Notes

Expeditious Preparation of η^3-Allylpalladium Tetrafluoroborates Using the 2,4,6-Triphenylpyridine Neutral Leaving Group

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Summary: N-Allyl-2,4,6-triphenylpyridinium tetrafluoroborates react with stoichiometric amounts of Pd(0) and phosphines to afford (η^3-allyl)palladium tetrafluoroborates, whereas allyltriphenylphosphonium tetrafluoroborates are produced if the amount of Pd(0) is kept catalytic.

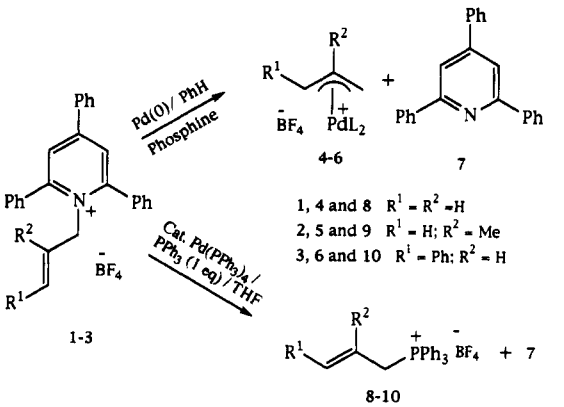
Preparation of cationic (η^3-allyl)palladium complexes of the general type **4–6** traditionally involves the reaction of the corresponding bis(μ-chloro)bis(η^3-allyl)dipalladium compounds with salts of noncoordinating anions.[1] Only a few examples of the use of other anionic leaving groups such as acetoxy,[1m] formyloxy,[2] and trifluoroacetoxy[1e,3] have been reported.

Neutral leaving groups have met with little popularity for the preparation of cationic allylpalladium complexes. To the best of our knowledge only tris(dimethylamino)-phosphine oxide and tetramethylthiourea were used for such purposes.[4]

In the course of a study on the electronic effects on the regioselectivity of the Pd(0)-catalyzed allylation of nucleophiles, we required cationic cinnamyl and 1,3-diarylallylpalladium complexes and we experienced difficulties in the isolation procedure when the usual method from chloroallylpalladium dimers was adopted.[1b] Therefore we deemed it interesting to find an expeditious method to prepare the title cationic complexes. In particular we were interested in maximal simplicity in the isolation procedure.

We focused our attention on the chemistry of pyridines

Scheme I



as neutral leaving groups, initiated by Balaban[5] and developed by Katritzky.[6] The required *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborates such as **1–3** are easily accessible from 2,4,6-triphenylpyrylium tetrafluoroborate[6] and allylamines. Our method rests ultimately upon the availability of allylamines, for which different synthetic methods covering a broad variety of structural types have been reported.[7-9]

Scheme I and Table I summarize our results. *N*-Allyl-2,4,6-triphenylpyridinium tetrafluoroborates **1–3**[10] react in benzene either with bis(dibenzylideneacetone)palladium(0) and 2 equiv of triphenylphosphine (or 1 equiv of a bidentate phosphine, see Table I) (method A) or with 1 equiv of tetrakis(triphenylphosphine)palladium(0) or of bis(1,2-(diphenylphosphino)ethane)palladium(0)[12]

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(8) For allylamine preparation through Pd(0)-catalyzed allylation of nucleophiles (Tsuji–Trost reaction), see: (a) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451. (b) Murahashi, S.-I.; Taniguchi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292.

(9) For allylamine preparation through Pd(0)-catalyzed coupling of aryl halides with olefin (Heck reaction), see: Malek, N. J.; Moormann, A. E. *J. Org. Chem.* **1982**, *47*, 5395.

(10) **1**, mp 117–118 °C (lit.[11] mp 164–166 °C); **2**, mp 189–191 °C; **3**, mp 138–142 °C. Salts **1–3** gave correct elemental analyses.

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Table I. η^3-Allylpalladium Tetrafluoroborates 4–6[a]

	R¹	R²	L₂	method (%) A[b]	method (%) B[c]	mp (dec), °C (dec)
4a	H	H	PPh_3, PPh_3	87	57[d]	188–194
4b	H	H	$Ph_2PCH_2CH_2PPh_2$	96	88	193–198
4c[e]	H	H	(2S,3S)-Ph_2PCHMe–$CHMePPh_2$	86	*f*	167–175
5a	H	Me	PPh_3, PPh_3	*f*	98	211–215[g]
5b	H	Me	$Ph_2PCH_2CH_2PPh_2$	90	78	99–105[h]
6a	Ph	H	PPh_3, PPh_3	61	42[i]	220–225
6b	Ph	H	$Ph_2PCH_2CH_2PPh_2$	65	77	195–200

[a] Elemental analysis within ±0.45 but for **4b** (C, +0.65). [b] $Pd(dba)_2$ + 2L. [c] PdL_4. [d] Product **8** (37%) was also formed. [e] $[\alpha]_D = +148°$ ($c = 0.5$, $HCCl_3$). [f] Experiment not performed. [g] Literature mp 219–222 °C.[17] [h] Literature mp 92–99 °C.[17] [i] Product **10** (33%) was also formed.

(method B). Method A is superior. Thus, (η^3-allyl)palladium tetrafluoroborates **4–6** precipitate out in pure form in the indicated yields. Sometimes evaporation and digestion with diethyl ether is required before filtration. The other reaction product, 2,4,6-triphenylpyridine, **7**, remains in solution. When **4a** and **6a** were prepared by method B, they were contaminated by other products identified as **8** and **10**, respectively. Therefore, initial experiments were performed to set up a method to prepare allyltriphenylphosphonium tetrafluoroborates, such as **8–10**. The results are in Scheme I. Treatment of **1–3** with 1 equiv of triphenylphosphine in the presence of 5% molar tetrakis(triphenylphosphine)palladium(0) in THF at room temperature gives in 4–6 h compounds **8–10**, which precipitate out upon evaporation of the solvent to half volume.[13] Palladium(0) is necessary for the formation of **8–10**, since refluxing equimolar amounts of **1** and triphenylphosphine in benzene for 6 h in the absence of palladium produced no reaction. In summary, phosphines are good nucleophiles toward cationic (η^3-allyl)palladium complexes, albeit they have been systematically chosen as stabilizing ligands in Pd(0)-catalyzed allylation of nucleophiles.[15] However, Pd(0)-catalyzed nucleophilic attacks of phosphorus nucleophiles on allylic systems are not without precedent.[1d,16]

(13) **8**, mp 164–166 °C (lit.[14] mp 161–162 °C); **9**, mp 185–188 °C; **10**, mp 188–191 °C.

(14) Takanami, T.; Suda, K.; Ohmori, H.; Masui, M. *Chem. Lett.* **1987**, 1335.

Experimental Section

Bis(triphenylphosphine)(η^3-allyl)palladium Tetrafluoroborate, 4a (Method A, General Procedure). A solution of bis(dibenzylideneacetone)palladium(0) (0.172 g, 0.3 mmol) and triphenylphosphine (0.157 g, 0.6 mmol) in anhydrous benzene (10 mL) was added to a solution of *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborate (0.131 g, 0.3 mmol) in anhydrous benzene (10 mL). The mixture was kept at room temperature for 5 h, and the formed solid was filtered off to afford practically pure **4a** (0.199 g, 87%), mp 188–194 °C dec (from methanol–diethyl ether): IR (KBr) 1481, 1435, 1094, 1058, 998, 748, 695 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.51–3.60 (m, 2H), 3.94–3.96 (m, 2H), 5.90–6.01 (m, 1H), 7.03–7.74 (m, 30H); ^{13}C NMR (62.5 MHz, C_2D_6CO) δ 76.0 (t, averaged $J_{CP} = 14.3$ Hz, 2C), 121.4 (t, $J_{CP} = 6.0$ Hz, 1C), 126.3 (t, $J_{CP} = 7.4$ Hz, 2C), 128.4 (s, 1C), 128.6 (t, $J_{CP} = 22.2$ Hz, 2C), 131.1 (t, $J_{CP} = 7.9$ Hz, 2C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.40 (reference H_3PO_4). Anal. Calcd for $C_{39}H_{35}BF_4P_2Pd$: C, 61.73; H, 4.65. Found: C, 61.80; H, 4.64.

Products **4–6** were all prepared by the same procedure. Sometimes it was necessary to evaporate partially the benzene solution to induce precipitation.

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