

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, $(C=C)_n$, 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 $Me_3C(C=C)_nCMe_3$ with n =4-8, 10, and 12 have been isolated, but that with n = 12decomposed within 8 min at room temperature to an insoluble black material.² In the triethylsilyl series, $Et_3Si(C=C)_nSiEt_3$, 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)silvl endgroups (n = 8, 10) to be stable to ≥ 105 °C.⁴ Hirsch has described two polypne series with 3,5disubstituted 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 (η^5 -C₅Me₅)Re(NO)(PPh₃), the complex with n = 10 was isolable, but noticeably more labile than lower homologues.⁶ With the pentafluorophenyl platinum fragment $(C_6F_5)(Pp-tol_3)_2Pt$, 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 longstanding consensus that polyynes with $n \ge 12$ 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 onedimensional 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-tol₃P)₂Pt(C=C)₂H (PtC₄H) and excess HC=CSiEt₃ (O₂, cat. CuCl, TMEDA, acetone) to give PtC_6Si (Si = SiEt₃).⁹ Reaction with wet n-Bu₄N⁺F⁻ gave the labile but isolable hexatriynyl complex PtC₆H, which could be similarly cross-coupled to PtC₈Si. When PtC₄H and PtC₆H were analogously reacted in the absence of HC=CSiEt₃, homocoupling to PtC₈Pt (74%, yellow) and PtC₁₂Pt (83%, orange) occurred (Scheme 1, route A). However, efforts to extend these sequences were unsuccessful. Problems included (a) the dramatically decreasing stability of PtC_xH with chain length, and (b) an increasing tendency for homocoupling of PtC_xH 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





^{*a*} Conditions: (a) wet n-Bu₄N⁺F⁻, acetone; (b) ClSiMe₃; (c) O₂, cat. CuCl, TMEDA, acetone.

Scheme 2. Four-Carbon sp Chain Extension Reaction



 $HC \equiv CSiEt_3$, which would be more acidic, would give better cross-coupling results.

As shown in Scheme 2 (top), an analogous cross-coupling of PtC_4H and the butadiyne $H(C \equiv C)_2SiEt_3$ (18 equiv)^{6,11} was at-

tempted. Chromatography gave, in inverse order of elution, the target complex PtC₈Si (29%), PtC₁₂Si (30%; orange), and a small amount of PtC₁₆Si (1%; deep red).¹² The simplest rationale for the formation of the higher homologues would involve the competing desilylation of PtC_xSi under the reaction conditions, a subject treated further below. Next, PtC₆Si and n-Bu₄N⁺F⁻ were combined (Scheme 2, bottom) to generate PtC₆H, which was treated in situ with $ClSiMe_3^{13}$ and then $H(C=C)_2SiEt_3$ under cross-coupling conditions. Chromatography gave PtC10Si (59%, orange) and PtC14-Si (7%, red). Similar smaller-scale sequences with PtC₈Si and PtC₁₀Si gave PtC₁₂Si (42%) and PtC₁₄Si (20%). To our knowledge, PtC₁₄Si and PtC₁₆Si are the longest polyynes with a single transition metal endgroup.

Homocouplings of PtC_xH were again investigated, but now with samples that had been generated from PtC_xSi and $n-Bu_4N^+F^-$ in situ and treated with ClSiMe₃.¹³ As shown in Scheme 1 (route B), reactions of PtC₆Si, PtC₈Si, and PtC₁₀Si gave PtC₁₂Pt (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 PtC₁₂Si (-25 or -45 °C) gave no tractable products. The rate of decomposition of the intermediate PtC₁₂H was presumed to be too rapid.

Thus, a modified protocol was investigated. Qualitatively, the rates of desilvlation of PtC_xSi 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 PtC₁₂Si might desilylate to PtC₁₂H under the homocoupling conditions, promoted by adventitious water or other nucleophiles.¹⁴ Since PtC₁₂H 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), PtC₁₂Si was so reacted at 10 °C (7 h). Chromatography gave PtC₂₄Pt (36%, deep red), along with recovered PtC12Si (38%). An analogous reaction of PtC14Si at 0 °C (58 h) gave PtC₂₈Pt (51%, deep red).

The PtC_xPt complexes were obtained as air-stable, analytically pure powders. PtC₂₀Pt, PtC₂₄Pt, and PtC₂₈Pt 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 PtC12Pt and PtC16Pt were ca. 200 °C, and those of PtC₂₀Pt, PtC₂₄Pt, and PtC₂₈Pt were 150-140 °C. In no case did any mass loss occur below 200 °C. From the crystal structure of PtC₁₂Pt,⁹ the platinum-platinum separation in PtC₂₈-Pt can be estimated as 38.8 Å.

As noted above, the colors of PtC_xPt 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 λ_{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_xH 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 PtC₂₈Pt. This



Figure 1. UV-visible spectra of PtC_xPt (1.25 × 10⁻⁶ in CH₂Cl₂).

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.

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Supporting Information Available: Experimental procedures and characterization¹² for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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