P–Ph bond (step b) is well known;[21] indeed, a particularly relevant example of such P–C bond activation has been observed during the formation of $[Pd_2(tBu_2PH)_2(\mu\text{-}tBu_2P)(\mu\text{-}C_6H_5O)]$, which is a closely related, isoelectronic analogue of **3**.[22] The reductive elimination from a Ni^{IV} intermediate (step c) is also quite reasonable, as is the rearrangement of the initially formed 1-phenyl-1,3-bis(trimethysilyl)indene to the observed 3-phenyl-1,3-bis(trimethysilyl)indene isomer by a silyl migration (step e).[23] Finally, comproportionation of Ni^{II} and Ni^0 species to give Ni^I dimers (step d) has been reported,[24] although the origin of the putative "$Ni^0(PPh_3)_2$" fragment is not known at this point.



Scheme 2. Suggested pathway for the conversion of **2** into **3**.

We conclude that the greater steric bulk in $[\{(SiMe_3)_n\text{-ind}\}Ni(PPh_3)Cl]$ indeed hinders the generation of the cationic bis(phosphane) side-products that form with less bulky analogues, and this might contribute to the observed increase in the catalytic reactivity of these complexes.[7] On the other hand, the presence of $SiMe_3$ substituents on ind also opens a new decomposition pathway that, in the case of the 1,3-$(SiMe_3)_2$-ind derivative **2**, results in the formation of the Ni^I dimer **3**. The observation of a $[(\mu,\eta^2,\eta^2\text{-Ph})BPh_3]^-$ ligand in **3** expands the range of coordination modes that should be taken into account when contemplating the use of BPh_4^- and its various analogues as weakly coordinating counterions. Preliminary experiments have shown that **3** does not react with $PhSiH_3$ or styrene, thus implying that this compound is not involved in the hydrosilylation catalysis promoted by its precursor. In view of the interesting catalytic reactivities exhibited by some Pd^I–Pd^I dimers,[25] however, future studies are planned to probe the reactivities of **3** towards other substrates.

Experimental Section

A slurry of $[\{1,3\text{-}(SiMe_3)_2\text{-ind}\}Ni(PPh_3)Cl]$ (191 mg, 310 μmol) and $Na[BPh_4]$ (113 mg, 330 μmol) was stirred in Et_2O (20 mL) at room temperature for two days. The reaction mixture was then filtered and the solid residues extracted with CH_2Cl_2 (total volume ca. 15 mL). (Analysis of the filtrate is described below.) Concentration of the extracts to about 2 mL and layering with hexane (ca. 5 mL) resulted in the formation of dark-brown crystals overnight, which were isolated, washed quickly with acetone, and dried under vacuum to give **3** (30 mg, 25% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.33$–6.50 (m, 55H; Ph-H), 5.92 (brs, 2H; benzene-$H^{2,6/3,5}$), 5,79 (brs, 1H; benzene-H^4), 5.52 ppm (brs, 2H; benzene-$H^{2,6/3,5}$); $^{13}C\{^1H\}$ NMR (100.56 MHz, $CDCl_3$, 25 °C): $\delta = 138.5$, 136.1, 135.6, 134.8, 133.3, 132.1, 129.5, 127.1, 125.8, 122.3, 102.6, 97.1, 86.2 ppm; $^{31}P\{^1H\}$ NMR (161.92 MHz, $CDCl_3$, 25 °C): $\delta = 126.5$ (t, $^2J_{P,P} = 35$ Hz), 22.3 ppm (d, $^2J_{P,P} = 35$ Hz); elemental analysis calcd (%) for $C_{72}H_{60}BP_3Ni_2$: C 75.44, H 5.28; found: C 74.70, H 5.25.

Crystal data for **3**: monoclinic ($P2_1/n$); $a = 18.6631(6)$, $b = 13.5095(5)$, $c = 25.0944(9)$ Å; $\beta = 110.350(2)°$; $V = 5932.1(4)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.283\ g\,cm^{-1}$; Bruker AXS diffractometer; $\mu = 1.869\ mm^{-1}$, $\lambda = 1.54178$ Å ($Cu_{K\alpha}$); ω scan, $\theta_{max} = 60.13°$; temperature: 223(2) K; h,k,l range: $-20 \leq h \leq 20$; $-14 \leq k \leq 15$; $-28 \leq l \leq 27$; 5072 reflections used ($I > 2\sigma(I)$); absorption correction multiscan SADABS; $R(F^2 > (2\sigma F^2))$, $wR(F^2)$: 0.0591, 0.1336; GOF: 0.929. CCDC-279748 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Analytical data for the filtrate from the reaction mixture: MS: m/z: 336 $[M]^+$, 321 $[M{-}\mathrm{CH_3}]^+$, 263 $[M{-}\mathrm{SiMe_3}]^+$, 248 $[M{-}\mathrm{SiMe_3}{-}\mathrm{CH_3}]^+$, 233 $[M{-}\mathrm{SiMe_3}{-}2\,\mathrm{CH_3}]^+$, 218 $[M{-}\mathrm{SiMe_3}{-}3\,\mathrm{CH_3}]^+$, 73 $[\mathrm{SiMe_3}]^+$; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 7.5$–6.9 (aromatic protons), 6.74 (s, H2 of the indenyl ring), -0.03 ppm (s, $\mathrm{SiMe_3}$).

Received: August 16, 2005

Keywords: bridging ligands · chloride abstraction · nickel · P ligands · zwitterions

---

[1] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283.

[2] D. Zargarian, *Coord. Chem. Rev.* **2002**, *233–234*, 157.

[3] a) R. Vollmerhaus, F. B. Gariépy, D. Zargarian, *Organometallics* **1997**, *16*, 4762; b) M.-A. Dubois, R. Wang, D. Zargarian, J. Tian, R. Vollmerhaus, Z. Li, S. Collins, *Organometallics* **2001**, *20*, 663; c) M.-A. Dubois, *MSc Dissertation*, Université de Montréal, **2000**.

[4] a) R. Wang, F. B. Gariépy, D. Zargarian, *Organometallics* **1999**, *18*, 5548; b) R. Wang, L. F. Groux, D. Zargarian, *J. Organomet. Chem.* **2002**, *660*, 98; c) R. Wang, L. F. Groux, D. Zargarian, *Organometallics* **2002**, *21*, 5531; d) E. Rivera, R. Wang, X. X. Zhu, D. Zargarian, R. Giasson, *J. Mol. Catal. A* **2003**, *204–205*, 325.

[5] a) F.-G. Fontaine, T. Kadkhodazadeh, D. Zargarian, *Chem. Commun.* **1998**, 1253–1254; b) F.-G. Fontaine, D. Zargarian, *Organometallics* **2002**, *21*, 401; c) F.-G. Fontaine, D. Zargarian, *J. Am. Chem. Soc.* **2004**, *126*, 8786; d) F.-G. Fontaine, *PhD Dissertation*, Université de Montréal, **2002**.

[6] F.-G. Fontaine, R.-V. Nguyen, D. Zargarian, *Can. J. Chem.* **2003**, *81*, 1299.

[7] Y. Chen, C. Sui-Seng, S. Boucher, D. Zargarian, *Organometallics* **2005**, *24*, 149.

[8] For example, the ^{31}P{^{1}H} NMR spectrum shows two very broad peaks at around $\delta = 30$ and 33 ppm (width at half-height approximately 400 Hz), which are assigned to the two inequivalent $\mathrm{PPh_3}$ groups that are in a dissociation/re-association equilibrium. The observation in the ^{1}H NMR spectrum of a significantly downfield-shifted signal for H3 (from $\delta = 3.5$ ppm in **1** to about $\delta = 5$ ppm in the product) is also consistent with the greater ind→Ni donation in such cationic species (ref. [2]). This spectrum also shows the anticipated signals for H2 and the aromatic protons at about $\delta = 6.5$–7.5 ppm, as well as an upfield singlet for the Si-$\mathrm{CH_3}$ protons at around $\delta = -0.12$ ppm.

[9] For comparison, the ^{31}P NMR signals of the μ-$\mathrm{PPh_2}$ moieties in $[(\mathrm{CNR})_2\mathrm{Ni_2}(\mu\text{-}\mathrm{PPh_2})_2(\mu\text{-}\mathrm{Ph_2PNHPPh_2})_2]$ (E. Simón-Manso, C. P. Kubiak, *Inorg. Chem. Commun.* **2003**, *6*, 1096) and $[\mathrm{Fe_2(CO)_6}(\mu\text{-}\mathrm{PPh_2})_2]$ (E. P. Kyba, R. E. Davis, C. N. Clubb, S.-T. Liu, H. O. A. Palacios, J. S. McKennis, *Organometallics* **1986**, *5*, 869) are found at around $\delta = 190$ and 143 ppm, respectively. On the other hand, the general range for the ^{31}P NMR signal of a $\mathrm{PPh_3}$ coordinated to Ni is $\delta = 25$–50 ppm.

[10] The main coordination modes of $\mathrm{BPh_4}^-$ and its derivatives have been reviewed: a) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927; b) M. Bochmann, *Angew. Chem.* **1992**, *104*, 1206; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1181.

[11] For examples of the various coordination modes encountered in complexes bearing $\mathrm{BPh_4}^-$ fragments, see: η^6-coordination: a) D. C. Ware, M. M. Olmstead, R. Wang, T. Henry, *Inorg. Chem.* **1996**, *35*, 2576; b) R. F. Winter, F. M. Hornung, *Inorg. Chem.* **1997**, *36*, 6197; c) M. Manger, J. Wolf, M. Laubender, M. Teichert, D. Stalke, H. Werner, *Chem. Eur. J.* **1997**, *3*, 1442; d) H. Werner, M. Manger, U. Schmidt, M. Laubender, B. Weberndoerfer, *Organometallics* **1998**, *17*, 2619; e) F. Torres, E. Sola, M. Martin, C. Ochs, G. Picazo, J. A. Lopez, F. J. Lahoz, L. A. Oro, *Organometallics* **2001**, *20*, 2716; η^2-coordination: f) M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, *Inorg. Chem.* **1980**, *19*, 1191; g) A. D. Horton, J. H. G. Frijns, *Angew. Chem.* **1991**, *103*, 1181; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1152; h) W. J. Evans, C. A. Seibel, J. W. Ziller, *J. Am. Chem. Soc.* **1998**, *120*, 6745; η^1-, η^2-, and η^4-coordination: i) G. B. Deacon, C. M. Forsyth, *Chem. Commun.* **2002**, 2522.

[12] Multiple searches of the CCSD (up to August 6, 2005) did not lead to any complex in which one of the Ph rings of $\mathrm{BPh_4}^-$ is coordinated to two or more metal centers. These searches also indicated that complex **3** is the first instance of a Ni complex bearing a coordinated $[\mathrm{PhBPh_3}]^-$.

[13] The following complexes featuring μ(η^2:η^2)-arene ligands coordinated through nonadjacent C=C bonds have been reported: a) $[\{(t\mathrm{Bu_3SiO})_3\mathrm{Ta}\}_2(\mu,\eta^2{:}\eta^2\text{-}\mathrm{C_6H_6})]$ (D. R. Neithamer, L. Párkányi, J. F. Mitchell, P. T. Wolczanski, *J. Am. Chem. Soc.* **1988**, *110*, 4421); b) $\{\mathrm{AgN(SO_2F)_2(C_6H_6)}\}_n$ (M. J. Begley, D. B. Sowerby, R. D. Verma, A. Vig, *J. Organomet. Chem.* **1994**, *481*, 243); c) $[\{\mathrm{Fe(CO)_3}\}_2\{\mu,\eta^2{:}\eta^2\text{-}1,4\text{-}(\mathrm{CH_2NPh})_2\text{-}3,6\text{-}\eta^1,\eta^1\text{-}\{\mathrm{Fe(CO)_3}\}_2\text{-}\mathrm{C_6H_2}\}]$ (W. Imhof, A. Göbel, *J. Organomet. Chem.* **2000**, *610*, 102); d) $[\mathrm{Pd_2(GaBr_4)_2}\{\mu(\eta^2{:}\eta^2\text{-arene})\}_2]$ (M. Gorlov, A. Fischer, L. Kloo, *J. Organomet. Chem.* **2004**, *689*, 489).

[14] Structural simulations have shown that rotating the borate anion in such a way as to orient a 1,3-diene moiety of the μ-$\mathrm{PhBPh_3}$ ligand towards the Ni atoms results in significant steric interactions between the Ph groups of the $\mathrm{PPh_3}$ ligand and the borate anion. The authors are grateful to Prof. F. Schaper for carrying out these simulations.

[15] For comparison, values of about 20° and 43° have been reported for the corresponding fold angles in the complexes $[\mathrm{Cp_2V_2}(\mu\text{-H})_2(\mu\text{-Ph})]$ (K. Jonas, V. Wiskamp, Y.-H. Tsay, C. Krüger, *J. Am. Chem. Soc.* **1983**, *105*, 5480) and $[\mathrm{Cp_2Fe_2}(\mu\text{-}\mathrm{C_6R_6})]$ (K. Jonas, G. Koepe, L. Schieferstein, R. Mynott, C. Krüger, Y.-H. Tsay, *Angew. Chem.* **1983**, *95*, 637; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 620).

[16] For a comprehensive review on the various bonding modes observed in μ-arene complexes, see: H. Wadepohl, *Angew. Chem.* **1992**, *104*, 253; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 247.

[17] I. Bach, K.-R. Pörschke, R. Goddard, C. Kopiske, C. Krüger, A. Rufinska, K. Seevogel, *Organometallics* **1996**, *15*, 4959.

[18] To our knowledge, the only other μ-arene complexes of Ni for which structural data are available are triple-decker complexes that involve, respectively, η^6- and η^3:η^3-arene ligands: a) J. L. Priego, L. H. Doerrer, L. H. Rees, M. L. H. Green, *Chem. Commun.* **2000**, 779; b) J. J. Schneider, D. Spickermann, D. Bläser, R. Boese, P. Rademacher, T. Labahn, J. Magull, C. Janiak, N. Seidel, K. Jacob, *Eur. J. Inorg. Chem.* **2001**, 1371; for the structure of a Ni dimer bridged by a novel benzdiyne ligand, (μ-$\mathrm{C_6H_2}$), see: M. A. Bennett, J. S. Drage, K. D. Griffiths, N. K. Roberts, G. B. Robertson, W. A. Wickramasinghe, *Angew. Chem.* **1988**, *100*, 1002; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 941.

[19] The Ni–Ni bond length of 2.4471(11) Å in **3** is within the expected range of 2.30–2.50 Å found in related Ni$^{\mathrm{I}}$–Ni$^{\mathrm{I}}$ dimers: a) B. L. Barnett, C. Krüger, Y. H. Tsay, *Chem. Ber.* **1977**, *110*, 3900; b) R. A. Jones, A. L. Stuart, J. L. Atwood, W. E. Hunter, R. D. Rogers, *Organometallics* **1982**, *1*, 1721; c) R. Hanko, *Angew. Chem.* **1985**, *97*, 707; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 704; d) M. J. Tenorio, M. C. Puerta, P. Valerga, *J. Chem. Soc. Dalton Trans.* **1996**, 1305; e) M. D. Fryzuk, G. K. B. Clentsmith, D. B. Leznoff, S. J. Rettig, S. J. Geiib, *Inorg. Chim. Acta* **1997**, *265*, 169–177; f) C. E. Kriley, C. J. Woolley, M. K. Krepps, E. M. Popa, P. E. Fanwick, I. P. Rothwell, *Inorg. Chim. Acta* **2000**, *300–302*, 200.

[20] L. Zhu, N. M. Kostic, *Organometallics* **1988**, *7*, 665.

[21] a) D. R. Fahey, J. E. Mahan, *J. Am. Chem. Soc.* **1976**, *98*, 4499; b) P. E. Garrou, *Chem. Rev.* **1985**, *85*, 171; c) R. A. Dubois, P. E. Garrou, *Organometallics* **1989**, *8*, 466; d) H. Omori, H. Suzuki, Y. Take, Y. Moro-oka, *Organometallics* **1989**, *8*, 2270.

[22] M. Sommovigo, M. Pasquali, P. Leoni, D. Braga, P. Sabatino, *Chem. Ber.* **1991**, *124*, 97.

[23] For a discussion of this type of rearrangements in indenes, see: a) M. Stradiotto, P. Hazendonk, A. D. Bain, M. A. Brook, M. J. McGlinchey, *Organometallics* **2000**, *19*, 590; b) M. Stradiotto, M. J. McGlinchey, *Coord. Chem. Rev.* **2001**, *219–221*, 311.

[24] For an example of a Ni^I–Ni^I dimer formed from the reaction of Ni^0 and Ni^{II} precursors, see ref. [19c]. For the analogous formation of Pd^I–Pd^I dimers, see: T. Murahashi, H. Kurosawa, *Coord. Chem. Rev.* **2002**, *231*, 207.

[25] a) J. P. Stambouli, R. Kuwano, J. F. Hartwig, *Angew. Chem.* **2002**, *114*, 4940; *Angew. Chem. Int. Ed.* **2002**, *41*, 4746; b) M. Prashad, X. Y. Mak, Y. Liu, O. Repic, *J. Org. Chem.* **2003**, *68*, 1163; c) U. Christmann, R. Vilar, A. J. P. White, D. J. Williams, *Chem. Commun.* **2004**, 1294.