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Communication

Synthesis of trans-Mono(silyl)palladium(II) Bromide Complexes

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Abstract: The stoichiometric reaction of cis-[Pd(ITMe)2(SiR3)2] (where (SiR3 = SiMe3 and SiMe2Ph and ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) with allyl bromide affords the corresponding allylsilanes along with complexes of the type trans-[Pd(ITMe)2(SiR3)(Br)]. The structure of trans-[Pd(ITMe)2(SiMe2Ph)Br] 2b has been determined in the solid state and displays a slightly distorted square-planar geometry with the two N-heterocyclic carbene ligands in a trans-configuration.

Keywords: palladium; silicon; N-heterocyclic carbene; allylsilane

1. Introduction

Mono(silyl)palladium(II) halide species are purported intermediates in a number of catalytic routes towards allylsilanes [1,2]. Palladium pincer chemistry accounts for such complexes are rather numerous, although examples of their isolation in this catalytic cycle are rare [3–7]. Trans-[PdCl(SiF2Ph)(L2)] (L = PMe3, PMe2Ph or PMePh2) and allyl bromide were shown to react to afford trans-[Pd(L2(SiF2Ph)(Br)] and the corresponding allylsilane [1], and [(BuPar2)Pd(SiMe3)(L)] (L = 3,5-Me2-C6H3) was synthesized from stoichiometric quantities of [(cod)Pd(CH2SiMe3)2] (cod = 1,5-cyclooctadiene), BuPar2 and Me2SiL [2]. Analogues have been used in silyl-Negishi couplings [8]. We wish to report here our preliminary findings on the reaction of (ITMe)2Pd(silyl)2 complexes with allyl bromide (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) [9–12].

2. Results and Discussion

The bis(silyl)palladium complexes, cis-[Pd(ITMe2)2(SiR3)2] (1a: SiR3 = SiMe3 and 1b: SiMe2Ph [13,14]) were reacted with excess allylbromide at room temperature under an nitrogen atmosphere to yield trans-[Pd(ITMe2)2(SiMe3)(Br)] 2a and trans-[Pd(ITMe2)2(SiMe2Ph)Br] 2b in 92 and 93% yield, respectively (Scheme 1). Reaction progress was monitored by 1H NMR spectroscopy. Characteristic resonances corresponding to silanes 3a and 3b were observed (in a 1:1 stoichiometry with 2a/2b, respectively, upon examination of the crude mixtures).

Scheme 1. Stoichiometric synthesis of mono(silyl)palladium bromide complexes.
In order to further characterize the organometallic complexes, single crystals of 2b suitable for X-ray analysis were grown by slow evaporation of a saturated deuterated benzene solution at room temperature. X-ray analysis revealed that 2b displays a marginally distorted square-planar geometry with the two NHCs in a trans-configuration and orthogonal to the Br-Pd-Si plane (Figure 1, Table 1).

![Figure 1. Molecular structure of 2b. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1-Br1 2.6333(7), Pd-Si1 2.2948(18), Pd1-C1 2.028(5), Pd1-C8 2.025(5); C1-Pd1-Br1 94.97(16), C1-Pd1-Si1 89.15(17), C8-Pd1-Br1 87.62(16), C8-Pd1-Si1 88.60(17), C1-Pd1-C8 177.2(2).](image)

Table 1. Crystal data and structure refinement for 2b.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C22H35BrN4PdSi                             |
| Formula weight                                | 569.94                                     |
| Temperature/K                                 | 173                                        |
| Crystal system                                | orthorhombic                               |
| Space group                                   | P212121                                    |
| a/Å                                           | 10.5467(4)                                 |
| b/Å                                           | 14.3455(3)                                 |
| c/Å                                           | 16.7301(4)                                 |
| α/°                                          | 90                                         |
| β/°                                          | 90                                         |
| γ/°                                          | 90                                         |
| Volume/Å³                                     | 2531.23(13)                                |
| Z                                             | 4                                          |
| ρ calc/cm³                                    | 1.496                                      |
| μ/mm⁻¹                                        | 2.374                                      |
| F(000)                                        | 1160.0                                     |
| Crystal size/mm³                              | 0.22 × 0.2 × 0.15                          |
| Radiation                                     | MoKα (λ = 0.71073)                         |
| 2θ range for data collection/°               | 6.836 to 52.744                            |
| Index ranges                                  | −13 ≤ h ≤ 8, −17 ≤ k ≤ 11, −14 ≤ l ≤ 20 |
| Reflections collected                         | 7612                                       |
| Independent reflections                       | 4799 [R int = 0.0320, R sigma = 0.0568]     |
| Data/restraints/parameters                    | 4799/0/272                                 |
| Goodness-of-fit on F²                         | 1.018                                      |
| Final R indexes [I >= 2σ (I)]                | R₁ = 0.0322, wR₂ = 0.0614                  |
| Final R indexes [all data]                   | R₁ = 0.0376, wR₂ = 0.0640                  |
| Largest diff. peak/hole/e Å⁻³                | 0.51/−0.34                                 |
| Flack parameter                               | 0.004(8)                                   |
| CCDC deposition number                        | 2076437                                    |
The carbenic carbon-Pd bond lengths in 2b [2.028(5) and 2.025(5) Å] are significantly shorter than in cis-[Pd(ITMe)₂(SiMe₂Ph)₂] [2.105(3) and 2.123(3) Å], suggesting SiMe₂Ph exhibits a stronger trans-influence than ITMe [15]. The decreased length of the Pd-Si bond in 2b [2.2948(18) Å] versus cis-[Pd(ITMe)₂(SiMe₂Ph)₂] [2.3445(8) and 2.3346(8) Å] infers a stronger Pd-Si bond in 2b and demonstrates the weak trans-influence of Br. Based on these data, the intensity of the trans-influence in these two structures follows the sequence: Br < ITMe < SiMe₂Ph. Thus, the preference for the trans-configuration observed in 2b may be attributed to the high trans-influence of SiMe₂Ph and the large steric size of Br.

A possible mechanism for the formation of 2 includes either a σ-bond metathesis between a Pd-Si, in cis-[Pd(ITMe)₂(SiR₃)₂], and Br-C bond, in allylbromide, or an S_N2/S_N2' by the nucleophilic Pd-Si bond at the electrophilic sites in the allyl halide, leading to a trans complex. As we have previously suggested using computational studies on related bis-ITMe complexes, an NHC would then dissociate from the palladium center followed by a cis to trans isomerization of the Br and Si moieties (Scheme 2) [11]. Finally, the dissociated NHC would re-coordinate, constrained by the bulk of the other ligands, in a cis-configuration [16,17].

![Scheme 2. Possible mechanistic routes for the formation of 2.](image_url)

3. Experimental

The handling of air-sensitive compounds and their spectroscopic measurements were undertaken using standard Schlenk line techniques using pre-dried Ar (using a BASF R3-11(G) catalyst and 4 Å molecular sieves), or in a MBraun glovebox under N₂ (O₂ < 10.0 ppm). All glassware was dried in a 160 °C oven prior to use. Celite was predried in a 200 °C oven and then dried with a heat gun under a dynamic vacuum prior to use. Filter cannulae equipped with microfiber filters were dried in an oven at 160 °C prior to use. Solvents employed in air-sensitive reactions were dried using vacuum distillation, followed by distillation over potassium or stored over activated 4 Å molecular sieves under an Ar atmosphere. NMR spectra were recorded on a Varian VNMRS 400 (Palo Alto, CA, USA) (¹H 399.5 MHz; ¹³C[¹H] 100.5 MHz; ¹¹B[¹H] 128.2 MHz; ¹⁹F 375.9 MHz; ²⁹Si[¹H]...
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79.4 MHz), or 500 (1H 499.9 MHz; 13C[1H] 125.7 MHz). Chemical shifts are reported in ppm. All other experimental details are outlined elsewhere [10].

Synthesis of trans-[Pd(ITMe)2(SiMe3)(Br)] (2a) and Allyltrimethylsilane (3a)

Allylbromide (0.032 g, 0.26 mmol) was added to a solution of cis-[Pd(dITMe)2(SiMe3)2] (0.043 g, 0.09 mmol) in C6D6 or toluene (3.0 mL) and the resulting reaction mixture was stirred at room temperature for 1.5 h. At this stage, the volatiles were removed in vacuo and the off-white powder was washed with hexane (3 × 4.0 mL).

2a, Yield: 0.040 g, 92%. 1H NMR (399.5 MHz, C6D6): δH = 3.68 [s, 12H, N(1,3)-CH3], 1.42 [s, 12H, C(4,5)-CH3], 0.12 [s, 9H, SiMe3]. 13C[1H] NMR (100.5 MHz, C6D6): δC = 184.9 [NCN], 124.0 [C(4,5)-CH3], 35.1 [N(1,3)-CH3], 8.5 [C(4,5)-CH3], 6.9 [SiMe3]. 29Si[1H] NMR (79.4 MHz, C6D6): δSi = 7.68. Elem. Anal. Calcd. for C17H33N4SiBrPd: C, 40.20%; H, 6.55%; N, 11.03%. Found: C, 40.15%; H, 6.54%; N, 10.95%. 3a (from crude reaction solution), 1H NMR (399.5 MHz, C6D6): δH = 5.77 [m, 1H, CH=], 4.92 [m, 1H, CH=], 4.89 [m, 1H, CH=], 1.44 [m, 2H, CH2]. −0.03 [s, 9H, SiMe3]. [Agrees with an independently taken 1H NMR sample of commercially available allyltrimethylsilane].

Synthesis of trans-[Pd(ITMe)2(SiMe2Ph)(Br)] (2b)

Allylbromide (6.0 µL, 0.07 mmol) and cis-[Pd(dITMe)2(SiMe2Ph)] (0.021 g, 0.03 mmol) were dissolved in C6D6 or toluene (1.0 mL). The resulting reaction mixture was stirred at room temperature for 2 h under an N2 atmosphere. At this stage, all volatiles were removed in vacuo and the resulting white solid was washed with hexane (3 × 2.0 mL). Yield: 0.018 g, 93%. 1H NMR (399.5 MHz, C6D6): δH = 7.20 [m, 2H, SiMe2Ph], 7.07 [m, 3H, SiMe2Ph], 3.51 [s, 12H, N(1,3)-CH3], 1.42 [s, 12H, C(4,5)-CH3], 0.31 [s, 6H, SiMe2Ph]. 13C[1H] NMR (100.5 MHz, C6D6): δC = 183.4 [NCN], 149.6 [SiMe2-i-Ph], 133.1 [SiMe2Ph], 127.0 [SiMe2Ph], 126.5 [SiMe2-p-Ph], 124.2 [C(4,5)-CH3], 34.9 [N(1,3)-CH3], 8.5 [C(4,5)-CH3], 4.2 [SiMe2Ph]. 29Si[1H] NMR (79.4 MHz, C6D6): δSi = 2.44. (It was not possible to obtain elemental analysis for 2b—every attempt resulted in numbers that were inconsistent with calculated values. A possible reason for this is decomposition of 2b by exposure to air or moisture on transit to data collection).

Crystal data for 2b: C22H35N4SiBrPd, M = 569.94 g mol−1, orthorhombic, space group P2121, a = 10.5467(4) Å, b = 14.3455(3) Å, c = 16.7301(4) Å, α = 90°, β = 90°, γ = 90°, V = 2531.23(13) Å3, Z = 4, T = 173 K, Mo(Kα) = 0.71073, R1 [I > 2σ(I)] = 0.0345, wR2 (all data) = 0.0677, GoF = 1.011.

Crude 1H NMR data are consistent with the formation of allyldimethylphenylsilane (3b) as a product of this reaction. However, this was not isolated in this instance [18].

4. Conclusions

Under mild conditions, non-pincer bis(NHC)(silyl)palladium halide complexes of the type trans-[Pd(ITMe)2(SiR3)(Br)] (SiR3 = SiMe2Ph (2a), and SiMe3 (2b)) were synthesized, by the reaction of allylbromide with the corresponding complexes cis-[Pd(ITMe)2(SiR3)2], 1a or 1b, respectively. A possible mechanistic route for the formation of 2 involves either a σ-bond metathesis or an Sn2/Sn2′ reaction between allylbromide and 1. This would necessitate a cis-trans isomerization via dissociation of an NHC ligand-[19]. The reactivity of trans-[Pd(ITMe)2(SiR3)(Br)] is unexplored but will soon be carried out. The facile formation and apparent stability of trans-2 may indeed hinder the catalytic silylation of ally halides mediated by ITMe2Pd-based complexes since the adoption of a cis-configuration is a prerequisite for reductive elimination and involvement in a catalytic cycle. Solutions to these unexplored questions are currently being sought, e.g., the potential for halide abstraction, and will be reported in due course.

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