

Cationic Lanthanide Alkyl Complexes. Evidence for an Unprecedented Tetraphenylborate Coordination Mode in $\text{La}(\text{C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}\text{BPh}_4$

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Summary: Reaction of $\text{La}(\text{C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}_2$ (**1**) with $[\text{PhNMe}_2\text{H}]\text{BPh}_4$ affords zwitterionic $\text{La}(\text{C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}\text{BPh}_4$ (**2a**), which reacts irreversibly with THF to displace the coordinated tetraphenylborate and afford the first cationic lanthanide alkyl complex $[\text{La}(\text{C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}(\text{THF})_3]\text{BPh}_4$ (**3a**).

A combination of the highly unsaturated Lewis acidic metal center, the vacant coordination site, and the reactivity of the M-R' bond in the cationic complexes $[\text{M}(\text{C}_5\text{R}_6)_2\text{R}]^+$ (M = Zr, R = H;¹ M = Zr, R = Me;^{1d,2} M = Th, R = Me³) are believed to be prerequisites for their olefin polymerization activity. This increasing interest in cationic Ti,⁴ Zr,^{1,2,5} and Th³ chemistry is, in part, associated with the realization that an important prerequisite is also a "noncoordinating" anion. Evidence suggests, however, that tetraphenylborates are not necessarily innocuous. For example, η^1 -coordination⁶ of one phenyl ring has been proposed in $\text{Zr}(\text{CH}_2\text{Ph})_3(\eta^1\text{-C}_6\text{H}_5)\text{BPh}_3$ ^{6a} and $\text{Cp}'_2\text{ZrMe}(\text{BPh}_4)$,⁷ cyclometalation occurs to afford $(\text{C}_5\text{Me}_5)_2\text{Zr}^+(\text{m-C}_6\text{H}_4)\text{BPh}_3$,^{2a} and weak σ -Me coordination has been observed in $(\text{C}_5\text{Me}_5)_2\text{Zr}^+\text{Me}(\mu\text{-Me})\text{BPh}_3$.^{1d} We report here the first examples of cationic lanthanide alkyl species, as well as an unprecedented coordination mode of the tetraphenylborate anion.

Results and Discussion

In order to access the chemistry of analogous cationic lanthanide alkyl complexes, a synthetic requirement is a monocyclopentadienyl precursor. We have previously

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(6) The evidence presented for $\text{Zr}(\text{CH}_2\text{Ph})_3(\eta^1\text{-C}_6\text{H}_5)\text{BPh}_3$ ^{6a} suggests, but does not unambiguously establish, η^5 -phenyl group coordination. In $\text{Cp}'_2\text{ZrMe}(\text{BPh}_4)$,⁷ the NMR evidence is consistent with η^3 -phenyl coordination or with the rapid equilibration of two diastereomers with η^2 -coordinated phenyl rings. η^6 -coordination of one phenyl ring of BPh_4^- is not common in electron-rich Ru(II) and Rh(I) chemistry. Kruger, G. J.; DuPrez, A. L.; Haines, R. J. *J. Chem. Soc., Dalton Trans.* 1974, 1302 and references therein. Uson, R.; Lahuerta, P.; Reyes, J.; Oro, L. A.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S. *Inorg. Chim. Acta* 1980, 42, 75.

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Scheme I

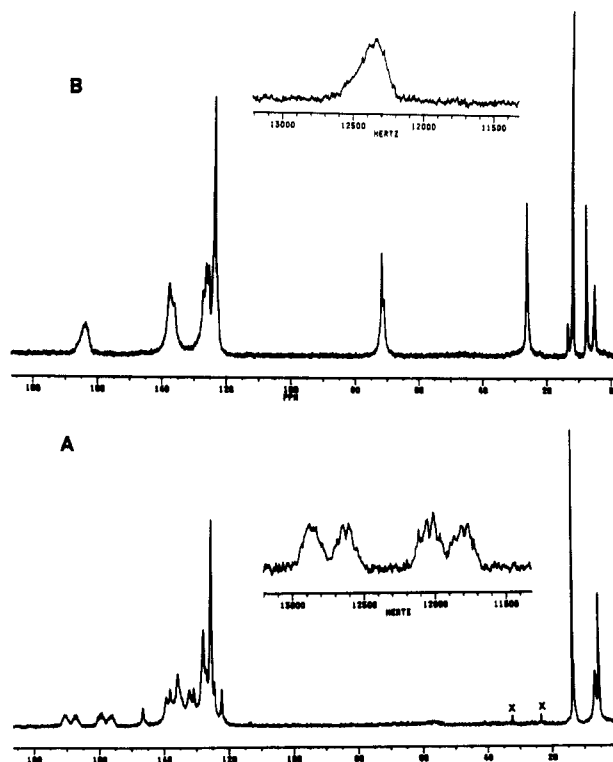
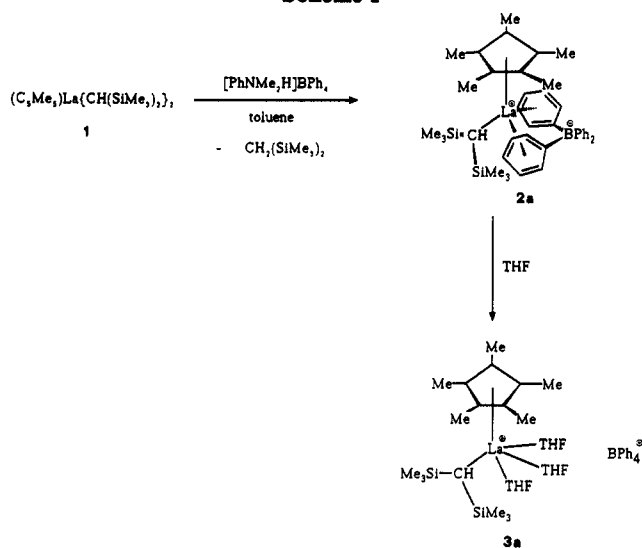


Figure 1. (A) ¹³C CPMAS NMR spectrum of **2a** (14728 scans; X = hexane). (B) ¹³C CPMAS NMR spectrum of **3a** (14916 scans).

developed a synthetic methodology to such a species.^{8a} Protonation of $\text{La}(\text{C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}_2$ (**1**)^{8a} with $[\text{PhNMe}_2\text{H}]\text{BPh}_4$ (1 equiv) in toluene (-30 to +20 °C) cleanly affords a new complex **2a** in 93% isolated yield with concomitant formation of 1 equiv of (uncoordinated)

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PhNMe₂ and CH₂(SiMe₃)₂ (by ¹H NMR). Characterization of **2a** by ¹H NMR, variable-temperature ¹³C and ²⁹Si NMR spectroscopy, and elemental analysis indicated the absence of coordinating solvents and the stoichiometry La(C₅Me₅){CH(SiMe₃)₂}BPh₄. (See Scheme I). Compound **2a** is insoluble in hexane and C₆H₁₂ but dissolves readily in benzene and toluene. It is soluble (and surprisingly stable) in CD₂Cl₂ and C₂D₂Cl₄, there being no evidence of decomposition and/or Cl⁻ abstraction after several hours at 25 °C.

The NMR data for the sterically unsaturated, formally 8-electron [La(C₅Me₅){CH(SiMe₃)₂}]⁺ fragment in **2a** are unexceptional, the chemical shifts (¹H, ¹³C, and ²⁹Si) being only slightly perturbed from those in **1**.^{8a,b} The tetraphenylborate phenyl groups are chemically equivalent, and all ¹³C NMR resonances remain sharp, down to -85 °C in solution (CD₂Cl₂). The ¹³C NMR chemical shift of the ipso carbons is very slightly solvent and temperature dependent (see Experimental Section). These C_{ipso} chemical shifts are perturbed upfield (albeit slightly) from those in the uncoordinated tetraphenylborate anion (ca. δ 164.0 ppm).^{1b,4c,7} The C_{ipso} peak shapes are also perturbed from that expected for the BPh₄ anion. We attribute this dependence to weak π-coordination of the anion and rapid inter- or intramolecular exchange in these weakly donor solvents (benzene, toluene,⁹ CH₂Cl₂.^{4b,10}). This explanation is also consistent with the solid-state NMR analysis. The ¹³C CPMAS NMR spectrum of **2a** (Figure 1A) displays two CH(SiMe₃)₂ methyl resonances in a 1:1 ratio due to rotation around each C_α-Si_β, exchanging methyl groups in the same (coordinated and uncoordinated) SiMe₃ group.^{8b} Single C₅Me₅ and C₅Me₅ peaks suggest that there are no magnetically inequivalent molecules present in the crystalline asymmetric unit cell giving rise to the multiple C_{ipso} resonances observed. Four ipso carbon resonances of equal intensity and similar line shape (multiplets, all with ^{10,11}B coupling¹¹) are observed at δ 170.4, 167.3, 159.5, and 156.3 ppm (average = 163.4 ppm). We attribute this to a (ηⁿ-C₆H₅)₂BPh₂ tetraphenylborate (in **2a**, **2n** is necessarily ≤10), giving a pseudotetrahedral lanthanum environment. This would give rise to just such a 1:1:1:1 ratio of BPh₄ C_{ipso} resonances, given the asymmetric^{8a} coordination of the CH(SiMe₃)₂ group.^{8b} Alternative structures for **2a**, such as La(C₅Me₅){CH(SiMe₃)₂}(ηⁿ-C₆H₅)BPh₃ or dinuclear [La(C₅Me₅){μ-CH(SiMe₃)₂}]₂(BPh₄)₂, are inconsistent with the (solution and solid-state) NMR evidence. Coordination of just one phenyl group would give rise to a 3:1 ratio of C_{ipso} resonances. In Zr(CH₂Ph)₃(ηⁿ-C₆H₅)BPh₃^{5a} and Cp₂ZrMe(ηⁿ-C₆H₅)BPh₃,⁷ π-coordination results in the ipso carbon of the ηⁿ-phenyl group resonating at significantly lower field (δ 178.5–181.0 ppm) and gives a 3:1 ratio of C_{ipso} resonances, as was also observed in the solid-state ¹³C NMR of cyclometalated (C₅Me₅)₂Zr⁺(*m*-C₆H₄)B-Ph₃.^{2a}

Despite the electronic saturation in **2a**, no evidence for a Si_β-C-La interaction was obtained, there being no significant upfield ²⁹Si NMR chemical shift (as was observed between [(C₆H₅)₂ZrC(SiMe₃)=CMe₂][B(p-C₆H₄F)₄]⁻ and its MeCN adduct^{5d}), compared with THF adduct **3a** (1 δ -14.62 ppm, C₇D₈, -40 °C;^{8b} **2a** δ -10.54 ppm, CD₂Cl₂, temperature invariant +25 to -80 °C; **3a** δ -10.79 ppm, CD₂Cl₂, 25 °C).

Reaction of **2a** with THF (3 equiv) in toluene leads to irreversible displacement of coordinated tetraphenylborate

and formation of cationic [La(C₅Me₅){CH(SiMe₃)₂}(THF)₃]BPh₄ (**3a**) in high (>85%) isolated yield. (See Scheme I.) The ¹H and ¹³C NMR spectra of both cation and anion are similar to those for **2a**, there being little significant perturbation of the chemical shift of diagnostic resonances. C_{ipso} resonates at δ 164.0 ppm (-30 °C, C₂D₂Cl₄) and displays the expected 1:1:1:1 quartet¹¹ (J_{BC} = 49 Hz) indicative of a noncoordinated, tetrahedral BPh₄ anion.^{1b,4c,7} The phenyl region of the ¹³C CPMAS NMR spectrum of **3a** is much simpler than that for **2a** (Figure 1B). In particular, just one broad resonance at δ 164.0 ppm is observed for all tetraphenylborate C_{ipso} carbons. The CH(SiMe₃)₂ resonance was not observed. THF resonances in a 2:1 ratio are observed, consistent with a pseudooctahedral geometry with *fac*¹² THF ligands, C₅Me₅, the La-C σ-bond, and the SiMe₃-La secondary interaction of the CH(SiMe₃)₂ group occupying the other three sites (see crystal structures of **1**^{8a} and **1**·THF^{8a}).

To determine the influence of the coordinated anion,¹³ La(C₅Me₅){CH(SiMe₃)₂}B(*p*-tolyl)₄ (**2b**) and [La(C₅Me₅){CH(SiMe₃)₂}(THF)₃]B(*p*-tolyl)₄ (**3b**) were prepared using [NH(ⁿBu)₃]B(*p*-tolyl)₄. In addition, and corroborating the formulation of **2a/b** as containing coordinated tetraphenylborate, incorporation of the poorer π-donor C₆H₄F group results in La(C₅Me₅){CH(SiMe₃)₂}B(*p*-C₆H₄F)₄ (**2c**) [prepared from **1** and [PhNMe₂H]B(*p*-C₆H₄F)₄]; δ 1.67 ppm, C₅Me₅; δ -0.12 ppm, CH(SiMe₃)₂ being much less thermally stable than **2a/b**. In the solid state, **2c** decomposes after 1 h at 25 °C. The relative instability of cationic zirconocene complexes with B(*p*-C₆H₄F)₄ as the counteranion has been reported.^{5d}

Consistent with the proposed stoichiometry, **2a** reacts with LiCH(SiMe₃)₂ (1 equiv) in benzene rapidly and quantitatively to give **1**. **2a** is also a potentially useful precursor for the formation of the mixed species La(C₅Me₅){CH(SiMe₃)₂}X, which are inaccessible by other synthetic methodologies. Thus, reaction with LiOC₆H₃^tBu₂·OEt₂ (1 equiv) gives La(C₅Me₅){CH(SiMe₃)₂}(OC₆H₃^tBu₂)₂.¹⁴

Formation of such ηⁿ-phenyl ring stabilized complexes is very dependent on the nature of the attendant ligands.^{2,5a} For example, in contrast to Zr(CH₂Ph)₄^{5a} and **1**, Lu{CH(SiMe₃)₂}₃ does not react with [PhNMe₂H]BPh₄.

In conclusion, the extreme electronic and steric unsaturation created by protonation of **1** allows ηⁿ-coordination of two phenyl rings in **2a**, rather than alternative pathways such as phenyl transfer^{1,7} to the metal, metalation,^{2a} or ηⁿ-coordination^{5a,7} of just one phenyl group. Although, in the absence of X-ray diffraction data, the coordination mode of tetraphenylborate in **2** cannot be unequivocally established, the available NMR evidence strongly indicates (ηⁿ-C₆H₅)₂BPh₂ coordination.

Experimental Section

All experiments were performed in an argon atmosphere using Schlenk type glassware or in a Braun single-station drybox equipped with a -40 °C refrigerator under a nitrogen atmosphere. Elemental analyses were performed at Analytische Laboratorien, Elbach, West Germany. ¹H NMR spectra were recorded on a

(12) Although a *mer* THF geometry is possible, this can be excluded by assuming that a CH(SiMe₃)₂ group having a secondary Si-C-La interaction occupies two adjacent coordination sites, given the electronically unsaturated nature of **3a**.

(13) Despite many efforts and mounting several crystals on the diffractometer, crystallization of **2a,b** and **3a** did not provide crystals suitable for X-ray diffraction purposes. A. G. Orpen, personal communication.

(14) Due to nonselective monosubstitution, La(C₅Me₅){CH(SiMe₃)₂}(OC₆H₃^tBu₂) cannot be prepared, either by reaction of **1** with HOC₆H₃^tBu₂ (1 equiv) or by reaction of La(C₅Me₅)(OC₆H₃^tBu₂)₂ with LiCH(SiMe₃)₂ (1 equiv).

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(11) The dipolar coupling of these resonances to quadrupolar ^{10,11}B confirms their assignment as C_{ipso}.

Varian XL-200 or Varian VXR-300 spectrometer. ^{13}C NMR spectra were at 75.4 or 125.76 MHz on the Varian VXR-300 or a Bruker 500 spectrometer, respectively. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants are reported in hertz. Coupling constants ($J_{\text{C-H}}$) were obtained from gated (^1H NOE enhanced) spectra. Solvents were PA grade. Ether, hexane, and toluene were dried initially over sodium wire, and THF was dried over solid KOH; then they were distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4-Å molecular sieves. High-resolution ^{13}C CPMAS NMR spectra of **2a** and **3a** were measured using conditions previously described.^{5b} Cross-polarization contact times were 10 ms and the 90° proton pulse was 3.3 μs with a recycle delay of 4 s between pulses. Line broadening was 2 Hz.

Preparation of $\text{La}(\text{C}_5\text{Me}_5)_2(\text{CH}(\text{SiMe}_3)_2)(\eta^3\text{-C}_3\text{H}_5)_2\text{BPh}_2$ (2a**).** To a stirred solution of 0.471 g (0.79 mmol) of $\text{La}(\text{C}_5\text{Me}_5)_2\text{CH}(\text{SiMe}_3)_2$ (**1**) in 20 mL toluene at -40°C was added 0.348 g (1 equiv) of $[\text{PhNMe}_2\text{H}]\text{BPh}_4$ as a solid. The resulting suspension was allowed to warm to room temperature. The initially colorless suspension became a light yellow solution concomitant with dissolution and reaction of $[\text{PhNMe}_2\text{H}]\text{BPh}_4$. After 30 min at 20°C , the toluene was removed in vacuo and the lemon-yellow powder washed with 2×5 mL of hexane to remove residual PhNMe_2 and $\text{CH}_2(\text{SiMe}_3)_2$. Crystallization from 5 mL of toluene/10 mL of hexane at -40°C afforded 0.555 g of **2a**. Yield: 93%. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 25°C): δ 7.37 (m, Ph), 7.2 (m, Ph), 2.02 (s, 15 H, C_5Me_5), -0.18 (s, 18 H, SiMe_3). The methyne resonance could not be unequivocally assigned. ^{13}C NMR (C_6D_6 , 25°C): δ 161.5 (m, C_{ipso}), 136.7 (C_o), 129.3 (C_m), 125.2 (C_p), 124.7 (C_5Me_5), 54.5 ($J_{\text{CH}} = 97$ Hz, CH), 12.1 (C_5Me_5), 5.0 (SiMe_3). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 25°C): δ 162.7 ("d", $J_{\text{BC}} = 63$ Hz), 136.4, 129.3, 125.2, 124.9 (C_5Me_5), 55.8 (CH), 12.55 (C_5Me_5), 5.1 (SiMe_3). ^{13}C NMR (CD_2Cl_2 , -60°C): δ 161.1 ("d", $J_{\text{BC}} = 54$ Hz), 134.8, 128.1, 124.0, 123.35 (C_5Me_5), 11.2 (C_5Me_5), 3.3 (SiMe_3). ^{13}C NMR (CD_2Cl_2 , -85°C): δ 160.73 (br, C_{ipso}), 134.84 (d, 155 Hz), 128.24 (d, 156 Hz), 124.22 (d, 161 Hz), 123.3 (s, C_5Me_5), 51.78 (d, 96 Hz, CH), 11.4

(q, C_5Me_5), 2.3 (q, SiMe_3). ^{13}C CPMAS NMR: δ 170.4, 167.3, 159.5, 156.3 (each m, C_{ipso}), 146.5, 139.3-122.2 (phenyls), 125.3 (C_5Me_5), 57.0 (v br, CH), 13.2 (C_5Me_5), 6.5 and 5.2 (SiMe_3). ^{13}C CPMAS spectra were also measured with CP times of 0.5, 5.0, and 20 ms. Anal. Calcd for $\text{C}_{41}\text{H}_{54}\text{LaSi}_2\text{B}$: C, 65.42; H, 7.23. Found: C, 65.15; H, 7.12.

Preparation of $[\text{La}(\text{C}_5\text{Me}_5)_2\text{CH}(\text{SiMe}_3)_2(\text{THF})_2]\text{BPh}_4$ (3a**).** In the drybox, 0.04 g of $\text{La}(\text{C}_5\text{Me}_5)_2\text{CH}(\text{SiMe}_3)_2\text{BPh}_4$ (**2a**) was dissolved in C_6D_6 and 40 μL of THF added. After standing in the box for ca. 1 h, yellow crystals began to precipitate. After 5 h the supernatant liquor was removed by pipet to yield $[\text{La}(\text{C}_5\text{Me}_5)_2\text{CH}(\text{SiMe}_3)_2(\text{THF})_2]\text{BPh}_4$ (**3a**). ^1H NMR (C_6D_6 , 25°C): δ 3.64 (m, 12 H, THF), 1.94 (s, 15 H, C_5Me_5), 1.77 (m, 12 H, THF), -0.134 (s, 18 H, SiMe_3). The methyne CH resonance could not be unequivocally assigned. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, -30°C): δ 164.0 (1:1:1 q, $J_{\text{BC}} = 49$ Hz), 136.4 (d, 152 Hz), 128.2 (d, 159 Hz), 123.2 (C_5Me_5), 122.1 (d, 162 Hz), 70.2 (t, 153 Hz, THF), 51.3 ($J_{\text{CH}} = 94$ Hz, CH), 25.9 (t, 134 Hz, THF), 12.3 (C_5Me_5), 5.0 (SiMe_3). ^{13}C CPMAS NMR: δ 164.0 (br, C_{ipso}), 137.5, 135.8, 127.0, 126.0, 125.2 (phenyls), 123.4 (C_5Me_5), 122.8 (sh, Ph), 122.4 (sh, Ph), 71.5 and 70.9 (THF), 26.0 and 25.7 (sh) (THF), 11.6 (C_5Me_5), 7.5 and 4.9 (SiMe_3). CH was not observed. Anal. Calcd for $\text{C}_{33}\text{H}_{79}\text{LaBO}_2\text{Si}_2$: C, 65.69; H, 8.11. Found: C, 65.52; H, 7.94.

$\text{La}(\text{C}_5\text{Me}_5)_2\text{CH}(\text{SiMe}_3)_2(\text{OC}_6\text{H}_5)_2\text{Bu}_2$. ^1H NMR (C_6D_6 , 25°C): δ 7.27 (d, 2 H, H_m), 6.82 (t, 1 H, H_p), 1.96 (s, 15 H, C_5Me_5), 1.44 (s, 18 H, CMe_3), 0.24 (s, 18 H, SiMe_3), 0.00 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$). ^{13}C NMR (C_6D_6 , 25°C): δ 162.3 (s), 136.5 (s), 128.3 (d, 159 Hz), 122.9 (C_5Me_5), 125.1 (d, 158 Hz), 117.4 (d, 155 Hz), 55.86 (d, 97 Hz, CH), 34.68 (s, CMe_3), 31.80 (q, CMe_3), 11.33 (q, C_5Me_5), 4.47 (q, SiMe_3).

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Oxygenation under UV Light of Allylsilanes Catalyzed by Palladium(II) and of (η^3 -Allyl)palladium Complexes: A Mechanistic Approach

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Summary: The use of 1-phenyl-3-(trimethylsilyl)-1-propene, 1-phenyl-1-(trimethylsilyl)-2-propene, and bis(μ -chloro)bis((1,2,3- η^3)-1-phenylpropenyl)dipalladium as substrates led us to reject a free-radical mechanism for the title reactions and to retain an incorporation of oxygen at the level of a common organopalladium intermediate.

A few years ago, we showed that the irradiation by UV light of oxygenated solutions of either allylsilanes in the presence of palladium(II) (path a)¹ or (η^3 -allyl)palladium complexes (path b)² leads to the oxygenation of the allyl groups (Scheme I). In the absence of oxygen, the irradiation of (η^3 -allyl)palladium complexes induces the cou-

pling of the allyl ligands (Scheme I, path c).³ The in situ formation of (η^3 -allyl)palladium complexes during the palladium-catalyzed oxidation of allylsilanes was suspected¹ from literature data.⁴ EPR⁵ and CIDNP⁶ studies

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