

Cationic Ni_2 Fragment

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

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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 $[(\text{R-ind})\text{Ni}(\text{PPh}_3)\text{Cl}]$ (R-ind = indenyl and its substituted derivatives)^[2] leads to the generation of a transient species (presumed to be $[(\text{R-ind})\text{Ni}(\text{PPh}_3)]^+$) that reacts with excess substrate to promote the oligomerization or polymerization of various olefins,^[3] $\text{PhC}\equiv\text{CH}$,^[4] and PhSiH_3 ,^[5] or catalyzes the hydrosilylation of olefins and ketones^[6]

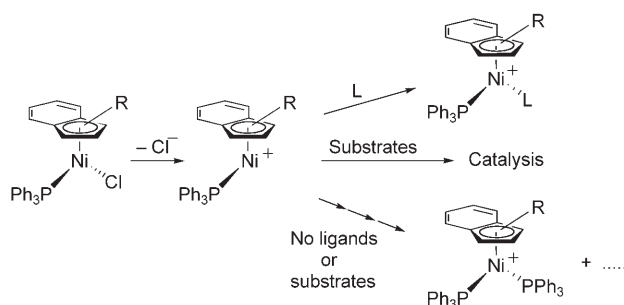
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(Scheme 1). We have also shown that abstraction of Cl^- in the presence of suitable ligands L gives $[(\text{R-ind})\text{Ni}(\text{PPh}_3)\text{L}]^+$ ($\text{L} = \text{PR}'_3$; $\text{R}''\text{CN}$, $t\text{BuNC}$).^[3a,4c,5d] If, on the other hand, Cl^- is



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

abstracted in the absence of sufficiently strong coordinating ligands or substrates, we obtain $[(\text{R-ind})\text{Ni}(\text{PPh}_3)_2]^+$ in low yields.^[3a] Varying amounts of the latter species also form during the above-noted catalytic reactions, thus resulting in lower catalytic activities.

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 $[(\text{R-ind})\text{Ni}(\text{PPh}_3)_2]^+$ during catalysis. An initial study showed that the catalytic activities of $[(\text{R-ind})\text{Ni}(\text{PPh}_3)\text{Cl}]$ for the hydrosilylation of styrene do increase with more bulky ind ligands ($1\text{-Me-ind} < 1\text{-SiMe}_3\text{-ind} < 1,3\text{-(SiMe}_3)_2\text{-ind}$).^[7] To answer this question more directly, we have studied the abstraction of Cl^- from $[(1\text{-SiMe}_3\text{-3-R-ind})\text{Ni}(\text{PPh}_3)\text{Cl}]$ ($\text{R} = \text{H}$, **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 $[(1\text{-SiMe}_3\text{-ind})\text{Ni}(\text{PPh}_3)_2][\text{BPh}_4]$,^[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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this product displays an A_2X system with a doublet at around $\delta = 22$ ppm and a triplet at around $\delta = 126$ ppm ($J_{\text{PP}} = 35$ Hz), while the ^1H and ^{13}C NMR spectra contain many signals in regions typical of phenyl groups (^1H : $\delta = 6.5\text{--}7.3$ ppm; ^{13}C : $\delta = 122\text{--}138$ ppm) in addition to a few peaks farther upfield (^1H : $\delta = 5.5\text{--}5.9$ ppm; ^{13}C : $\delta = 86\text{--}102$ ppm). Significantly, the signals expected for the $(\text{SiMe}_3)_2\text{-ind}$ 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 ^1H 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 $(\text{PPh}_3)\text{Ni}^+$ cations bridged by the anions $\mu\text{-[PPh}_2\text{]}^-$ and $\text{syn},\mu\text{-[(}\eta^2\text{:}\eta^2\text{-Ph)BPh}_3\text{]}^-$ (Figure 1). The main features of this crystal structure are consistent with the solution spectra: the A_2X signals observed in the ^{31}P NMR spectrum of **3** can be assigned to a $\mu\text{-PPh}_2$ and two PPh_3 moieties,^[9] while the upfield signals in the ^1H and ^{13}C NMR spectra can be assigned to the $(\eta^2\text{:}\eta^2\text{-Ph)BPh}_3$ moiety.

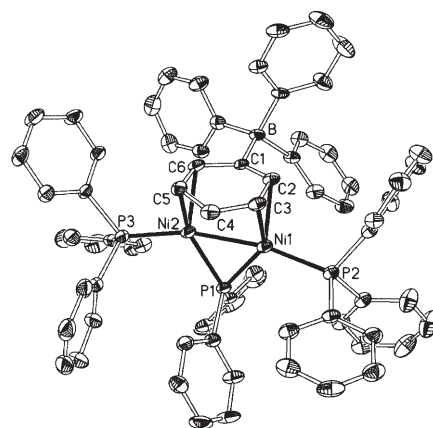
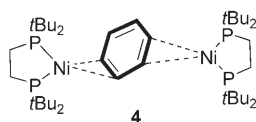


Figure 1. ORTEP view of **3**. Thermal ellipsoids are shown at the 30% probability level. Selected distances [Å] and angles [°]: Ni1–Ni2 2.4471(11), Ni1–P1 2.1397(16), Ni2–P1 2.1395(13), Ni1–P2 2.2055(15), Ni2–P3 2.1841(16), Ni1–C1 2.670(4), Ni1–C2 2.120(4), Ni1–C3 2.094(4), Ni1–C4 2.617(4), Ni2–C1 2.666(5), 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 $[(\eta^{2-6}\text{-Ph})_n\text{BPh}_{4-n}]^-$,^[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 $\mu\text{-PhBPh}_3$ moiety interacts with the two NiL_2 moieties through two nonadjacent double bonds from opposite edges of the $\mu\text{-arene}$ 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 $\text{Ni}_2\text{-}[\mu,\eta^2,\eta^2\text{-PhBPh}_3]$ moiety emerges from a careful inspection of the individual Ni–C distances, which show that the $\mu\text{-Ph}$ 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 $\mu\text{-Ph}$ 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]

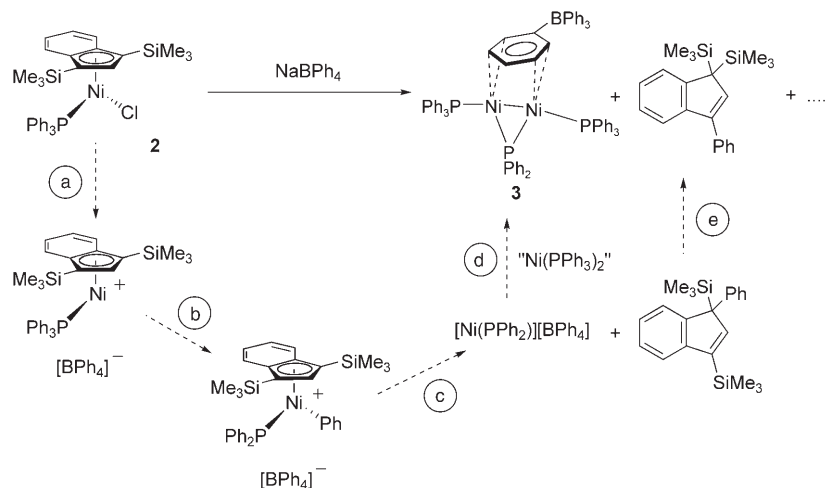
It is instructive to compare the unusual Ni–arene interactions found in **3** to those in complex **4**^[17], which is a rare



$\text{Ni}_2(\mu\text{-arene})$ species.^[18] In contrast to **3**, the $\text{Ni}_2(\mu\text{-C}_6\text{H}_6)$ interactions in **4** are antiferro 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 $(\mu\text{-PhBPh}_3)$ 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 $[(\mu, \eta^2, \eta^2\text{-Ph})\text{BPh}_3]^-$; 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 $[(\text{PPh}_3)_2\text{Pd}]_2(\mu\text{-Br})^+$ has only two low-lying vacant orbitals of appropriate symmetry to interact with the two HOMO orbitals of a $(\mu\text{-C}_6\text{H}_6)$ 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



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

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 $[\text{Pd}_2(\text{tBu}_2\text{PH})_2(\mu\text{-tBu}_2\text{P})(\mu\text{-C}_6\text{H}_5\text{O})]$, 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(trimethylsilyl)indene to the observed 3-phenyl-1,3-bis(trimethylsilyl)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 “ $\text{Ni}^0(\text{PPh}_3)_2$ ” fragment is not known at this point.

We conclude that the greater steric bulk in $[(\text{SiMe}_3)_n\text{-ind}]\text{Ni}(\text{PPh}_3)\text{Cl}$ 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- $(\text{SiMe}_3)_2$ -ind derivative **2**, results in the formation of the Ni^{I} dimer **3**. The observation of a $[(\mu, \eta^2, \eta^2\text{-Ph})\text{BPh}_3]^-$ 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 $\text{Pd}^{\text{I}}\text{--Pd}^{\text{I}}$ dimers,^[25] however, future studies are planned to probe the reactivities of **3** towards other substrates.

Experimental Section

A slurry of $[(1,3\text{-}(\text{SiMe}_3)_2\text{-ind})\text{Ni}(\text{PPh}_3)\text{Cl}]$ (191 mg, 310 μmol) and $\text{Na}[\text{BPh}_4]$ (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): δ = 7.33–6.50 (m, 55H; Ph-H), 5.92 (brs, 2H; benzene- $\text{H}^{2,6/3,5}$), 5.79 (brs, 1H; benzene- H^4), 5.52 ppm (brs, 2H; benzene- $\text{H}^{2,6/3,5}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.56 MHz, CDCl_3 , 25°C): δ = 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; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.92 MHz, CDCl_3 , 25°C): δ = 126.5 (t, $^2J_{\text{PP}} = 35$ Hz), 22.3 ppm (d, $^2J_{\text{PP}} = 35$ Hz); elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{60}\text{BP}_3\text{Ni}_2$: 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; β = 110.350(2)°; V = 5932.1(4) Å³; Z = 4; ρ_{calcd} = 1.283 g cm^{−3}; Bruker AXS diffractometer; μ = 1.869 mm^{−1}, λ = 1.54178 Å ($\text{CuK}\alpha$); ω scan, θ_{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 $[M-CH_3]^+$, 263 $[M-SiMe_3]^+$, 248 $[M-SiMe_3-CH_3]^+$, 233 $[M-SiMe_3-2CH_3]^+$, 218 $[M-SiMe_3-3CH_3]^+$, 73 $[SiMe_3]^+$; 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.5–6.9 (aromatic protons), 6.74 (s, H2 of the indenyl ring), –0.03 ppm (s, $SiMe_3$).

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