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Bent and Stretched but Not Yet to the Breaking Point: C_8−C_{16} sp Carbon Chains That Span Two Platinum Atoms and the First Structurally Characterized 1,3,5,7,9,11,13,15-Octayne

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In recent years, there has been rapidly increasing interest in compounds with long sp carbon chains.[1−4] One goal has been improved synthetic methodology or chain growth efficiency. Key variables here are the carbon−carbon bond forming steps[5] and the building-block lengths.[6] Another goal has been to approach the limit of the polymeric sp carbon allotrope “carbyne”,[7] the one-dimensional counterpart of graphite and diamond. It has been suggested that carbyne might easily bend and generate other allotropes,[7b] but characterization has remained problematic. Model compounds of increasing lengths would allow key physical properties to be extrapolated, and presage chemical behavior.

There is an extensive older literature of conjugated polyynes with organic endgroups such as *tert*-butyl and trialkylsilyl.[8] These become less stable as the chains are extended and have only been structurally characterized through the pentayne stage (phenyl termini).[9,10] Modern efforts have emphasized cyano[3] and transition metal endgroups.[2,4] There are now two structurally characterized hexaynes, one with (η^5-C_5Me_5)(CO)$_2$Fe and the other with (*p*-tol)(*p*-tol$_3$P)$_2$Pt termini.[4] Longer chain compounds with chiral rhenium endgroups are known, but have so far resisted crystallization.[2b] In this communication, we report a new (pentafluorophenyl)platinum endgroup that is easily elaborated to C_8, C_{12}, and C_{16} systems, and interesting crystal structures of each. The last features the longest sp carbon chain structurally characterized to date.

The reaction of tetrahydrothiophene (SR_2) complex [(C_6F_5)Pt(SR_2)(μ-Cl)]$_2$[11] and *p*-tol$_3$P gave *trans*-(C_6F_5)(*p*-tol$_3$P)$_2$PtCl (**1**) in 93% yield after workup.[12,13] Complex **1**, as all others below, showed one ^{31}P NMR signal and virtual coupling patterns typical of trans square planar bis(phosphine) complexes.[14] The chlorine was replaced by a butadiynyl group as previously described for (*p*-tol)(Ar_3P)$_2$Pt endgroups (excess HC$\equiv$CC$\equiv$CH in HNEt$_2$/THF, cat. CuI),[4b] affording *trans*-(C_6F_5)(*p*-tol$_3$P)$_2$PtC$\equiv$CC$\equiv$CH (**2**) in 81% yield.

Longer chain monoplatinum complexes were sought. Since higher homologues of HC$\equiv$CC$\equiv$CH become increasingly explosive, iterative chain growth strategies were investigated. As shown in Scheme 1, reaction of **2** and excess HC$\equiv$CSiEt$_3$ under Hay conditions (excess O_2, 0.20−0.25 equiv of CuCl/TMEDA in acetone) gave the cross-coupled Pt(C$\equiv$C)$_3$SiEt$_3$ species **3** in 53% yield. Treatment with *n*-Bu$_4$N$^+$ F$^-$ in wet THF gave the Pt(C$\equiv$C)$_3$H complex **4** as a white powder in 85% yield after a low-temperature workup. This material darkened within a few minutes at room temperature, but was stable at −18 °C for several days.

The enhanced lability of longer hydrogen-capped polyynes is well documented.[2b,4b] Thus, we sought coupling conditions that would allow **4** and higher homologues to be used in situ. Accordingly, an *acetone* solution of **3** was treated with *n*-Bu$_4$N$^+$ F$^-$ (wet THF) to generate **4**, followed by ClSiMe$_3$ and the Hay heterocoupling components (O_2, cat. CuCl/TMEDA, excess HC$\equiv$CSiEt$_3$). Chromatography gave the Pt(C$\equiv$C)$_4$SiEt$_3$ complex **5** (Scheme 1) in 30% yield. When ClSiMe$_3$ was omitted, only traces of **5** formed. We hypothesize that fluoride ion must be scavenged prior to coupling. The modest yield is ameliorated by a useful byproduct (**8**, below).

Homocoupling reactions were investigated next. Reaction of **2** under Hay conditions gave the C_8 complex **7** (Scheme 1) in 97% yield. Acetone solutions of **3** and **5** were treated with *n*-Bu$_4$N$^+$ F$^-$ (wet THF), followed by ClSiMe$_3$ and the Hay recipe. Workups gave the C_{12} and C_{16} complexes **8** and **9** in 89−92% yields. Such an impressive yield of **9** would be impossible without the in situ desilylation/coupling protocol. Complexes **7**−**9** were air-stable yellow to apricot powders of extraordinary thermal stability (decomposition points from 234 to 288 °C).[13]

The ^{13}C NMR spectra showed a gradual downfield shift of the PtC$\equiv$ signal (δ 100.6, 106.5, 109.1), a nearly constant PtC$\equiv$*C* signal (δ 96.7−95.0), and the remaining sp carbons clustered between δ 55.9 and 66.7. IR spectra gave two, three, and four

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(13) All new complexes were characterized by IR, NMR, and mass spectroscopy (and many by additional means; see Supporting Information). All except **4** gave correct microanalyses. IR $\nu_{C\equiv C}$ (powder film): **7**, 2152 s, 2011 m; **8**, 2127 m, 2088 s, 1992 m; **9**, 2154 w, 2088 w, 2054 s, 1984 m.

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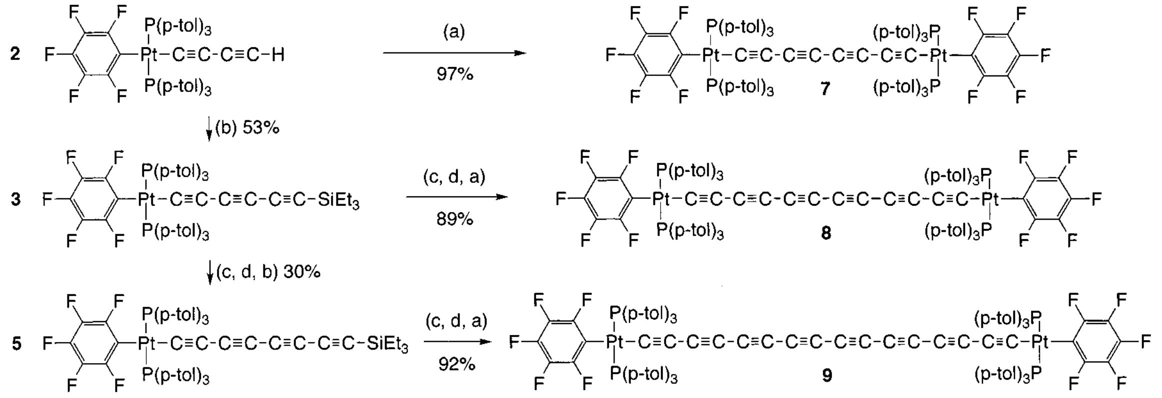
Scheme 1. Syntheses of PtC_xPt Complexes[a]



[a] (a) O_2, acetone, cat. CuCl/TMEDA. (b) $HC\equiv CSiEt_3$ (excess), O_2, acetone, cat. CuCl/TMEDA. (c) Wet n-Bu_4N^+ F^-. (d) $ClSiMe_3$.

$\nu_{C\equiv C}$ bands, respectively.[13] UV−vis spectra (cover, Supporting Information) exhibited increasing numbers of increasingly intense bands, with extinction coefficients topping 600,000 M^{-1} cm^{-1}. Those at longest wavelengths (325, 359, 397 nm) were always the most intense and, from previous studies of conjugated polyynes, may be taken as the $\pi \rightarrow \pi^*$ transitions.[3,15] Cyclic voltammetry (CH_2Cl_2) showed a partially reversible oxidation of **7** ($E°$ vs ferrocene 0.74 V, $i_c > i_a$), and no reductions prior to the solvent limit. Complexes **8** and **9** gave thermodynamically more difficult and less reversible oxidations.

Crystal structures of **7**−**9** were determined (Supporting Information). The features of **7** are routine, similar to those of the (p-tol)($Ph_3P)_2$Pt analogue.[4b] In contrast, **8** shows the most dramatic curvature of any polyyne to date (Figure 1, top). The average of the 12 M−C−C and C−C−C bond angles, 174.6°, is not so different from 180°. However, all of the bends reinforce each other. Accordingly, the Pt−Pt distance (17.009(6) Å) is 5.9% shorter than the sum of the intervening bond lengths (18.067 Å). The Pt−Pt vector defines 33.85(2)° and 19.7° angles, respectively, with C1 and the midpoint of the C6−C7 bond. If the atoms were arrayed in a semicircle, the latter would be 45°. The corresponding values in the most highly curved tetrayne are 17.1(2)° and 8.0°.[9b] The (p-tol)(p-tol$_3$P)$_2$Pt-capped C_{12} complex crystallizes with a much straighter chain.[4b]

Interestingly, the longer chain in **9** is also much straighter, with a slight S-shape (Figure 1, bottom). The average bond angle (178.0°) is greater than in **8**, and the difference between the Pt−Pt distance (23.071(4) Å) and the sum of the intervening bond lengths (23.145 Å) is only 0.3%. Our earlier analyses of bending in tetraynes implicated crystal packing forces.[9b] Indeed, **8** ($P2_1/c$, $Z = 4$; two perpendicular sets of "parallel" chains) and **9** ($P\bar{1}$, $Z = 1$; all chains parallel) exhibit different packing motifs. However, a detailed examination of the lattice of **8** reveals no obvious single-parameter explanation for the curvature (e.g., van der Waals contacts, π interactions, solvate molecules). Otherwise, **7**−**9** exhibit bond lengths and angles very similar to those in other structurally characterized bis(phosphine)platinum(II) alkynyl complexes.[4b,16]

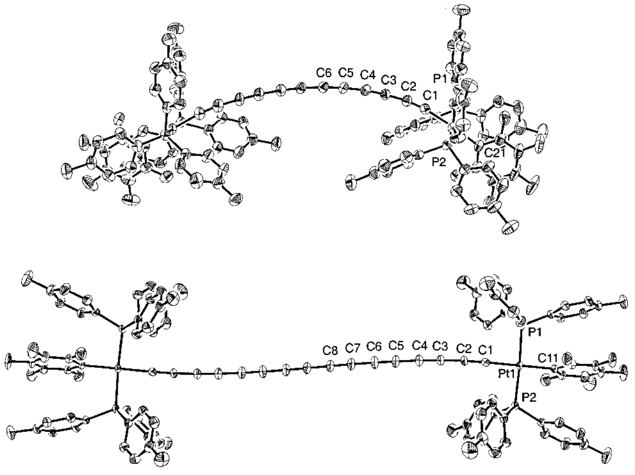


Figure 1. Structures of **8**·(benzene)$_4$(ethanol) (top) and **9**·(benzene)$_{10}$ (bottom) with solvent molecules omitted. Key distances (Å, **8**/**9**): Pt1−Pt2, 17.009(6)/23.071(4); Pt1−C1, 1.972(6)/1.981(2); Pt1−C21(C11), 2.048(5)/2.065(2); Pt1−P1, 2.3088(13)/2.3106(6); Pt1−P2, 2.3129(13)/2.3136(6); C1−C2, 1.234(8)/1.220(3); C2−C3, 1.361(8)/1.355(3); C3−C4, 1.209(8)/1.214(3); C4−C5, 1.363(8)/1.350(3); C5−C6, 1.216(7)/1.217(4); C6−C7, 1.358(8)/1.349(3); C7−C8, 1.210(7)/1.212(3); C8−C8′, −/1.349(5). Key angles (deg, **8**/**9**): C1−Pt1−C21(C11), 176.8(2)/177.35(10); P1−Pt1−P2, 175.66(5)/176.537(19); Pt1−C1−C2, 172.9(5)/175.7(2); C1−C2−C3, 173.2(7)/176.9(3); C2−C3−C4, 178.3(7)/178.2(3); C3−C4−C5, 175.6(7)/178.0(3); C4−C5−C6, 175.3(6)/178.7(3); C5−C6−C7, 175.7(6)/179.1(3); C6−C7−C8, 175.7(6)/178.3(3); C7−C8−C8′, −/179.3(4).

In summary, we have established that sp carbon chains comparable to the longest known to date can be efficiently constructed between platinum endgroups (C_6F_5)(p-tol$_3$P)$_2$Pt, using in situ desilylation/coupling procedures that avoid the isolation of terminal polyynes. The products are exceedingly stable, despite unprecedented curvature in the solid state. Hence, we are optimistic that still longer chains will prove possible. Efforts in this direction, as well as novel complexes described from the above species, will be described in future reports.

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Supporting Information Available: Experimental procedures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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