

"Click" Chemistry in Metal Coordination Spheres: Copper(I)-Catalyzed 3+2 Cycloadditions of Benzyl Azide and Platinum Polyynyl Complexes trans- $(C_6F_5)(p-tol_3P)_2Pt(C\equiv C)_nH$ (n = 2-6)

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Summary: Benzyl azide and the terminal polyynyl complexes trans- $(C_6F_5)(p-tol_3P)_2Pt(C \equiv C)_nH$ (n = 2-6) undergo 3+2"click" cycloadditions in the presence of $CuSO_4/ascorbic$ acid to give the 1,2,3-triazoles trans- $(C_6F_5)(p-tol_3P)_2Pt(C \equiv C)_{n-1}$ -

 $C = CHN(CH_2C_6H_5)N = N$, four of which are structurally characterized.

Over the course of the last seven years, the copper(I)catalyzed "click" 3+2 cycloaddition of azides and terminal alkynes^{1,2} has been extended to virtually every class of molecules. Furthermore, numerous *in vivo* applications³ and means of functionalizing a variety of types of solid phases⁴ have been developed. However, the inorganic and organometallic communities have come relatively late to this game. Outside of robust ferrocenyl systems,⁵ there have only been a handful of click reactions conducted in metal coordination spheres. These include the derivatization of bridging formamidinate, porphyrin, carbene, and pincer ligands that contain aryl C=CH moieties as described by Ren,⁶ Collman,⁷ Casarrubios and Sierra,⁸ and van Koten.^{9,10}

We have had an ongoing interest in platinum terminal polyynyl complexes of the formula trans-(Ar)(p-tol₃P)₂Pt-(C=C)_nH (PtC_{2n}H) and their oxidative homocoupling to diplatinum polyynediyl complexes trans,trans-(Ar)(p-tol₃-

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P)₂Pt(C=C)_{2n}Pt(Pp-tol₃)₂(Ar) (PtC_{4n}Pt).¹¹ The latter exhibit surprisingly high stabilities, with decomposition temperatures in excess of 150 °C even at chain lengths of 20 to 28 carbon atoms (Ar = p-tol). However, the educts become exceedingly labile at longer chain lengths, with hexatriynyl complexes (PtC₆H) representing the limit for isolability in spectroscopically pure form. This also generally applies to purely organic systems.¹² The trick to synthesizing PtC₂₄Pt and PtC₂₈Pt (Ar = p-tol) is to generate the dodecahexaynyl and tetradecaheptaynyl complexes PtC₁₂H and PtC₁₄H under conditions that maximize the chances for subsequent bimolecular coupling as opposed to unimolecular or solvent-mediated decomposition.^{11b}

As such, we were interested in investigating the potential utility of copper(I)-promoted azide cycloadditions as diagnostic tests for the generation of labile $PtC_{2n}H$ species. Importantly, Tykwinski has established the applicability of such trapping reactions to organic conjugated terminal diynes, triynes, and tetraynes.¹³ In this communication, we report that analogous reactions can be realized with platinum derivatives, including the first click cycloadditions involving any type of terminal pentayne or hexayne. The resulting organometallic triazoles are exceedingly stable and readily crystallize.

As shown in Scheme 1 (top), equimolar quantities of the pentafluorophenyl-substituted complex *trans*-(C_6F_5)(*p*-tol₃-P)₂Pt($C\equiv C$)₂H (**Pt'C₄H**)^{11a} and benzyl azide were combined in DMF. Then aqueous CuSO₄ and ascorbic acid, a standard recipe for generating copper(I),² were added. After ca. 16 h at room temperature, a chromatographic workup gave a new complex, 1 (65% based upon the structure established below), which was characterized by microanalysis and NMR (¹H, ¹³C, ³¹P, ¹⁹F) and IR spectroscopy, as summarized in the Supporting Information.

The ¹³C NMR spectrum of **1** (CDCl₃) showed only a single C=C linkage (δ 109.0, 101.9 ppm), and the =CH ¹H NMR signal of **Pt'C₄H** (δ 1.46 ppm) was replaced by one with a chemical shift plausible for a triazole =CH moiety (s, 6.15 ppm). Crystals were obtained from CH₂Cl₂/pentane, and the X-ray structure was determined as described in the Supporting Information. The resulting thermal ellipsoid diagram, depicted in Figure 1, confirmed **1** to be the expected

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Scheme 1. Syntheses of "Click" Adducts $1-5^a$



^{*a*} Conditions A₁: THF, wet *n*-Bu₄N⁺F⁻ in THF and then ClSiMe₃. Conditions A₂: DMF, benzyl azide, cat. CuSO₄ and ascorbic acid, H₂O. Conditions B: THF, then benzyl azide in DMF, then cat. aqueous CuSO₄ and ascorbic acid, then wet *n*-Bu₄N⁺F⁻ in THF.

1,4-disubstituted 1,2,3-triazole. Metrical parameters are supplied in the Supporting Information.

Next, $Pt'C_6H$ and $Pt'C_8H$ were generated by the protodesilylation of the corresponding triethylsilyl derivatives $Pt'C_6SiEt_3$ and $Pt'C_8SiEt_3$ with wet *n*-Bu₄N⁺F⁻ in THF ("conditions A₁" in Scheme 1).^{11a} This was followed by the addition of ClSiMe₃, an additive that has proved beneficial in subsequent homocoupling reactions.¹¹ A DMF solution of benzyl azide and aqueous solutions of CuSO₄ and ascorbic acid were then introduced ("conditions A₂"). Workups gave the 3+2 cycloadducts 2 and 3 in 70% and 60% yields. These were characterized analogously to 1.

When a similar reaction was attempted with $Pt'C_{10}SiEt_3$,¹⁴ no tractable products were obtained. This was seen as consistent with a rapid independent decomposition of $Pt'C_{10}H$, in accord with results obtained in oxidative homocouplings.¹¹ Thus, protodesilylations of $Pt'C_{2n}SiEt_3$ were attempted in the *presence* of all reactants required for

subsequent 3+2 cycloadditions (conditions B, Scheme 1). Slight excesses of benzyl azide were now employed (2.0-1.5 equiv), and wet *n*-Bu₄N⁺F⁻ was the last species added. A model reaction with Pt'C₆SiEt₃ gave 2 in 62% yield after workup, establishing the compatibility of the various reactants. Analogous procedures were then applied to Pt'C₁₀SiEt₃ and Pt'C₁₂SiEt₃. As shown in Scheme 1, the target 3+2 cycloadducts 4 and 5 were isolated in 74% and 78% yields.

Crystals of 2-4 or solvates thereof could also be obtained. Those of 3 and 4 were yellow, whereas 1 and 2 were colorless. The X-ray structures were determined, and the resulting thermal ellipsoid plots are given in Figure 1. Although the bond lengths and angles about platinum (Supporting Information) are similar, there are minor conformational differences. For example, 3 exhibits the most linear Pt-C=C-C= segment (sum of bond angles 355.3° vs $337.7-345.5^{\circ}$).¹⁵ Also, 1 and 4 exhibit pronounced

^{(14) (}a) This complex is available from the cross-coupling of $Pt'C_6H$ and HC_4SiEt_3 , analogously to closely related procedures described earlier.¹¹ (b) Kuhn, H. *Doctoral Dissertation*, Universität Erlangen-Nürnberg, **2009**.

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Figure 1. Thermal ellipsoid plots (50% probability level) of the crystal structures of (top to bottom) 1, 2, 3, and 4.

 $C_6H_4CH_3/C_6F_5/C_6H_4CH_3$ stacking interactions, as found in many other crystal structures of *trans*- $(C_6F_5)(p$ -tol₃P)₂Pt species.^{11a,16} This can be quantified by the average distances between the centroids of the C_6F_5 and $C_6H_4CH_3$ rings (3.497–3.554 Å for **1**, **4** vs 3.955–3.975 Å for **2**, **3**), and the near-zero C_{ipso} –P–Pt– C_{ipso} torsion angles (4.74(15)° and $-5.75(15)^{\circ}$ for **1**, 10.21(15)° and 14.27(15)° for **4**, and higher average values for **2** and **3**).

A few spectroscopic trends merit note. For example, the C=CC=CHN ¹H NMR signals of 1-5 show a pronounced monotonic downfield shift (δ 6.15, ca. 7.09 (overlapping signals), 7.39, 7.51, 7.56 ppm). The Brønsted acidities of conjugated terminal polyynes R(C=C)_nH are known to increase with chain length.¹⁷ Hence, the Pt(C=C)_n- moieties become increasingly more electron withdrawing. The ³¹P NMR chemical shifts exhibit a weaker monotonic trend (18.0 to 17.2 ppm), paralleled by an increase in the ¹J_{PPt} values (2613, 2624, 2631, 2651, 2687 Hz).

Finally, $Pt'C_4H$ and the rhenium azide complex $(\eta^5 - C_5H_5)Re(NO)(PPh_3)(N_3)^{18}$ were combined under conditions analogous to those in Scheme 1. However, no reaction was observed. Nonetheless, other types of cycloadditions of metal azide complexes and alkynes have been reported.¹⁹

In summary, we have shown that platinum polyynyl complexes with terminal CH linkages readily undergo copper(I)-promoted "click" 3+2 cycloadditions with organic azides. These reactions can furthermore be effected by conducting protodesilylations of triethylsilyl polyynyl complexes in the presence of the azide and copper(I) catalyst. This enables the trapping of labile terminal polyynes that would undergo rapid independent decomposition of the time scale of sequential reactions. There are a number of obvious extensions of this work, such as to reactants with still longer sp carbon chains and ruthenium catalysts that afford complementary cycloaddition regiochemistries,²⁰ and further efforts will be reported in due course.

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Supporting Information Available: Experimental procedures and characterization for all new compounds, and CIF files with crystallographic data for 1–4. This material is available free of charge via the Internet at http://pubs.acs.org.

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