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A Case of Slow Isomerization of a (σ–π-Hexenyl)palladium Complex and Its Relevance to Organic Synthesis

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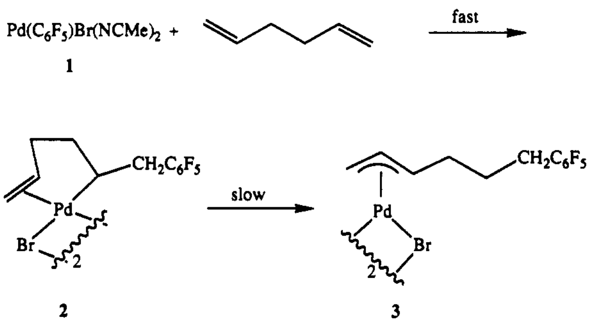
Summary: Reaction of 1,5-hexadiene with [$Pd(C_6F_5)Br(NCMe)_2$] (**1**) at room temperature gives in seconds the dimeric σ–π complex [$Pd_2(\mu\text{-}Br)_2(6\text{-}C_6F_5\text{-}(1,2,5\text{-}\eta^3)\text{-}C_6H_{10})_2$] (**2**), which isomerizes in solution *in hours* at room temperature to give the allyl derivative [$Pd_2(\mu\text{-}Br)_2(6\text{-}C_6F_5\text{-}(1\text{-}3\text{-}\eta^3)\text{-}C_6H_{10})_2$] (**3**) as the sole product. This slow isomerization shows that the usually fast rate of the Pd-migration step can be noticeably slowed down in some systems, thus giving rise to the possibility of formation of different organic products in some Pd-initiated organic synthesis.

Scheme I



Palladium-promoted cis and trans additions of nucleophiles to olefinic bonds are currently widely employed in organic synthesis because of the excellent regio- and stereoselectivity of these processes.[1,2] When a second double bond is present in the organic substrate, the palladium often migrates rapidly along the hydrocarbon chain (via β-hydride elimination–readdition)[3] to give an (η^3-allyl)palladium complex without isomerization of the second double bond.[4] Exceptions are good chelating dienes such as norbornadiene and 1,5-cyclooctadiene, which lead to σ–π palladium complexes. The latter can also produce a mixture of σ–π and η^3-allyl palladium complexes as competing products;[5] it is sometimes possible to isomerize the σ–π complex to the thermodynamically more stable η^3-allyl complex, but this only happens under conditions much more stringent than those used for insertion or for Pd-elimination reactions in organic synthesis.

Only two extreme situations ((i) very fast Pd migration and (ii) extremely slow migration) seem to have been reported so far, and emphasis has been given to the ease of this palladium migration; this might lead to the impression that the lapse allowed between the beginning of the insertion step and the Pd-elimination step in an organic synthesis has little relevance to the products. The process represented in Scheme I shows that, in appropriate sys-

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(1) Trost, B. M.; Verhoeven, T R. Organopalladium Compounds in Organic Synthesis and in Catalysis. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 854.

(2) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(3) (a) Albelo, G.; Wiger, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510. (b) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 180. (c) Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013. (d) Larock, R. C.; Takagi, K. *J. Org. Chem.* **1984**, *49*, 2701. (e) Larock, R. C.; Leung, W.-Y. *J. Org. Chem.* **1990**, *55*, 6244.

(4) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. *Organometallics* **1990**, *9*, 1079 and references therein.

(5) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594 and references therein.

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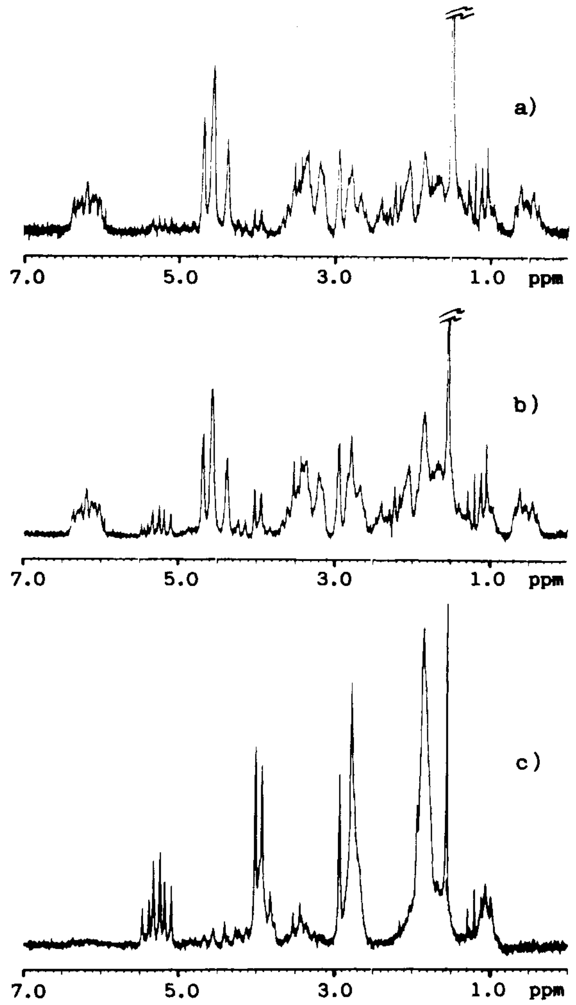

Figure 1. ^1H NMR ($CDCl_3$, 80 MHz, 307 K) sequence of the isomerization **2** → **3** after (a) 10 min, (b) 45 min, and (c) 180 min.

tems, the palladium migration can take place within the range of times used in the manipulation of an organic synthesis.

The reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ (**1**)[4] with the stoichiometric amount of 1,5-hexadiene in $CDCl_3$ can be followed by ^1H and ^{19}F NMR spectroscopy.[6] The first recording (less than 1 min after mixing the reactants, T = 298 K) shows only signals of **2**, and no traces of **1** or **3** are observed. In successive recordings, **3** begins to be formed at the expense of **2**, and the isomerization **2** → **3** (which shows a first-order dependence on **2**; $k_{obs} = 5.37 \times 10^{-5}$ s^{-1}, studied by ^{19}F NMR spectroscopy)[7] is complete after 10 h; at 307 K complete isomerization takes about 3 h. Figure 1 shows the ^1H NMR spectra of the initial, intermediate, and final situations. The reaction can be carried out on a preparative scale, and both **2** (white) and **3** (yellow) have been isolated as solids and fully characterized.[8]

We have previously studied the insertion of 1,5-cyclooctadiene into the $Pd-C_6F_5$ bond[5] and shown that a $\sigma-\pi$ and an η^3-allyl complex are competitively formed from a common η^1 precursor; furthermore, the isomerization $\sigma-\pi \rightarrow \eta^3$-allyl is undetectable at room temperature. Here the situation is different, since only **2** is initially formed; hence, all **3** is produced as a result of the isomerization **2** → **3**. This means that (i) coordination of the unattacked double bond is much faster here than H abstraction (the initial step for Pd migration) or occurs previous to insertion (further studies are needed to discriminate between these two possibilities) and (ii) the isomerization $\sigma-\pi \rightarrow \eta^3$-allyl is noticeably faster here than for 1,5-COD. Since isomerization involves decoordination of the unattacked double bond,[5] the activation energy of the process (and consequently its rate) is dependent on the stability of the metallacycle formed in the $\sigma-\pi$ complex, which is lower in the corresponding derivative of 1,5-hexadiene.

It is remarkable that, under the conditions used, neither 1-perfluorophenyl)-1,5-hexadiene nor products derived from it are observed, which indicates that, in the hydride–olefin palladium intermediate, hydride readdition is faster than olefin decoordination, thus ruling out competing processes.

If a Pd-elimination reaction were applied to the process in Scheme I, the organic products obtained would be different, depending on the complexes actually present in the solution at that moment, unless the elimination process happens to promote fast isomerization to **3**. If both **2** and **3** are present, a mixture of two organic derivatives will be obtained in spite of the regio- and stereoselectivity of the different steps involved.

In conclusion, the user of Pd-initiated addition of nucleophiles should be aware that, when this addition is applied to complex systems (which is becoming more and more usual), the usually very fast rate of Pd migration can be slowed down noticeably if stabilized intermediates can be formed. Furthermore, in a case such as the one discussed here, the slowness of isomerization might afford a new tool for selective functionalization of either of two different carbons at will, by producing Pd elimination either in **2** or in **3**. We are pursuing these findings further.

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(6) For details about the application of ^{19}F NMR spectroscopy, see refs 4 and 5.

(7) Complex **1** and 1,5-hexadiene (1:1) were mixed at 298 K in $CDCl_3$, and ^{19}F NMR spectra were recorded by use of a microprogram with a fixed delay (10 min) between spectra. Successive concentrations of **2** and **3** were determined by integration of their distinct F_{ortho} resonances at −142.6 (**2**) and −145.3 (**3**) ppm; a pulse delay of at least five T_1's was used to ensure complete relaxation (total acquisition time for each spectrum was 2.37 min). A plot of $\ln [\mathbf{2}]_0 - \ln [\mathbf{2}]_t$ versus time is linear (for 20 data and a final transformation of nearly 50% of **2** into **3**) and provided the *first*-order rate constant k_{obs} (rate = $k_{obs}[\mathbf{2}]$).

(8) Complex **2** was prepared by stirring **1** with 1,5-hexadiene (1:1) in CH_2Cl_2 at 0 °C for 5 min. The solvent and the displaced NCMe were pumped off, and the dry residue was triturated in diethyl ether. For **3** the reaction was maintained at room temperature for 24 h, followed by filtration of any palladium traces, evaporation to a small volume, addition of *n*-hexane, and cooling. Anal. Calcd for both **2** and **3**: C, 33.09; H, 2.31. Found for **2**: C, 33.40; H, 2.35. Found for **3**: C, 33.18; H, 2.31. ^1H NMR (δ, at 250 MHz in $CDCl_3$, reference TMS): for **2**, 6.18 (m, 1 H, H^2), 4.63 (d (8 Hz), 1 H, H^1), 4.48 (d (14 Hz), 1 H, $H^{1'}$), 3.5 (m, 1 H, H^5), 3.25 (m, 1 H, H^6), 2.8 (m, 1 H, $H^{6'}$), 2.4 (m, 1 H, H^3), 2.0 (m, 1 H, $H^{3'}$), 1.5 (m, 1 H, H^4), 0.53 (m, 1 H, $H^{4'}$); for **3**, 5.3 (ddd (11.6, 11.2, 6.8 Hz), 1 H, H^2), 3.95 (m, 1 H, H^3 anti), 3.85 (d (6.8 Hz), 1 H, H^1 syn), 2.8 (d (11.6 Hz, 1 H, H^1 anti), 2.7 (m, 2 H, $H^6 + H^7$), 1.7–1.9 (m, 4 H). Double-resonance techniques were used to assign the resonances listed above. ^{19}F NMR (δ, at 75.4 MHz in $CDCl_3$, reference $CFCl_3$): for **2**, −142.6 (m, 2 F_o), −158.0 (t, F_p), −163.3 (m, 2 F_m); for **3**, −145.3 (m, 2 F_o), −158.9 (t, 1 F_p), −164.0 (m, 2 F_m).