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Communication

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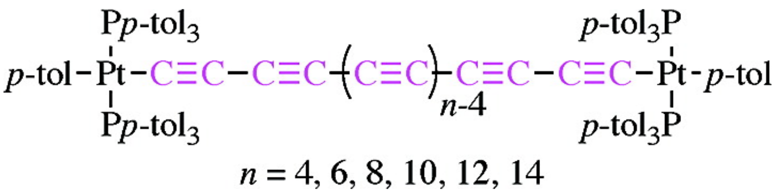

$$p\text{-tol}-\underset{Pp\text{-tol}_3}{\overset{Pp\text{-tol}_3}{Pt}}-C\equiv C-C\equiv C-(C\equiv C)_{n-4}-C\equiv C-C\equiv C-\underset{p\text{-tol}_3P}{\overset{p\text{-tol}_3P}{Pt}}-p\text{-tol}$$

$n = 4, 6, 8, 10, 12, 14$

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A Synthetic Breakthrough into an Unanticipated Stability Regime: Readily Isolable Complexes in which $C_{16}-C_{28}$ Polyynediyl Chains Span Two Platinum Atoms

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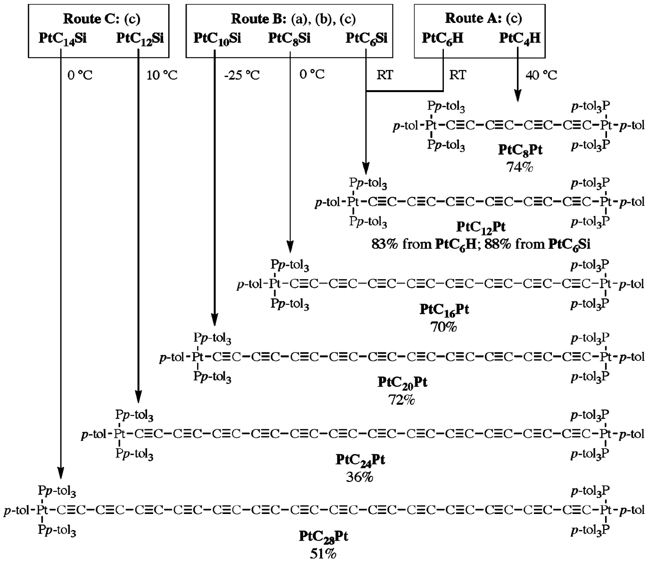
Polyynediyl moieties, $(C{\equiv}C)_n$, are seeing increasing use as connectors in sophisticated molecular assemblies.[1] There are many applications for which very long segments would be desirable. However, available data suggest certain stability thresholds. For example, *tert*-butyl-capped polyynes $Me_3C(C{\equiv}C)_nCMe_3$ with $n = 4-8$, 10, and 12 have been isolated, but that with $n = 12$ decomposed within 8 min at room temperature to an insoluble black material.[2] In the triethylsilyl series, $Et_3Si(C{\equiv}C)_nSiEt_3$, species with $n = 6$ and 8 were isolable, but decomposed at room temperature or below; higher homologues ($n = 10$, 12, 16) were only generated in solution.[3] In more recent work, Tykwinski has shown analogues with bulkier tri(isopropyl)silyl endgroups ($n = 8$, 10) to be stable to ≥105 °C.[4] Hirsch has described two polyyne series with 3,5-disubstituted aryl endgroups, the highest members of which ($n = 8-10$) were stable solids at room temperature.[5] We have studied polyyne series with transition metal endgroups.[6,7] With the rhenium fragment $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$, the complex with $n = 10$ was isolable, but noticeably more labile than lower homologues.[6] With the pentafluorophenyl platinum fragment $(C_6F_5)(P\textit{p}\text{-tol}_3)_2Pt$, only complexes with $n \leq 8$ could be synthesized in quantity. However, traces of higher homologues with appreciable lifetimes at room temperature were detected by HPLC.[7]

Given the earlier studies sketched above, there has been a long-standing consensus that polyynes with $n \geq 12$ should not be stable as solids at room temperature. However, some of the more recent data have provided grounds for cautious optimism, provided that various synthetic problems with carbon chain extension could be surmounted. In this communication, we report new methodology that enables previous chain length "records" for stable polyynes to be shattered. The resulting air-stable, *p*-tolyl-substituted diplatinum complexes provide the closest models yet for the elusive one-dimensional carbon allotrope, carbyne.[8] Furthermore, there is every indication that the stability regime extends considerably beyond the title compounds.

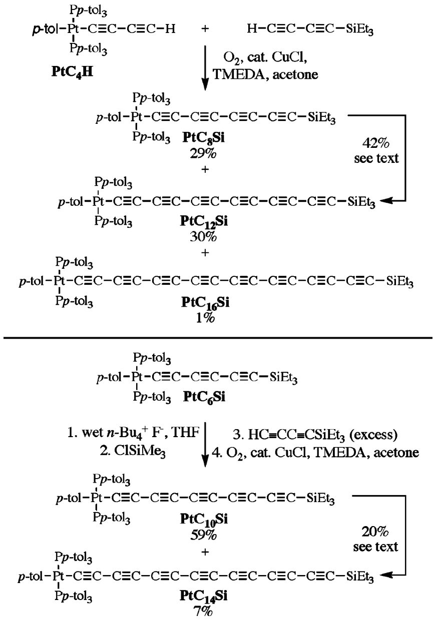
In earlier work, we described the oxidative cross-coupling of *trans*-(*p*-tol)(*p*-tol$_3$P)$_2$Pt(C≡C)$_2$H (PtC$_4$H) and excess $HC{\equiv}CSiEt_3$ (O_2, cat. CuCl, TMEDA, acetone) to give **PtC$_6$Si** (Si = SiEt$_3$).[9] Reaction with wet $n\text{-}Bu_4N^+F^-$ gave the labile but isolable hexatriynyl complex **PtC$_6$H**, which could be similarly cross-coupled to **PtC$_8$Si**. When **PtC$_4$H** and **PtC$_6$H** were analogously reacted in the absence of $HC{\equiv}CSiEt_3$, homocoupling to **PtC$_8$Pt** (74%, yellow) and **PtC$_{12}$Pt** (83%, orange) occurred (Scheme 1, route A). However, efforts to extend these sequences were unsuccessful. Problems included (a) the dramatically decreasing stability of **PtC$_x$H** with chain length, and (b) an increasing tendency for homocoupling of **PtC$_x$H** at the expense of cross-coupling. The same difficulties were encountered with related pentafluorophenyl platinum complexes.[7] The homocoupling rates show an empirical correlation with the Brønsted acidities, which increase with chain length for terminal polyynes.[10] We therefore wondered whether higher homologues of $HC{\equiv}CSiEt_3$, which would be more acidic, would give better cross-coupling results.

Scheme 1. Syntheses of Diplatinum Complexes[a]



[a] Conditions: (a) wet $n\text{-}Bu_4N^+F^-$, acetone; (b) $ClSiMe_3$; (c) O_2, cat. CuCl, TMEDA, acetone.

Scheme 2. Four-Carbon sp Chain Extension Reaction



As shown in Scheme 2 (top), an analogous cross-coupling of **PtC$_4$H** and the butadiyne $H(C{\equiv}C)_2SiEt_3$ (18 equiv)[6,11] was at-

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tempted. Chromatography gave, in inverse order of elution, the target complex **PtC$_8$Si** (29%), **PtC$_{12}$Si** (30%; orange), and a small amount of **PtC$_{16}$Si** (1%; deep red).[12] The simplest rationale for the formation of the higher homologues would involve the competing desilylation of **PtC$_x$Si** under the reaction conditions, a subject treated further below. Next, **PtC$_6$Si** and n-Bu$_4$N$^+$F$^-$ were combined (Scheme 2, bottom) to generate **PtC$_6$H**, which was treated in situ with ClSiMe$_3$[13] and then H(C≡C)$_2$SiEt$_3$ under cross-coupling conditions. Chromatography gave **PtC$_{10}$Si** (59%, orange) and **PtC$_{14}$Si** (7%, red). Similar smaller-scale sequences with **PtC$_8$Si** and **PtC$_{10}$Si** gave **PtC$_{12}$Si** (42%) and **PtC$_{14}$Si** (20%). To our knowledge, **PtC$_{14}$Si** and **PtC$_{16}$Si** are the longest polyynes with a single transition metal endgroup.

Homocouplings of **PtC$_x$H** were again investigated, but now with samples that had been generated from **PtC$_x$Si** and n-Bu$_4$N$^+$F$^-$ in situ and treated with ClSiMe$_3$.[13] As shown in Scheme 1 (route B), reactions of **PtC$_6$Si**, **PtC$_8$Si**, and **PtC$_{10}$Si** gave **PtC$_{12}$Pt** (88%) and the new complexes **PtC$_{16}$Pt** (70%, red) and **PtC$_{20}$Pt** (72%, red).[12] Note the progressively lower temperatures required (RT, 0 °C, −25 °C). However, similar sequences with **PtC$_{12}$Si** (−25 or −45 °C) gave no tractable products. The rate of decomposition of the intermediate **PtC$_{12}$H** was presumed to be too rapid.

Thus, a modified protocol was investigated. Qualitatively, the rates of desilylation of **PtC$_x$Si** appeared to increase with chain length, in accord with the C$_x$ leaving group abilities expected from the Brønsted acidity trends noted above.[10] Also, desilylation occurs under the conditions of Scheme 2 (top), in which fluoride ion is absent. We therefore wondered whether **PtC$_{12}$Si** might desilylate to **PtC$_{12}$H** under the homocoupling conditions, promoted by adventitious water or other nucleophiles.[14] Since **PtC$_{12}$H** would be generated *in the presence* of an oxidizing agent, homocoupling might better compete with decomposition (similar factors likely facilitate multiple heterocouplings in Scheme 2). As shown in Scheme 1 (route C), **PtC$_{12}$Si** was so reacted at 10 °C (7 h). Chromatography gave **PtC$_{24}$Pt** (36%, deep red), along with recovered **PtC$_{12}$Si** (38%). An analogous reaction of **PtC$_{14}$Si** at 0 °C (58 h) gave **PtC$_{28}$Pt** (51%, deep red).

The **PtC$_x$Pt** complexes were obtained as air-stable, analytically pure powders. **PtC$_{20}$Pt**, **PtC$_{24}$Pt**, and **PtC$_{28}$Pt** showed no significant decomposition after several days, although they slowly decomposed in solution. Lower homologues were stable for months. Thermolyses were monitored by DSC and TGA (Supporting Information). The decomposition points of **PtC$_{12}$Pt** and **PtC$_{16}$Pt** were ca. 200 °C, and those of **PtC$_{20}$Pt**, **PtC$_{24}$Pt**, and **PtC$_{28}$Pt** were 150−140 °C. In no case did any mass loss occur below 200 °C. From the crystal structure of **PtC$_{12}$Pt**,[9] the platinum−platinum separation in **PtC$_{28}$Pt** can be estimated as 38.8 Å.

As noted above, the colors of **PtC$_x$Pt** progressively shifted from yellow to deep red, consistent with the UV−visible spectra in Figure 1. As usual for series of polyynes,[2−7] increasing numbers of progressively more intense and red-shifted bands were observed. In the case of **PtC$_{28}$Pt**, the molar extinction coefficient ϵ remained above 185 000 M^{-1} cm^{-1} from 360 through 515 nm (402 000 M^{-1} cm^{-1} at $\lambda_{\max}$ (489 nm)), tailing to less than 10 000 M^{-1} cm^{-1} only at 560 nm. The nature of the transitions has been analyzed in detail elsewhere.[15] The NMR and IR properties were similar to those of other metal-capped polyynes[6,7] and will be discussed in our full paper.

In summary, diplatinum adducts of polyynediyls consisting of as many as 28 carbon atoms have been synthesized by generating the labile **PtC$_x$H** complexes in the presence of a suitable oxidizing agent (Scheme 1, route C). There is no indication that a feasibility limit has been reached with the highest homologue **PtC$_{28}$Pt**. This represents a breakthrough into an unanticipated stability regime, which we expect can be extended to other polyynes with bulky and/or electropositive endgroups. Although product mixtures are obtained in Scheme 2, we anticipate that this can be avoided with other silicon endgroups; however, for many purposes, easily separated mixtures of oligomers are advantageous. The elaboration of the compounds reported herein to diplatinum complexes with *odd* numbers of triple bonds and still longer C$_x$ chains, as well as more complex assemblies[16,17] will be described in future publications.

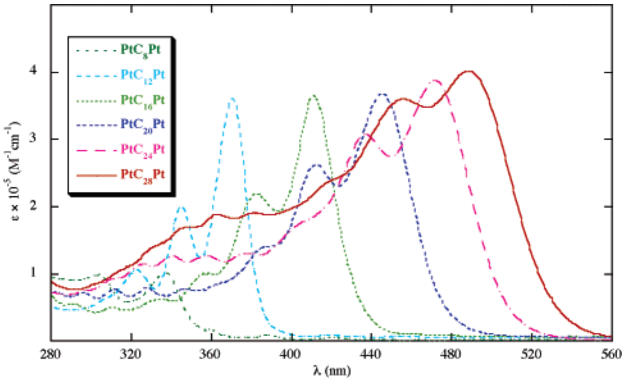

Figure 1. UV−visible spectra of **PtC$_x$Pt** (1.25×10^{-6} in CH$_2$Cl$_2$).

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Supporting Information Available: Experimental procedures and characterization[12] for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) All new compounds were characterized by IR, NMR (^{1}H, ^{13}C, ^{31}P), and UV−visible spectroscopy, mass spectrometry, microanalysis, and DSC/TGA, as summarized in the Supporting Information.
(13) This reagent, which is necessary for the success of the couplings, is believed to serve as a F$^-$ ion scavenger.[7]
(14) For the in situ desilylation and homocoupling of R(C≡C)$_n$SiMe$_3$ species (K$_2$CO$_3$, Cu(OAc)$_2$·H$_2$O, pyridine), see: Haley, M. M.; Bell, M. L.; Brand, S. C.; Kimball, D. B.; Pak, J. J.; Wan, W. B. *Tetrahedron Lett.* **1997**, *38*, 7483.
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