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First 2,3-Dialkynyl-1,4-diazabutadienes by Pd-Catalyzed Cross-Coupling of Bis(imidoyl chlorides) and Alkynylstannanes

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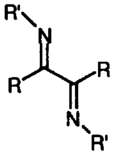
Abstract: A general procedure for a palladium-mediated organyl group transfer from organostannanes to bis(imidoyl chlorides) has been developed on the basis of the $Pd_2(dba)_3{\cdot}CHCl_3$ / $AsPh_3$ catalyst system. This protocol allows the synthesis of 2,3-dialkynyl-1,4-diazabutadienes and of trialkynyl-1,3,5-triazines from cyanuric chloride. © 1997 Elsevier Science Ltd.

Vicinal diimines (1,4-diazabuta-1,3-dienes) **1**, in addition to their established usefulness in constructing heterocyclic ring systems of the imidazole type,[1] have been used frequently as chelating ligands in transition metal complexes.[2] Currently, these complexes attract considerable attention as the integral part of efficient catalyst systems for olefin polymerizations and cross polymerization.[3]



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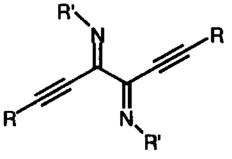
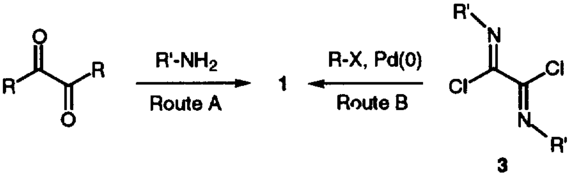


2

We became interested in diazabutadienes as part of our project directed at the synthesis of alkynylated NIR chromophores in which we have identified small acetylenic building blocks as versatile precursors.[4] Surprisingly, and despite many synthetic efforts to explore the chemistry of vicinal diimines, 2,3-dialkynyl substitution of the diazabutadiene backbone as in **2** was previously not realized. Typically, compounds **1** are obtained by condensation of the corresponding diketones with primary amines (route A), a protocol that succeeds only in specific cases with acetylenic precursors due to dominant 1,4-addition of the primary amines to the ynone moiety.[5]

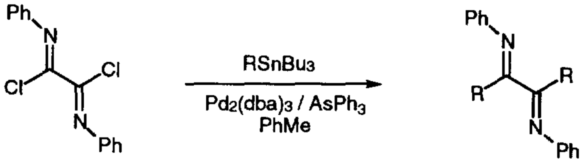


3

A more general strategy to dialkynyl diazabutadienes starts from the bis(imidoyl chlorides) **3**,[6] which should lend themselves to alkynylation by means of a palladium-mediated cross coupling procedure (Route B). While there is literature precedence for this kind of transformation with simple (mono) imidoyl chlorides[7] or *N*-substituted isocyanide dichlorides[8] and organotin derivatives, the bis(imidoyl chlorides) **3** pose a considerable challenge as substrates in palladium catalysis due to their potential as chelating ligands to transition metals. Complexation of one or two molecules of **3** to palladium(0)[9] would most likely interfere with the catalytic activity of the transition metal.

It was therefore not entirely unexpected that initial experiments using standard palladium sources, such as $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, $Pd(PhCN)_2(PPh_3)_2$ or the palladacycle[10] formed from $Pd(OAc)_2$ and P(*o*-tolyl)$_3$, in conjunction with organostannanes and *N,N'*-diphenyl bis(imidoyl chloride) **4** failed to give the desired coupling products. Gratifyingly, however, the dinuclear "ligandless" palladium(0) complex $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylidene acetone) when activated by the addition of excess $AsPh_3$[11] efficiently catalyzes this transformation in toluene at temperatures around 70 °C (table 1).[12]

Table 1. Pd-catalyzed CC-bond forming reactions between bis(imidoyl chlorides) and organostannanes

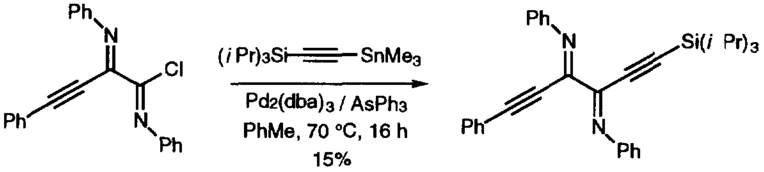


4 **5-9**

Entry	R	t [h] / T [°C]	Yield[a]	Product
1	Bu	72 / 70	11	**5**
2	Ph	24 / 70	67	**6**
3	2-thienyl	3 / 60	28	**7**
4	Ph-C≡C	5 / 50	50	**8**
5	$(i\text{Pr})_3$Si-C≡C[b]	3 / 85	49	**9**

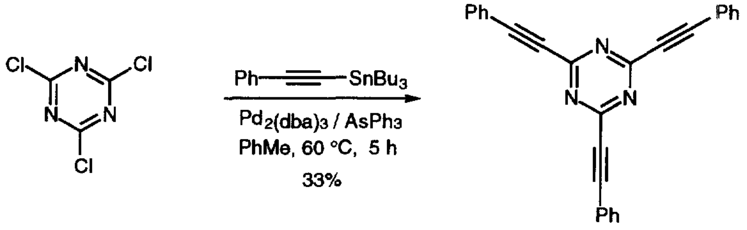
[a]Isolated yields. [b]The analogous Me_3Sn derivative was used.

The yields of isolated coupling products generally reflect the transfer rates of organic groups in palladium mediated Stille coupling reactions.[13] In case of the 2-thienyl derivative (entry 3), the conversion remains incomplete after an initial rapid consumption of the starting material, a behaviour suggestive of product inhibition by 7. The products derived from simple alkenyl (e.g. tributyl-2-phenylethenylstannane or tributyl-1-propenylstannane) or cycloalkenyl (e.g. tributyl-1-cyclohexenylstannane) substrates defied chromatographic isolation. Most important for the design of alkynylated NIR chromophores is the fact that this protocol allows the preparation of the targeted dialkynyl diazabutadienes **8**[14] and **9** in yields of about 70% per coupling step (entries 4 and 5). In addition, the syntheses of **8** always furnished some of the mono-alkynylated derivative **10** as a byproduct which can be converted to the unsymmetrical dialkynyl diazabutadiene **11** in low yield. Methods to obtain compounds like **11** more efficiently using a related palladium-based strategy are currently being explored.



10 **11**

The fact that the catalyst system $Pd_2(dba)_3{\bullet}CHCl_3/AsPh_3$ provides a rather general entry to substituted imines from imidoyl chlorides is highlighted by the peralkynylation of 2,4,6-trichloro-*s*-triazine (cyanuric chloride) **12**, which proceeds in 33% overall yield, again *ca.* 70% per alkyne transfer. Previously, the preparation of alkynyltriazines, an attractive venue for the development of advanced materials and compounds with interesting electrooptical properties, was restricted to the additon of lithium acetylides to prohibitively expensive 2,4,6-trifluoro-*s*-triazine.[15]



12 **13**

In conclusion, the preparation of dialkynyl diazabutadienes proceeds smoothly from bis(imidoyl chlorides) using the $Pd_2(dba)_3{\bullet}CHCl_3/AsPh_3$ catalyst system. Studies to use the dialkynyl diazabutadienes as precursors for acetylenic *N*-heterocycles are under way. First transition metal complexes of the dialkynyl diazabutadienes have been prepared and are being examined for their chemical reactivity.

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12. *General procedure*: A mixture of bis(imidoyl chloride) (1 mmol), organostannane (2 mmol), 10 mol% $Pd_2(dba)_3 \cdot CHCl_3$ and 45 mol% $AsPh_3$ in 20 ml toluene was heated in an argon atmosphere under the conditions specified in table 1. The mixture was filtered through a pad of silica and residual stannane was removed by precipitation with aqueous NaF solution. The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent the residue was chromatographed on SiO_2 using hexane / ethyl acetate 20:1. Analytically pure compounds could be obtained by recrystallization from diethyl ether (**6** and **8**) or hexane (**7** and **10**).
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14. *Analytical data for N,N'*-diphenyl-1,6-diphenylhexa-1,5-diyne-3,4-diimine (**8**): yellow solid, m.p. 174 °C. – IR (KBr): ν = 2213 cm^{-1} (s, C≡C), 1575 (s, C=N). – UV (CH_2Cl_2): λ_{max} (ε) = 252 nm (31700), 282 nm (sh, 23700), 298 nm (sh, 22400), 376 nm (8400). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.5-7.2 (m, 20 H). – ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 150.6 (C), 149.8 (C), 132.6 (CH), 129.8 (CH), 128.5 (CH), 128.3 (CH), 125.9 (CH), 121.4 (C), 121.0 (CH), 99.7 (C≡C), 82.5 (C≡C). – MS (70 eV), *m/z* (%): 408 (36) [M$^+$], 204 (100) [M$^+$/2], 77 (38) [Ph]. – $C_{30}H_{20}N_2$ (408.16): calcd. C 88.20, H 4.94, N 6.86; found C 87.97, H 5.14, N 7.02.
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