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# Palladium-Catalyzed Syntheses of Oxygen- and Nitrogen Heterocycles via Transmetalation of Functionalized Alkynyl Stannanes

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***Abstract:*** The reaction between $CpFe(CO)_2I$, hydroxy- or aminoalkynyl stannanes, and $PdCl_2(CH_3CN)_2$ (8.0 mol. %) generates a reactive iron-alkynyl intermediate that reacts *in situ* with $RCHO/BF_3{\cdot}Et_2O$ to yield an iron oxa- or azacarbeniums quantitatively, further producing oxygen- and nitrogen heterocycles in high yields after $Me_3NO$-oxidation of these carbenium salts. © 1998 Elsevier Science Ltd. All rights reserved.

Alkynyl organometallics of silanes, boranes and stannanes[1] are not as useful as their allyl- propargyl and allenyl species.[2] These alkynyl compounds undergo electrophilic addition with organic carbonyls at the $C_\alpha$ carbon. $CpM(CO)_n(\eta^1$-alkynyl) (M=W, n=3; M=Fe, n=2) compounds may serve as a complementary mode to main group metal analogues in organic syntheses because the regioselectivity for addition of aldehydes to transition metal alkynyl is at the $C_\beta$ carbon via metal-allenylidene intermediate.[3] We recently reported[4] that the reactions between $CpW(CO)_3(\eta^1$-alkynol) and aldehydes/$BF_3.Et_2O$ led to cycloalkenation to yield tungsten-oxacarbenium species as shown in Scheme 1. One major drawback in this cycloalkenation is the requirement for isolation of air-sensitive tungsten-alkynols although the yields were reasonable (60-75%). Since main group metal compounds are more frequently used in organic chemistry,[1-2] it is desired to have a transmetalation catalyst to convert alkynyl complexes of silanes, boranes or stannanes into their corresponding iron species at ambient conditions to expand the reaction scopes. In this study, we choose iron compounds due to its low cost as well as its high reactivity toward electrophiles;[3] iron-mediated cycloalkenation has not been investigated yet. Toward this direction, we report here a palladium-catalyzed transmetalation of functionalized alkynyl stannanes into their iron analogues, and further into oxygen- and nitrogen heterocyclics via iron-mediated cycloalkenation. The whole sequence of reactions were carried out in one-pot operation to avoid isolation of air-sensitive iron-alkynyl compounds and to demonstrate its efficiency.

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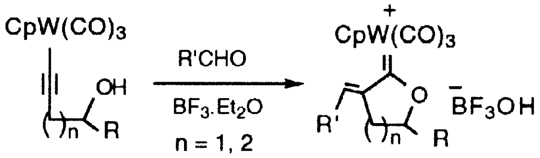
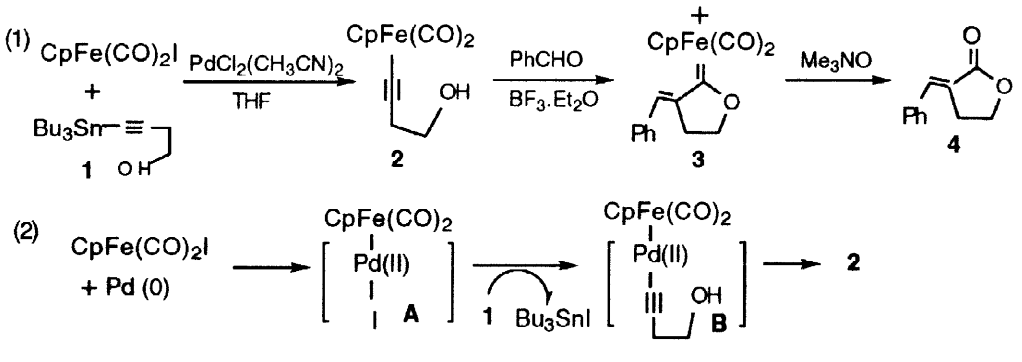
**Scheme 1**

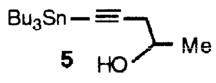
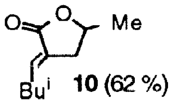
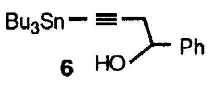
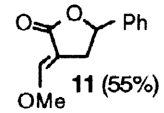
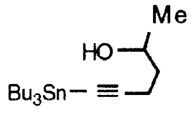
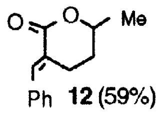
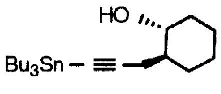
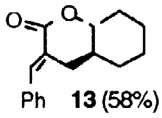
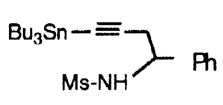
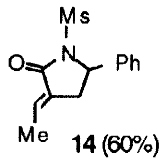


Shown in Scheme 2 (eq 1) is the reaction between α,δ-hydroxyalkynyl stannane **1** (ca. 1.5 g, 1.1 equiv.) and $CpFe(CO)_2I$ (, 1.0 equiv) in the presence of $PdCl_2(CH_3CN)$ catalyst (8.0 mol %) in THF (30 mL, 23 °C, 16 h) to yield iron-alkynyl complex **2**.[5] Formation of **2** presumbly involves the oxidative addition of Pd(0) with $CpFe(CO)_2I$ to yield the bimetallic intermediate **A**;[6] further ligand exchange of this intermediate with alkynyl stannane **1** introduces an alkynyl group,[7] yielding species **B** that subsequently undergoes reductive elimination to afford iron-alkynyl complex **2**. The mother liquor of **2** was reduced in volume (ca. 10-12 mL) under vacuum and further treated with a diethyl ether solution (25-30 mL) of $PhCHO/BF_3{\cdot}Et_2O$ in equimolar proportion to yield a black precipitate, presumbly iron-oxacarbenium **3**. Demetalation of this iron-salt with $Me_3NO$ (3.0 equiv) in $CH_2Cl_2$ at 23 °C delivered α-benzylidene γ-lactone **4** in 81% yield.

**Scheme 2**

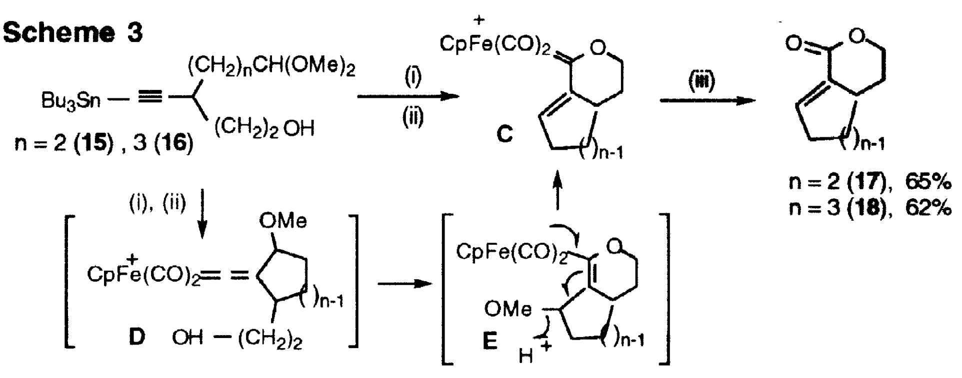


The preceding palladium-catalyzed transmetalation expands the reaction scope of alkynyl stannanes via utilization of iron-mediated cycloalkenation reaction. Table 1 shows more examples for the syntheses of oxygen- and nitrogen heterocyclics with alternations of alkynyl stannanes and aldehydes. The entire syntheses of these heterocyclics were carried out in one-pot operation to demonstrate its efficiency. Sequential treatment of alkynyl stannanes (1.1 equiv) with $CpFe(CO)_2I$ (1.0 equiv) and $PdCl_2(CH_3CN)$ catalyst (8 mol%) in THF (23 °C, 12 h), then with aldehyde/$BF_3.Et_2O$ (1.1 equiv, -40 °C, 2h) produced an iron-oxabenium precipitate; the mother THF liquor was subsequently decanted away and replaced with $CH_2Cl_2$ for $Me_3NO$-demetalation of this salt. The heterocyclics **10-14** were purified on preparative silica-TLC; the isolated yields reported in Table 1 were based on alkynyl stannanes. Entry 1 provides another example for the synthesis of γ-lactone **10** (62 % yield) derived from α,δ-alkynyl stannane **5** and isobutyr-aldehyde; This reaction can also be applied to the system where trimethoxymethane is the electrophile (entry 2) to afford functionalized γ-lactones **11** in 55% yield. We also examined the reaction on α,ε-alkynyl stannanes **7** and **8** to deliver the δ-lactones **12** and **13** in 59 % and 58 % yields respectively. This synthetic method is also useful for the syntheses of γ-lactam **14**, and the yield is 60 % based on α,δ-aminoalkynyl stannane **9**.

| entry | alkynyl stannanes | electrophiles | heterocyclics |
|---|---|---|---|
| 1 |  **5** | Bu$^i$CHO |  **10** (62 %) |
| 2 |  **6** | CH(OMe)$_3$ |  **11** (55%) |
| 3 |  **7** | PhCHO |  **12** (59%) |
| 4 |  **8** | PhCHO |  **13** (58%) |
| 5 |  **9** | EtCHO |  **14** (60%) |

To enhance synthetic utility of this method, we further prepared functionalized alkynylstannanes **15-16** having both a tethered hydroxy and an acetal groups for intramolecular cyclization. Treatment of **15-16** (1.1 equiv) with CpFe(CO)$_2$I (1.0 equiv) and PdCl$_2$(CH$_3$CN)$_2$ (8.0 mol %) in THF (23 °C, THF) , then added BF$_3$·Et$_2$O (1.5 equiv), generated a precipitate believed to be a bicyclic iron-oxacarbenium **C**; formation of this cationic salt is envisaged to derive from a reaction pathway involving two iron ntermediates **D** and **E**. Further oxidation of these salts with Me$_3$NO (3.0 equiv) in CH$_2$Cl$_2$ delivered the unsaturated lactone **17** and **18** in 66% and 62 % yields respectively based on alkynylstannanes **15-16**.

**Scheme 3**



(i) CpFe(CO)$_2$I ( 1.0 equiv), PdCl$_2$(CH$_3$CN)$_2$( 8 mol %), THF (23 °C, 12 h)
(ii) BF$_3$.Et$_2$O (1.5 equiv), (iii) Me$_3$NO (3.0 equiv.), CH$_2$Cl$_2$

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## References and Notes

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(5) The iron-alkynol compounds **2** could be isolated in 65% yield after purification from column chromatography. NMR data for **2**: $^1$H NMR (300 Mz, $CDCl_3$): δ 4.90 (s, 5H), 3.00 (t, *J* = 6.3 Hz, 2H), 2.48 (t, *J* = 6.3 Hz, 2H), 2.10 (br s, 1H); $^{13}$C NMR (300 Mz, $CDCl_3$): 212.6, 110.4, 85.0, 74.3, 61.9, 26.4.

(6) For oxidative addition of Pd(0) species with metal-iodide M-I to form bimetallic M-Pd(II)-I species, see representative examples: a) Hoskins, B. F.; Steen, R. J.; Turney, T. W. *J. Chem. Soc. Dalton. Trans.* **1984**, 1831. b) Braunstein, P.; Knorr, P.; Tiripicchio, A.; Tiripicchio Carmellini, M. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1361.

(7) For the palladium-catalyzed coupling reaction between $CpFe(CO)_2I$ and unfunctionalized alkynyl stannanes, see the precedent example: Crescenzi, R.; Sterzo, C. L. *Organometallics* **1992**, *11*, 4301.