Ag NMR as a Tool for Mechanistic Studies of Ag-Catalyzed Reactions: Evidence for in Situ Formation of Alkyn-1-yl Silver from Alkynes and Silver Salts

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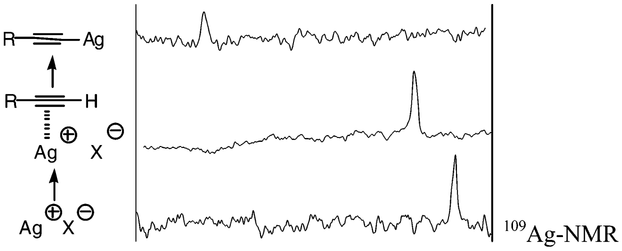


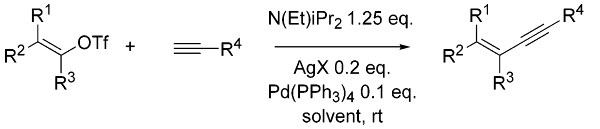
As demonstrated by ^{1}H, ^{13}C, and ^{109}Ag NMR, a π-alkyne-Ag complex and then an alkynyl silver are in situ formed from alkyne and silver salt in conditions related to those used for Ag-catalyzed alkynylation or for Ag/Pd-catalyzed sp−sp^2 cross-coupling reactions. This finding allows for a rationale of the mechanisms of these reactions.

Introduction

In recent years, silver salts have increasingly gained interest as catalysts for various alkynylation reactions[1] as well as cocatalysts in various cross-coupling reactions involving alkynes and different partners, especially alkenyl triflates.[2]

In connection with our interest in the synthesis of antitumoral dienediynes,[3,4] we have developed mild sp−sp^2 cross-coupling reactions, catalyzed by a new combination of catalysts: Pd(PPh$_3$)$_4$ and silver salts[2] (Scheme 1). For a better understanding of these reactions and other Ag-catalyzed reactions, we embarked on mechanistic studies and tried to characterize some intermediates.[5]

SCHEME 1. Pd/Ag-Catalyzed Synthesis of Enynes: (a) X = Cl or I; (b) solvent: DMF, PhH, CHCl$_3$, CH$_2$Cl$_2$



Since our coupling reactions involve palladium and a group 11 metal salt, i.e., silver, as catalysts, they are strongly related to the well-known Sonogashira coupling reactions.[6] Although this reaction is widely used, the exact mechanism is still unknown. Using palladium and copper as catalysts, the Sonogashira reaction is believed

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(1) Wei, C.; Li, Z.; Li, C.-J. *Org. Lett.* **2003**, *5*, 4473−4475. Ji, J.-X.; Au-Yeung, T. T.-L.; Wu, J.; Yip, C. W.; Chan, A. S. C. *Adv. Synth. Catal.* **2004**, *346*, 42−44.

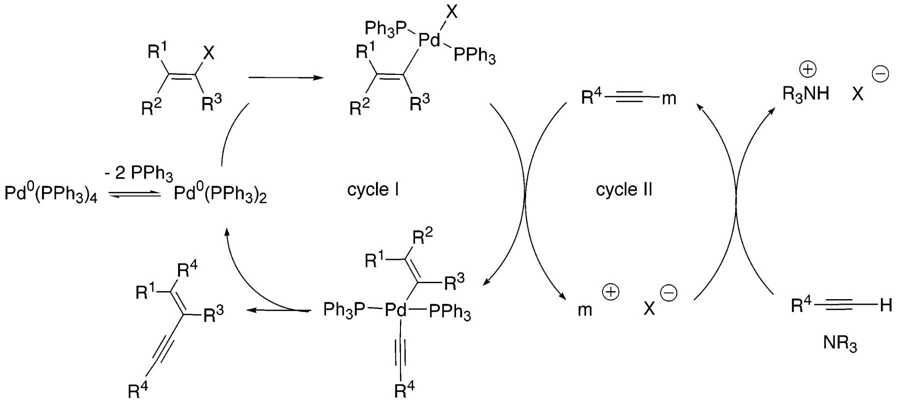
(2) (a) Bertus, P.; Pale, P. *J. Organomet. Chem.* **1998**, *567*, 173−180. (b) Bertus, P.; Halbes, U.; Pale, P. *Eur. J. Org. Chem.* **2001**, *23*, 4391−4393. (c) Halbes, U.; Bertus, P.; Pale, P. *Eur. J. Org. Chem.* **2001**, 4391−439. (d) Halbes, U.; Bertus, P.; Pale, P. *Tetrahedron Lett.* **2001**, *42*, 8641−8644. (e) Halbes, U.; Pale, P. *Tetrahedron Lett.* **2002**, *43*, 2039−2042. (f) Halbes, U.; Pale, P. *J. Organomet. Chem.* **2003**, *687*, 420−424. (g) Halbes, U.; Vasiliev, A.; Pale, P. *Eur. J. Org. Chem.* **2005**, 2828−2834.

(3) Dienediynes: (a) Ishida, N.; Miyazaki, K.; Kumagai, K. M.; Rikimura, M. *J. Antibiot.* **1965**, *18*, 68−76. (b) Edo, K.; Mizugaki, M.; Koide, Y.; Seto, H.; Furihata, K.; Otake, N.; Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331−334. (c) Ishii, M.; Ando, T.; Kajiura, T.; Kameyama, T.; Nihey, Y. *Jpn. Kokai Tokkyo Koho* JP 07291955; *Chem. Abstr.* **1996**, *124*, 115564h. (d) Ando, T.; Ishii, M.; Kajiura, T.; Kameyama, T.; Miwa, K.; Sugiura, Y. *Tetrahedron Lett.* **1998**, *39,* 6495−6498. (e) Hofstead, S. J.; Matson, J. A.; Malacko, A. R.; Marquard, H. *J. Antibiot.* **1992**, *45*, 1250−1254. (f) Leet, J. E.; Schroeder, D. R.; Hofstead, S. J.; Golik, J.; Colson, K. L.; Huang, S.; Klohr, S. E.; Doyle, T. W.; Matson, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 7946−7948. For reviews on enediynes and dienediynes, see: (g) Nicolaou, K. C.; Smith, A. L. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; pp 203−287. (h) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453−6518. (i) Lhermitte, H.; Grierson, D. *Contemp. Org. Synth.* **1996**, *3*, 41−63 and 93−124.

(4) (a) Bertus, P.; Zhang, J. H.; Sir, G.; Weibel, J. M.; Pale, P. *Tetrahedron Lett.* **2003**, *44*, 3391−3395. (b) Klein, S.; Zhang, J. H.; Holler, M.; Weibel, J. M.; Pale, P. *Tetrahedron Symp. Print* **2003**, *59*, 9793−9802.

10.1021/jo0511546 CCC: $30.25

SCHEME 2. Proposed Catalytic Cycle for Sonogashira Type Reactions



to take place through two independent catalytic cycles. The generally accepted catalytic cycle for the palladium catalysis was based on successive oxidative addition, transmetalation, and reductive elimination (cycle I in Scheme 2).[7] In a second catalytic cycle, the terminal alkyne would react with amine in the presence of copper salt, yielding a copper acetylide, which could then transmetalate to palladium (cycle II in Scheme 2).[8] However, in situ formation of copper acetylide as intermediate has never been proven.[8,9]

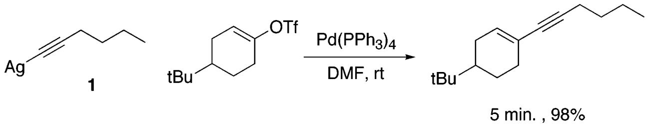
In our reaction, silver salts used as cocatalyst would probably behave in a similar way and thus lead to silver acetylide intermediates. We already demonstrated that such silver organometallics behave as magnesium, zinc, or tin organometallics and were indeed able to enter the Pd catalytic cycle at the transmetalation step.[5a] Ag-catalyzed alkynylation reactions also probably occur via the formation of alkynyl silver from alkyne.[1]

In this contribution, we provide evidence for in situ formation of π-alkyne-Ag complexes and alkyn-1-yl silver under sp−sp^2 cross-coupling conditions, shedding some light on the mechanism of Ag-catalyzed coupling reactions and alkynylations.

Results and Discussion

Other than its synthetic advantages,[1−2] using silver as cocatalyst offers a unique opportunity to study reaction mechanisms by NMR spectroscopy. Indeed in this case, all occurring nuclei, i.e., proton, carbon, and silver, are NMR active. Silver consists of two NMR active nuclei, ^{107}Ag and ^{109}Ag, the 109-isotope being the more sensitive.[10] Although far from common, silver NMR can provide useful information about the environment around silver atoms, a key element in our coupling reactions.[2] We have therefore followed by multinuclear NMR the course of our reactions.

SCHEME 3



In a preliminary study, we determined the characteristic NMR features in common NMR solvents of alkyn-1-yl silver in order to be able to detect its possible formation. Hexyn-1-yl silver **1**[11] was selected due to its efficiency as coupling partner (Scheme 3)[5] and due to its favorable solubility properties.

After having set the right parameters,[12] proton, carbon, and silver NMR spectra of **1** were recorded in deuterated benzene, chloroform, and DMF (Figure 1, Table 1), solvents in which our cross-coupling reactions and some alkynylations can be carried out (Scheme 1). The proton spectra were referenced to the internal standard tetramethylsilane; the carbon and silver spectra were referenced to tetramethylsilane via the Ξ scale.[13]

The proton spectrum of **1** was poorly resolved at 300 K in $CDCl_3$, CD_2Cl_2, and DMF-d_7 but not in C_6D_6. Whatever the solvent, it nevertheless clearly exhibited the expected four signal groups with the corresponding 2:2:2:3 integration. Compared to 1-hexyne **2**, all methylene protons are deshielded, with the propargylic methylene protons being the most deshielded (2.50 vs 2.13 ppm in $CDCl_3$ and 2.77 vs 1.92 ppm in C_6D_6 , see Table 1).

The carbon spectra of **1** showed the expected four signals in the aliphatic region and two signals in the unsaturated carbons region. The assignment of the

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[5] (a) Dillinger, S.; Bertus, P.; Pale, P. *Org. Lett.* **2001**, *3*, 1661−1664. (b) Létinois-Halbes, U.; Pale, P.; Berger, S. *Magn. Reson. Chem.* **2004**, *42*, 831−834.

[6] (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 2004. (b) Negishi, E.-i.; De Meijere, A. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, 2002. (c) Farina, V. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 222−225. (d) Sonogashira, K. In *Comprehensive Organic Chemistry*; Fleming, I., Trost, B. M., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 521−549.

[7] The actual Pd cycle is probably more complex. See: (a) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254−278. (b) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314−321. (c) Amatore, C.; Bensalem, S.; Ghalem, S.; Jutand, A.; Medjour, Y. *Eur. J. Org. Chem.* **2004**, 366−371.

[8] Geissler, H. In *Transition Metals for Organic Synthesis*, Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; pp 158−183.

[9] Indirect evidence has nevertheless been presented. See: Bertus, P.; Fécourt, F.; Bauder, C.; Pale, P. *New J. Chem.* **2004**, *28*, 12−14.

[10] Goodfellow, R. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York and London, 1983; pp 563−589.

[11] Davis, R. B.; Scheiber, D. H. *J. Am. Chem. Soc.* **1956**, *78*, 1675−1677.

[12] The silver spectra were recorded on a 600 MHz Bruker spectrometer at a frequency of 27 927 MHz using a 10 mm TBI probe head. The 90° pulse was set to 65 μs with a power of 3 dB. Further, d1 was 5 s and DE was set to 40 μs to prevent important baseline rolling. The spectral width was 2000 ppm and the acquisition time 1.170 s. For a 1 M solution, 200 scans were used as a minimum value.

[13] Harris, R. K. *Pure Appl. Chem.* **2001**, *73*, 1795−1818, Ξ = 4 653 533 for ^{109}Ag.

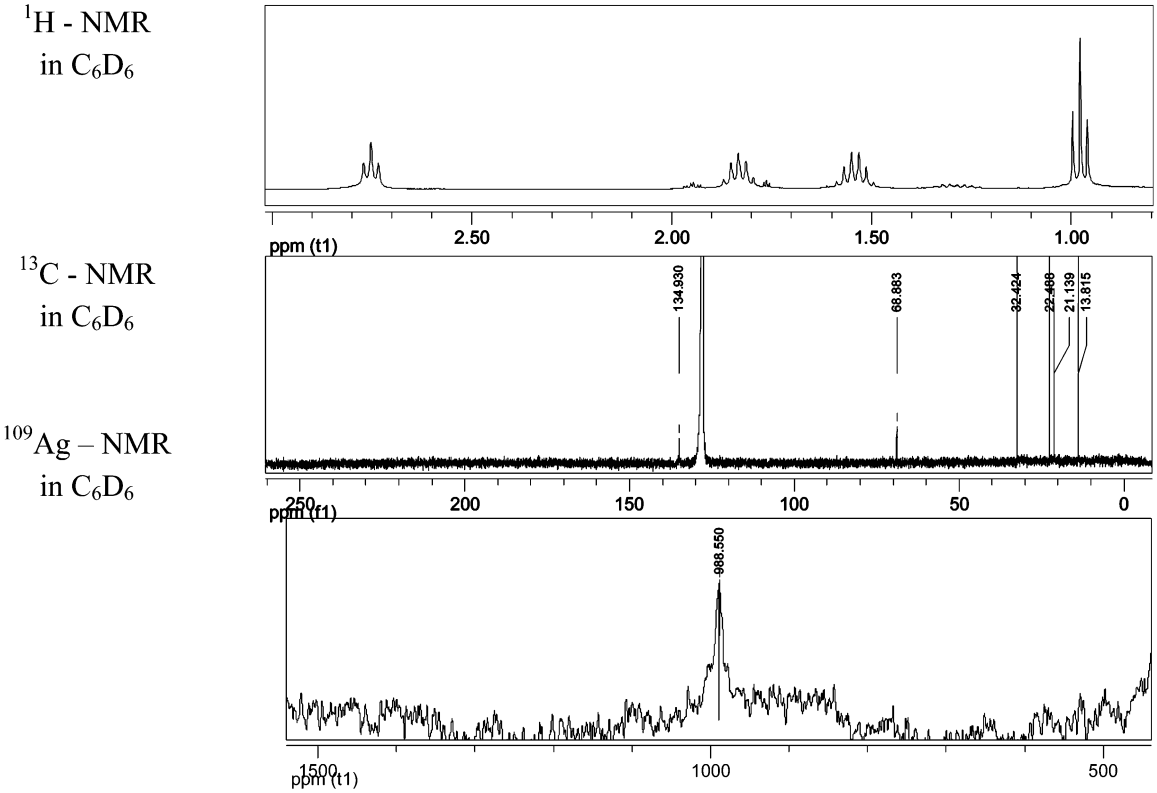

FIGURE 1. Typical NMR spectra of hexynyl silver **1** in C_6D_6.

TABLE 1. Comparison of Some ^{1}H NMR Chemical Shifts of Hexyn-1-yl Silver 1 and Hex-1-yne 2 in Various Solvents[a]

solvent		δ (H3)	δ (H4)	δ (H5)	δ (H6)
$CDCl_3$	**2**	2.13	1.40−1.53	1.40−1.53	0.92
	1	2.50	1.68	1.46	0.94
CD_2Cl_2	**2**	2.19	1.51	1.42	0.91
	1	2.50	1.69	1.45	0.93
C_6D_6	**2**	1.92	1.22−1.31	1.22−1.31	0.72
	1	2.77	1.85	1.55	0.97
DMF-d_7	**2**	2.18	1.37−1.46	1.37−1.46	0.88
	1	2.64	1.77	1.52	0.97

[a] Numbering refers to IUPAC nomenclature.

signals was established by HMQC and HMBC experiments. Both sp carbons are deshielded with respect to 1-hexyne, but the inner sp carbon is more deshielded than the terminal sp carbon (134.9 and 86.8 ppm vs 83.9 and 68.2 ppm in C_6D_6). Both sp carbons signals and the signal for the methylene group adjacent to the triple bond appear broad.

^{109}Ag spectra showed for a $CDCl_3$ solution of **1** a chemical shift of 1061 ppm relative to $AgNO_3$. In deuterated benzene and DMF, very similar chemical shifts were observed (δ = 988 and 1055 ppm, respectively). Compared to the chemical shift of a 1 M solution of $AgNO_3$ in D_2O set to zero by convention,[14] hexynyl silver appears strongly deshielded. These data are consistent with the electronic density expected from d^{10} ion conjugated with adjacent π-system.[15] In $CDCl_3$, CD_2Cl_2, and DMF-d_7, the silver signal appeared as a very broad singlet. With a nuclear spin quantum number $I = 1/2$ for ^{109}Ag and ^{107}Ag, one could expect to detect the coupling between silver and the propargylic protons. The values of ^4J {^{109}Ag, ^{1}H} coupling constants should lie between 0.4 and 1.8 Hz.[16] However, experiments for the inverse detection through proton−silver coupling unfortunately did not afford any results. Due to the line width of at least 75 Hz, this ^4J coupling could not be measured. Moreover, HMBC experiments on different spectrometers showed only one cross-peak, which suggested a coupling between H6 and silver.[17] Agostic interactions between the methyl group and silver were however ruled out, as the coupling constant ^1J{^{13}C, ^{1}H} = 125 Hz of the methyl group did not show any weakening of the bond. ^{109}Ag spectra recorded at lower temperatures between 180 and 270 K in CD_2Cl_2 did not lead to a better quality of the spectra either. On the contrary, heating the sample to 335 K in C_6D_6 led to the smallest observed line width of 75 Hz. Such behavior suggests that relaxation of the silver nucleus occurs predominantly by chemical shift anisotropy (CSA),[18] and this relaxation would also explain the large line widths.

With these data in hand, we started investigating the in situ formation of alkynyl silver in various solvents

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(14) Garth Kidd, R.; Goodfellow R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; pp 195−257.

(15) Elschenbroich, C.; Salzer, A. *Organanometallics*, 2nd ed.; VCH: Weinheim, 1992. Crabtree, R. A. *The Organometallic Chemistry of Transition Metals*; Wiley: New York, 1988.

(16) Zangger, K.; Armitage, I. M. *Metal Based Drugs* **1999**, *6*, 239−244.

(17) The cross-peak Ag−H6 in HMBC experiments was not an artifact, as shown by different experiments on several spectrometers of different magnetic fields.

(18) Claridge, T. D. W. In *High-Resolution NMR Techniques in Organic Chemistry*; Baldwin, J. E., Williams, F. R. S., Williams, R. M., Eds.; Pergamon: Oxford, 1999; p 39.

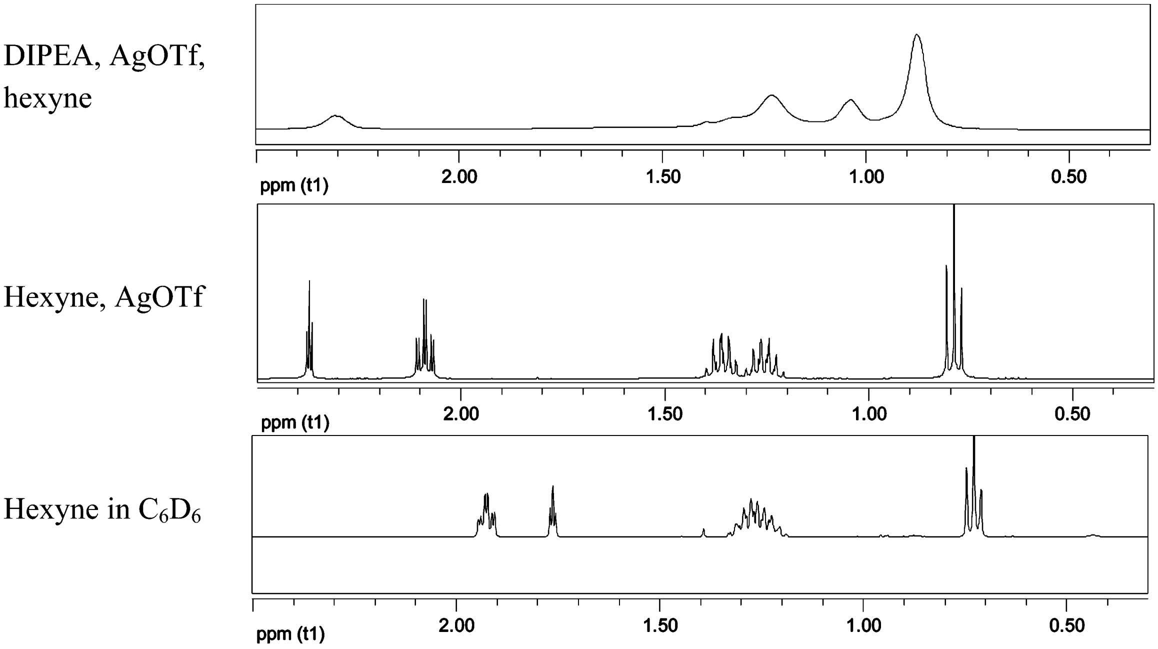

FIGURE 2. Formation of hexynyl silver **1** from hexyne and silver triflate followed by ^1H NMR in C_6D_6.

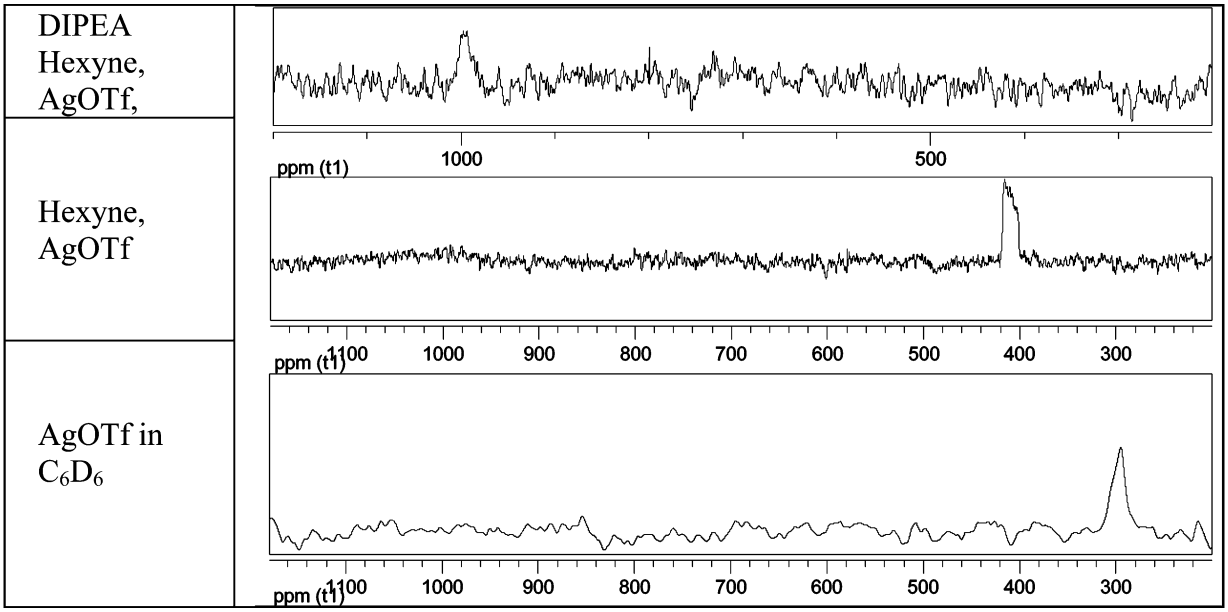

FIGURE 3. Formation of hexynyl silver **1** from hexyne and silver triflate followed by ^{109}Ag NMR in C_6D_6.

under conditions similar to those used for our cross-coupling reactions.[2]

Hexyne was thus dissolved in C_6D_6, and AgI and *N*,*N*-diisopropylethylamine (DIPEA) were successively added. To follow the evolution of this reaction mixture, proton, carbon, and silver NMR spectra were recorded after each addition of the products and then every hour. Surprisingly, almost no evolution could be observed in these conditions. The signals observed in the spectra corresponded to a simple mixture of hexyne and DIPEA. As solids always remained on the bottom of the NMR tube, this lack of conversion could be due to the poor solubility of silver iodide in this apolar solvent.[19] Silver iodide was therefore replaced by silver triflate because of its better solubility in organic solvents. Silver triflate is also an effective catalyst in alkynylation reactions[1] as well as in our coupling reactions,[2] and due to the Pd catalysis, triflate anions are present during our cross-coupling reaction involving vinyl triflates and alkynes. Thus, triflate anion should not disturb the reaction. The proton, carbon, and silver spectra of the mixture of hexyne, AgOTf, and DIPEA were successively recorded in various solvents and evolution clearly occurred (Figures 2 and 3).

The ^1H spectrum of 1-hexyne **2** in C_6D_6 clearly showed the acetylenic proton at 1.77 ppm with its characteristic coupling pattern (t, $^4J\{^1H, ^1H\} = 2.47$ Hz) to the adjacent

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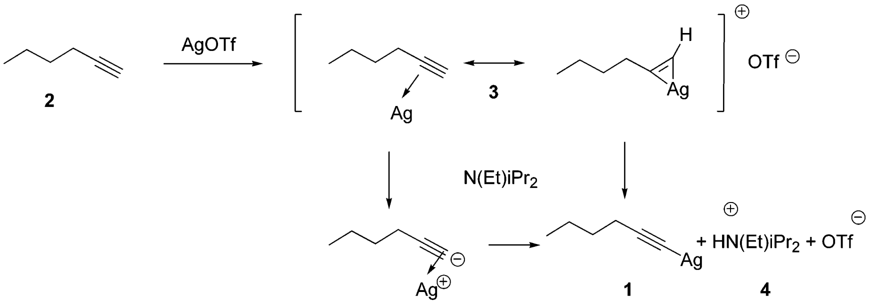
(19) Cross-coupling reactions in the presence of AgI always seem to be heterogeneous; solids always remain in the flask whatever the solvent used. However, in the absence of AgI, no reaction takes place.

SCHEME 4



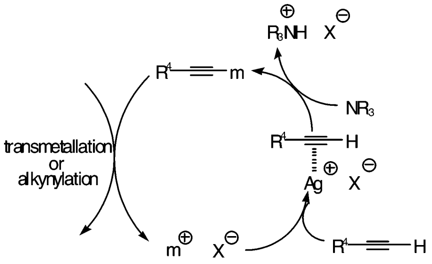
methylene group (Figure 2, bottom trace). Upon addition of silver triflate, all five signals were still present, but all protons became deshielded (Figure 2, middle trace). The large multiplet around 1.2 ppm corresponding to two methylene units split into two distinct multiplets at 1.4 and 1.5 ppm. The most important effect was observed for the signal of the acetylenic proton, with a shift of almost 1 ppm, from 1.77 to 2.67 ppm. The coupling constant $^4J\{^1H, ^1H\}$ decreased to 1.76 Hz, indicating a loss of electron density of the H−C(sp) bond. Changes in ^{13}C spectra were also obvious when compared to free 1-hexyne spectra. Deshielding of the internal sp carbon (87.0 vs 83.9 ppm) was observed, but this was accompanied by a shielding of the terminal carbon (66.2 vs 68.2 ppm).

The most dramatic modifications were observed in the ^{109}Ag spectra (Figure 3). AgOTf dissolved in DMF-d_7 showed a ^{109}Ag signal at 80 ppm and at 294 ppm in C_6D_6. When hexyne was added, the silver signal was shifted to 750 ppm in DMF-d_7 and to 416 ppm in C_6D_6. A large line width (600 Hz) was observed for this signal in DMF-d_7; this large value could be due to a dynamic process in this coordinating solvent. Indeed, in C_6D_6, a sharper signal was observed (line width 250 Hz).

These results supported the in situ formation of a silver π-complex. The observed deshielding of the protons upon addition of silver triflate and the presence of the same number of signal groups can indeed be explained by the formation of a π-complex between the silver cation and the triple bond of the alkyne. In this case, electron density is partly transferred to the silver cation, therefore weakening the H−C(sp) bond and deshielding the protons as well as the silver ion. Therefore, we assigned these signals to the acetylene π-complex **3** (Scheme 4).

The ESI-MS spectrum confirmed the assumption of the in situ formation of the π-complex **3**. Indeed, when the mixture of silver triflate and 1-hexyne in C_6D_6 was directly introduced into the mass spectrometer (diluted by 1:1000 in MeCN), two sets of peaks were observed with two major and two minor peaks (see Supporting Information). The first set at 189.0 (100%) and 190.0 amu (7%) corresponds to the π-complex that contains the ^{107}Ag isotope and one ^{13}C, respectively (exact mass found 188.9618, calcd 188.9833 for $C_6H_{10}{}^{107}Ag$). The second set at 191.0 (93%) and 192.0 amu (6%) corresponds to the complex containing the ^{109}Ag isotope and one ^{13}C. The ratio of both sets fits exactly the natural abundance of ^{107}Ag (51.82%) and ^{109}Ag (48.18%).

SCHEME 5. Observed Mechanism for the Formation of Alkynyl Silver in the Presence of Silver Salt



Upon addition of DIPEA to this silver acetylene π-complex, a white precipitate formed in the NMR tube, leading to some resolution loss. Coupling constants could not be determined anymore in the ^1H spectra (Figure 2, top trace). Nevertheless, some of the signal groups corresponded to those obtained with the independently prepared diisopropylethylammonium triflate **4**, and the precipitate proved to be identical with this ammonium triflate. The formation of diisopropylethylammonium triflate should be due to the formation of **1**. Some of the signals in the ^1H spectra indeed corresponded to **1**. However, due to the poor resolution, the exact nature of the newly formed product could not be determined without ambiguity. ^{13}C spectra were not conclusive either, since the typical broad signals for the sp carbons could hardly be distinguished from the noise in the spectra. The same behavior was observed whatever the solvent.

^{109}Ag NMR proved to be more helpful, as measured in DMF-d_7 and C_6D_6 (Figure 3). When DIPEA was added, the silver signal was further shifted to 1050 ppm in DMF-d_7 and to 990 ppm in C_6D_6 and the line got sharper, with a line width of 300 Hz in DMF-d_7 and of 100 Hz in C_6D_6. These values are very close to those obtained for the independently prepared hexynyl silver (1060 ppm in $CDCl_3$, 1055 in DMF-d_7, and 988 ppm in C_6D_6). It is worth noting that such differences are very small compared to the enormous range of chemical shifts in silver NMR (−250 to 2519 ppm).

These results clearly demonstrated that the alkynyl silver **1** was indeed produced from a π-complex after addition of DIPEA. Therefore, we assume that the second catalytic cycle in our coupling reaction follows the steps shown in Scheme 5 (m = Ag), the alkynyl silver being transmetalated to palladium species. We also assume that alkynylation reactions proceed through the same pathway, the alkynyl silver acting then as a nucleophile.[1,20]

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[20] (a) Shahi, S. P.; Koide, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 2525−2527. (b) Naka, T.; Koide, K. *Tetrahedron Lett.* **2003**, *44*, 443−445.

In conclusion, we have shown that alkynyl silver **1** is formed by deprotonation of a π-complex in situ obtained after mixing the corresponding alkyne and silver salt in different solvents. As silver alkynes do form in situ under a variety of conditions, it is very likely that the silver catalysts in alkynylation reactions and in our coupling reactions proceed through such intermediates. Due to its similarity and other indirect evidence,[9] the Sonogashira cross-coupling reaction should proceed through the same reaction steps (Scheme 5, m = Cu).

Experimental Section

General Comments. NMR spectra were recorded using a forward multinuclear probe head with z-gradients. The proton spectra were recorded at a frequency of 400 MHz and the ^{13}C spectra at 100.577 MHz. During recording ^{13}C spectra protons were decoupled. Decoupling showed no line-narrowing effect. The ^{109}Ag spectra were recorded on a 600 MHz spectrometer using a 10 mm TBI probe head. The ^{109}Ag spectra have been recorded at a frequency of 27.912 MHz. The 90° pulse was set to 65 μs with a power of 3 dB. Further, d1 was 5 s, and DE was set to 40 μs to prevent important baseline rolling. The spectral width was 2000 ppm and the acquisition time 1.170 s. For 1 M solution, 200 scans were used as a minimum value. The chemical shift is given in ppm with respect to TMS and to $CDCl_3$ in ^{13}C spectra (77.0 ppm). The ^{109}Ag spectra as well as ^{13}C spectra in solvents other than $CDCl_3$ were referenced to the Ξ scale using the recommended IUPAC Ξ values for $^{13}C = 25.145020$ MHz and $^{109}Ag = 4.653533$ MHz. The coupling constants are given in hertz. The ESI-MS spectra were performed with a triple quadripole spectrometer in the positive mode.

Preparation of Hexyn-1-yl silver 1.[5a] In a flask protected from light, 2.2 equiv (with respect to hexyne) of silver nitrate were dissolved in 5 equiv of methanol and 3 equiv of water. A 25% aqueous ammonia solution was then added dropwise until the solution became clear. 1-Hexyne was added dropwise, and the solution was stirred at room temperature for 30 min. The precipitate formed was filtered off and washed with water until the washing water reached pH 7. The solid was dried in a vacuum for one night.

^1H ($CDCl_3$): δ 0.94 (t, $J = 7.6$ Hz, 3H, H6); 1.46 (sext, $J = 7.6$ Hz, 2H, H5); 1.68 (m, 2H, H4); 2.50 (2H, t, $J = 5.9$ Hz, H3). ^{13}C ($CDCl_3$): δ 13.7 (C6); 21.7 (C3); 22.5 (C5); 31.8 (C4); 80.2 (C1); 129.9 (C2). ^{109}Ag ($CDCl_3$): δ 1061. IR ($1/\nu$ [cm^{-1}]): 151, 722, 820, 894, 937, 1030, 1103, 1244, 1287, 1318, 1377, 1402, 1463, 1709, 2041, 2857, 2928, 2955, 3457. Anal. Calcd for C_6H_9Ag: C 38.13, H 4.80. Found: C 37.99, H 4.95.

In-Situ Generated Silver Hexyne π-Complex 3. ^1H (C_6D_6): δ 0.72 (t, $J = 7.2$ Hz, 3H, H6); 1.15 (m, 2H, H5); 1.25 (m, 2H, H4); 2.02 (dt, $J = 1.8$ Hz, $J = 7.2$ Hz, 2H, H3), 2.71 (d, $J = 1.76$ Hz, 1H, H1). ^{13}C (C_6D_6): δ 13.6 (C6); 18.8 (C5); 22.1 (C4); 31.0 (C3); 64.2 (C1); 88.1 (C2); 121.4 (CF_3). ^{109}Ag (C_6D_6): δ 416. HR-MS: calcd for $C_6H_{10}Ag$ 188.9833, found 188.9618.

***N,N*-Diisopropylethylammonium Triflate 4.**[21] A 87 μL (0.5 mmol) portion of DIPEA was dissolved in 0.5 mL of DMF-d_7 in an NMR tube, and 44 μL (1 equiv) of trifluoromethane sulfonic acid was added. The tube was shaken well until the precipitate dissolved.

^1H (DMF-d_7): δ 1.37 (t, $J = 5.4$ Hz, 3H, CH_2CH_3); 1.39 (d, $J = 6$ Hz, 12H, CH_3CH); 3.31 (sept, $J = 6$ Hz, 2H, CH_3CH); 3.81 (q, $J = 5.4$ Hz, 2H, CH_3CH_2); 8.20 (s br, 1H, NH). ^{13}C (DMF-d_7): δ 12.8; 17.5; 43.0; 54.9; 121.5 (q, $J = 1280$ Hz, CF_3).

NMR Survey of the Reaction: A 41 mg sample of hexyne (0.5 mmol) was placed in an NMR tube, and 0.5 mL of the corresponding deuterated solvent was added, giving a 1 M solution. Then 0.5 equiv of silver triflate was added, and the ^1H and ^{13}C NMR spectra were recorded. Then, 1.25 equiv of DIPEA was added. A voluminous white precipitate was formed. The NMR spectra were also recorded. For all silver NMR spectra, the quantity of product and solvents was multiplied by 6 and a 10 mm diameter tube was used.

MS Survey of the Reaction. The same procedure as for the NMR survey was followed, but a nondeuterated solvent was used.

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Supporting Information Available: ^1H, ^{13}C, and ^{109}Ag NMR spectra of hexyn-1-yl silver in C_6D_6 and a ^{109}Ag NMR spectrum of AgOTf in C_6D_6 are provided. ^1H, ^{13}C, and ^{109}Ag NMR spectra and an ESI-MS spectrum of a 1:1 mixture of 1-hexyne and AgOTf and ^1H, ^{13}C, and ^{109}Ag NMR spectra of a 1:1:1 mixture of 1-hexyne, AgOTf, and DIPEA are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753–1755. Gionta, G.; Lillocci, C. *J. Phys. Org. Chem.* **1993**, *6*, 187–192.