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C₈ and C₁₂ sp Carbon Chains That Span Two Platinum Atoms: The First Structurally Characterized 1,3,5,7,9,11-Hexayne

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Summary: Reaction sequences involving *trans*-(*p*-tol)-(Ar₃P)₂PtCl (Ar = Ph, *p*-tol), HC≡CC≡CH, HC≡CSEt₃, and oxidative ≡CH/HC≡ cross- or homocoupling (O₂, cat. CuCl/TMEDA) give the C_x complexes *trans*,*trans*-(*p*-tol)(Ar₃P)₂Pt(C≡C)_nPt(PAr₃)₂(*p*-tol) (*n* = 4, 6), which have been characterized by crystallography and by IR, NMR, and UV–visible spectroscopy.

Over the past few years, there has been rapidly increasing interest in compounds where sp carbon chains span two metal atoms,^{1–3} as well as sp carbon rich organic systems.^{4,5} One important objective involves methodology for the construction of longer sp carbon chains. Such species constitute models for the polymeric sp carbon allotrope “carbyne”,⁶ the precise physical and chemical characterization of which continues to present

many challenges. For example, the possibility that carbyne might easily bend and generate other allotropes has received considerable speculation,⁶ but experimental probes remain scant.

Several metal-capped octatetraynediyl systems L_nMC≡CC≡CC≡CC≡CML_n are now known.³ However, higher C₁₀–C₂₀ homologues have so far only been accessed with the chiral rhenium end group (η⁵-C₅Me₅)Re(NO)(PPh₃).^{2e} These dirhenium compounds have yielded much valuable data. Nonetheless, the *meso* and *dl* diastereomers are often inseparable, complicating some analyses. Hence, we sought to develop parallel chemistry with achiral end groups. In this communication, we report that bis(phosphine)arylplatinum termini can also support C₈–C₁₂ chains, as well as crystal structures of C₈ and C₁₂ systems. The latter represents the longest polyyne structurally characterized to date.⁷

We first prepared the building block (*p*-tol)(COD)PtCl (**1**),⁸ which features (1) easily displaced diene and chloride ligands and (2) a *p*-tol group to facilitate NMR analyses. Reaction of **1** and *p*-tol₃P (2.4 equiv) gave the new bis(phosphine) complex *trans*-(*p*-tol)(*p*-tol₃P)₂PtCl (**2**) in 94% yield after workup.⁹ As with all other complexes below, **2** showed a single set of phosphine NMR signals and virtual coupling patterns¹⁰ typical of square-planar *trans*-bis(phosphine) complexes. As depicted in Scheme 1, a HNET₂ solution of **2** and CuI (0.12 equiv) was treated with excess HC≡CC≡CH^{11a} in THF. Workup gave the 1,3-butadiynyl complex *trans*-(*p*-tol)(*p*-tol₃P)₂PtC≡CC≡CH (**3**) as a tan powder in 79% yield.^{9,12} The ¹³C NMR coupling constant patterns (*J*_{CP}, *J*_{CPt}, *J*_{CH}) allowed unambiguous assignment of the sp carbon signals.

(7) All crystallographically characterized 1,3,5,7-tetraynes (seven) and 1,3,5,7,9-pentaynes (one) are tabulated in the following papers: (a) Bartik, B.; Dembinski, R.; Bartik, T.; Arif, A. M.; Gladysz, J. A. *New J. Chem.* **1997**, 21, 739. (b) Dembinski, R.; Lis, T.; Szafer, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, 578, 229.

(8) (a) The reaction of (COD)PtCl₂^{8b} and *p*-tolMgBr (2.5 equiv) gave (COD)Pt(*p*-tol)₂.^{8c} Subsequent addition of acetyl chloride (1.0 equiv) in MeOH/CH₂Cl₂ yielded **1**.^{8d} (b) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, 59, 411. (c) Alternative synthesis: Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357. (d) Alternative synthesis: Ertl, J.; Grafl, D.; Brune, H. A. *Z. Naturforsch.* **1982**, 37B, 1082.

(9) All new complexes were characterized by IR and NMR spectroscopy (and many by additional means), as detailed in the Supporting Information. Most gave correct microanalyses.

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[§] This paper is dedicated to a pioneer in this field and a neighbor in Franconia, Prof. Dr. Helmut Werner, on the occasion of his 65th birthday.

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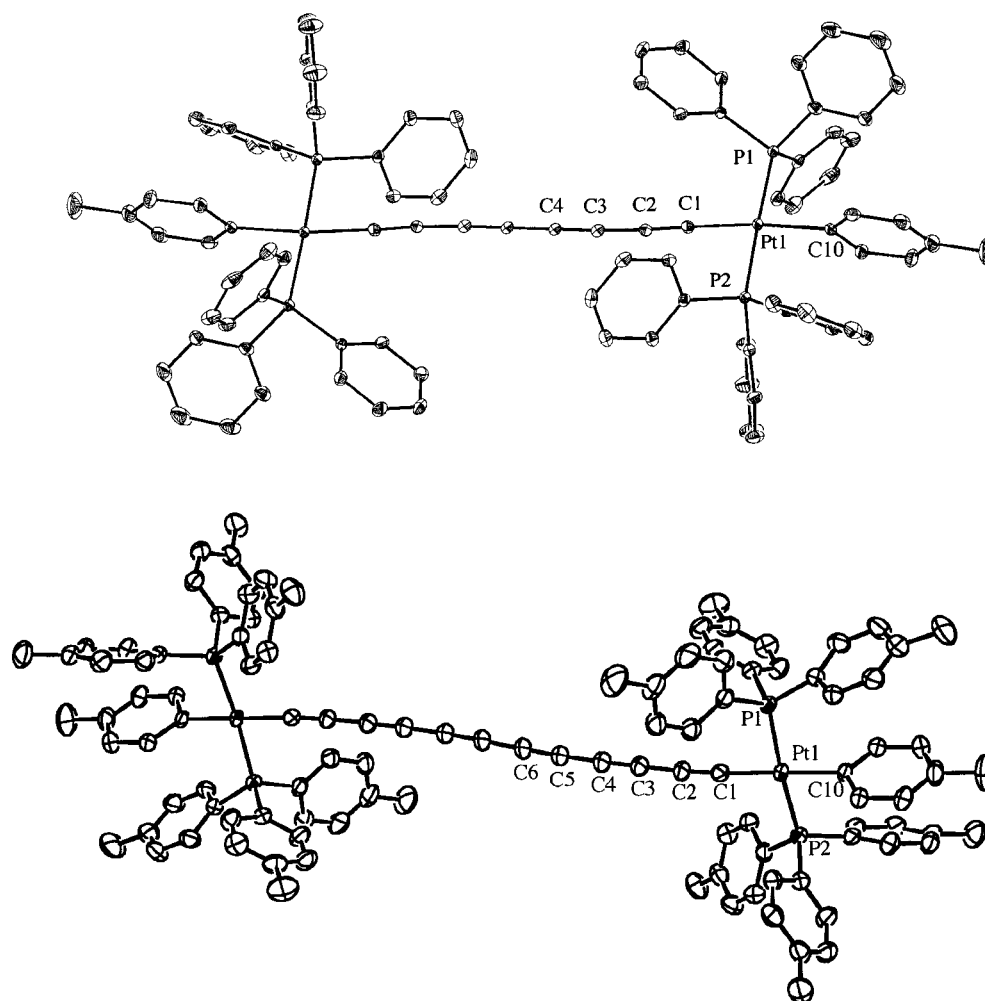


Figure 1. Molecular structures of **4'** (top) and **7** (bottom). Key distances (in Å; **4'**/**7**): Pt1–C1, 2.011(4)/1.990(3); Pt1–C10, 2.064(4)/2.060(3); Pt1–P1, 2.3073(11)/2.3055(8); Pt1–P2, 2.3002(11)/2.3164(8); C1–C2, 1.218(6)/1.233(4); C2–C3, 1.368(6)/1.358(4); C3–C4, 1.223(6)/1.210(5); C4–C4, 1.367(9)/–; C4–C5, –/1.356(5); C5–C6, –/1.211(5); C6–C6, –/1.344(7); Pt1–Pt1, 12.998(1)/17.9564(4). Key angles (in deg; **4'**/**7**): C1–Pt1–C10, 172.92(19)/177.86(13); P1–Pt1–P2, 178.22(4)/174.45(3); Pt1–C1–C2, 178.0(4)/174.0(3); C1–C2–C3, 176.5(5)/174.5(4); C2–C3–C4, 177.8(5)/178.6(4); C3–C4–C4, 179.5(9)/–; C3–C4–C5, –/178.3(4); C4–C5–C6, –/177.5(4); C5–C6–C6, –/178.9(6).

oxidations (V vs ferrocene: 0.96/1.33 and 1.19/1.34) but no reduction prior to the solvent limit.

Crystals suitable for X-ray diffraction could be grown at will, but always with solvent incorporation. Figure 1 shows two structures, **4'** and **7**. The bond lengths and angles about platinum are unexceptional.¹³ The C≡C and ≡C–C≡ bond lengths in **7** (1.210(5)–1.233(4) and 1.344(7)–1.356(4) Å) are near the upper and lower extremes of those in 1,3,5,7-tetraynes,⁷ suggesting asymptotic approaches to limiting values of ca. 1.24 and 1.34 Å at infinite chain length. The chain in **7** also curves gracefully. The PtCC and PtCCC angles are the most bent (174.0(3), 174.5(4)°; others 177.5(4)–178.9(6)°). Although the platinum–platinum distance (17.9564(4) Å) is just slightly less than the sum of the intervening bond lengths (18.06 Å), only one tetrayne shows distinctly greater nonlinearity.^{7b} Both **4'** and **7** pack with

parallel chains, the shortest carbon–carbon distances between which are 8.890 and 7.884 Å, respectively. The PtC atom of one chain aligns approximately with the midpoint of the neighbor. This offsets the bulky end groups, and solvent molecules fill some but not all of the remaining voids.

In summary, the preceding data establish that medium-length polyyne diyl complexes can easily be constructed with platinum end groups of the formula Ar(Ar₃P)₂Pt. Yields of individual steps are high, and intermediates and products are especially stable. Furthermore, the ancillary ligands are easily varied. Novel assemblies derived from such substitutions, as well as the pursuit of higher chain lengths, will be described in future reports.

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Supporting Information Available: Text giving experimental procedures and tables of crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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