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C_8 and C_{12} 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)(Ar_3P*)*$_2$*PtCl (Ar = Ph, p-tol), HC*$\equiv$*CC*$\equiv$*CH, HC*$\equiv$*CSiEt*$_3$*, and oxidative* $\equiv$*CH/HC*$\equiv$ *cross- or homocoupling (*O_2*, cat. CuCl/TMEDA) give the* C_x *complexes trans,trans-(p-tol)(*Ar_3P*)*$_2$*Pt(C*$\equiv$*C)*$_n$*Pt(PAr*$_3$*)*$_2$*(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 $L_nMC\equiv CC\equiv CC\equiv CC\equiv CML_n$ are now known.[3] However, higher $C_{10}-C_{20}$ homologues have so far only been accessed with the chiral rhenium end group (η^5-C_5Me_5)Re(NO)(PPh_3).[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 C_8-C_{12} chains, as well as crystal structures of C_8 and C_{12} 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*-tol$_3$P (2.4 equiv) gave the new bis(phosphine) complex *trans*-(*p*-tol)(*p*-tol$_3$P)$_2$PtCl (**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 patterns[10] typical of square-planar *trans*-bis(phosphine) complexes. As depicted in Scheme 1, a $HNEt_2$ solution of **2** and CuI (0.12 equiv) was treated with excess $HC\equiv CC\equiv CH$[11a] in THF. Workup gave the 1,3-butadiynyl complex *trans*-(*p*-tol)(*p*-tol$_3$P)$_2$PtC$\equiv$CC$\equiv$CH (**3**) as a tan powder in 79% yield.[9,12] The ^{13}C NMR coupling constant patterns (J_{CP}, J_{CPt}, J_{CH}) allowed unambiguous assignment of the sp carbon signals.

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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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(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.; Szafert, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, *578*, 229.

(8) (a) The reaction of (COD)$PtCl_2$[8b] and *p*-tolMgBr (2.5 equiv) gave (COD)Pt(*p*-tol)$_2$.[8c] Subsequent addition of acetyl chloride (1.0 equiv) in $MeOH/CH_2Cl_2$ 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.

(10) Pregosin, P. S.; Venanzi, L. M. *Chem. Br.* **1978**, 276.

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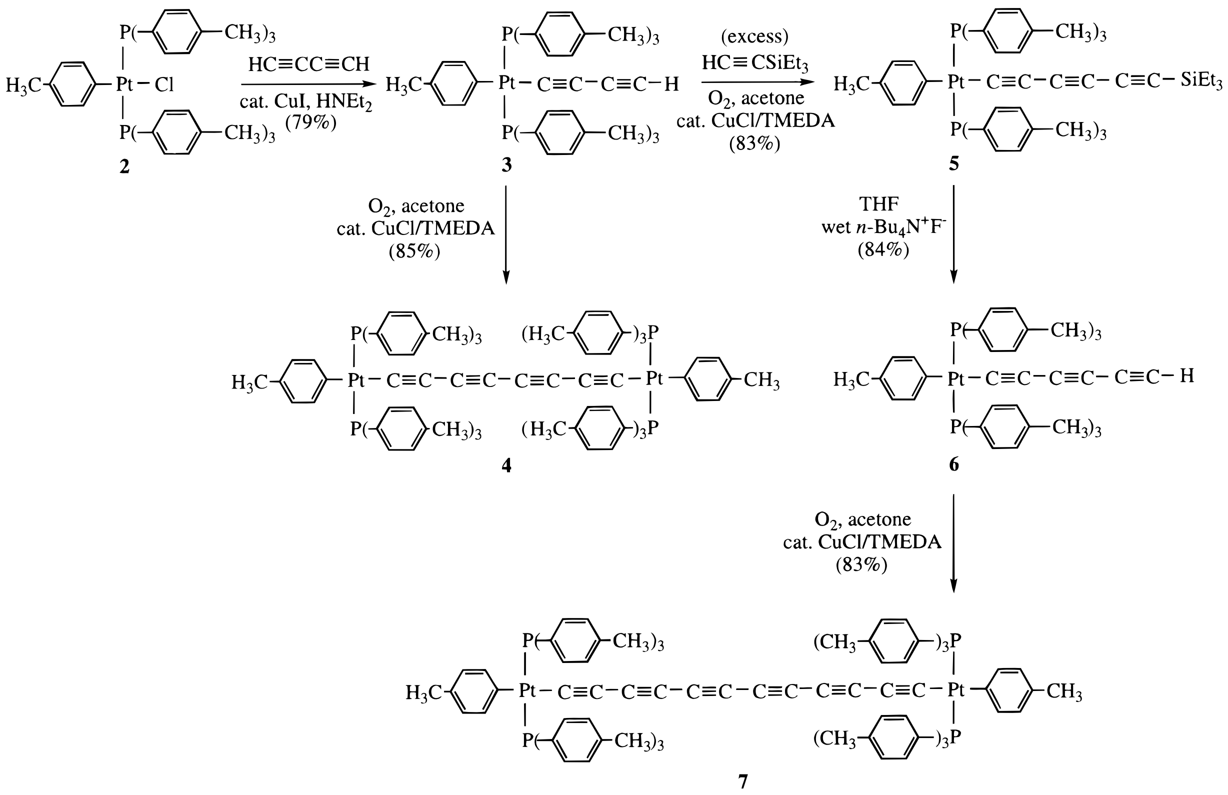
10.1021/om990448c CCC: $18.00

Scheme 1. Syntheses of PtC_xPt Complexes



The oxidative homocoupling of **3** was attempted. The Eglinton recipe that proved optimal for chiral rhenium educts $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)Re(C{\equiv}C)_nH$ (1 equiv of $Cu(OAc)_2$ in pyridine)[2b,e] did not afford detectable quantities of the target C_8 complex *trans*,*trans*-(*p*-tol)(*p*-$tol_3P)_2Pt(C{\equiv}C)_4Pt(P$*p*-$tol_3)_2$(*p*-tol) (**4**). However, Hay conditions (excess O_2, 0.20−0.25 equiv of CuCl and TMEDA in acetone)[12b] gave **4** in 85% yield after workup (Scheme 1). The structure followed from the mass spectral parent ion and spectroscopic properties, which are discussed with those of homologues below.

Efforts were next directed at compounds with longer sp carbon chains. As analyzed previously,[2e,7] this requires either longer building blocks or "second generation" chain growth in a metal coordination sphere. Since higher homologues of 1,3-butadiyne become very explosive,[11b] the latter strategy was investigated. As shown in Scheme 1, **3** and excess $HC{\equiv}CSiEt_3$ were subjected to the Hay conditions. Workup gave the heterocoupling product *trans*-(*p*-tol)(*p*-$tol_3P)_2PtC{\equiv}CC{\equiv}CC{\equiv}CSiEt_3$ (**5**) in 83% yield. Unfortunately, similar reactions with $HC{\equiv}CC{\equiv}CSiEt_3$ gave only homocoupling products, possibly due to the decreased steric bulk of the organosilicon partner.

Reaction of **5** with *n*-$Bu_4N^+F^-$ (1.3 equiv) in wet THF afforded the 1,3,5-hexatriynyl complex *trans*-(*p*-tol)(*p*-$tol_3P)_2PtC{\equiv}CC{\equiv}CC{\equiv}CH$ (**6**) in 84% yield. A Hay coupling then gave the desired C_{12} complex *trans*,*trans*-(*p*-tol)(*p*-$tol_3P)_2Pt(C{\equiv}C)_6Pt(P$-*p*-$tol_3)_2$(*p*-tol) (**7**) in 83% yield. In efforts to further extend the chain, **6** and excess $HC{\equiv}CSiEt_3$ were reacted under Hay conditions. Workup gave the heterocoupling product *trans*-(*p*-tol)(*p*-$tol_3P)_2PtC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CSiEt_3$ (**8**, 48%), sought unsuccessfully from **3** and $HC{\equiv}CC{\equiv}CSiEt_3$ above. However, attempts to elaborate **8** to a C_{16} complex have to date been unsuccessful, an outcome presently ascribed to the apparent instability of the corresponding 1,3,5,7-octatetraynyl complex. Finally, PPh_3 homologues of **2**−**7** were similarly prepared (**2′**−**7′**), but these exhibited much lower solubilities. Hence, the Hay couplings were heterogeneous and required heating, and ^{13}C NMR spectra were of lower quality.

The monoplatinum complexes $Pt(C{\equiv}C)_nX$ gave *n* or *n* − 1 IR $\nu_{C\equiv C}$ bands (2176−1991 cm^{-1}). However, the diplatinum complexes **4**/**4′** and **7**/**7′** exhibited *n*/2 bands, consistent with their higher symmetry. In all cases, ^{13}C NMR spectra showed $PtC{\equiv}$ signals at 120.9−111.2 ppm. These were coupled to phosphorus ($^2J_{CP}$ 14.8−13.5 Hz) and platinum ($^1J_{CPt}$ 875−650 Hz; satellites). The $PtC{\equiv}\boldsymbol{C}$ signals ranged from 98.3 to 96.0 ppm and gave smaller phosphorus and platinum couplings (<2 and 212−237 Hz). The remaining $C{\equiv}C$ signals of **7** were at 66.6−56.9 ppm. The colors of **4**/**4′** and **7**/**7′** (bright yellow and orange) were less intense than those of dirhenium analogues, and UV−visible spectra were less complex. The two longest wavelength bands intensified and red-shifted with increasing chain length (nm, CH_2Cl_2 (ϵ, M^{-1} cm^{-1}): **4**, 305 (95 000), 343 (100 000); **7**, 347 (125 000), 371 (215 000)) but then simply tailed into the visible.

All compounds exhibited excellent stability, including a surprising tolerance to O_2 in solution. Only concentrated solutions of **6** appeared labile. When heated, solid samples decomposed without melting (**4**/**7**, 185/204 °C, sealed capillary). Cyclic voltammograms of **4** and **7** were recorded in CH_2Cl_2. Each showed two irreversible

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[12] Related platinum butadiynyl complexes have been similarly prepared: (a) Fujikura, Y.; Hagihara, N.; Sonogashira, K.; Takahashi, S.; Toyoshima, N. *J. Organomet. Chem.* **1978**, *145*, 101. (b) Bruce, M. I.; Ke, M.; Low, P. J. *J. Chem. Soc., Chem. Commun.* **1996**, 2405. (c) AlQaisi, S. M.; Galat, K. J.; Chai, M.; Ray, D. G., III; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149.

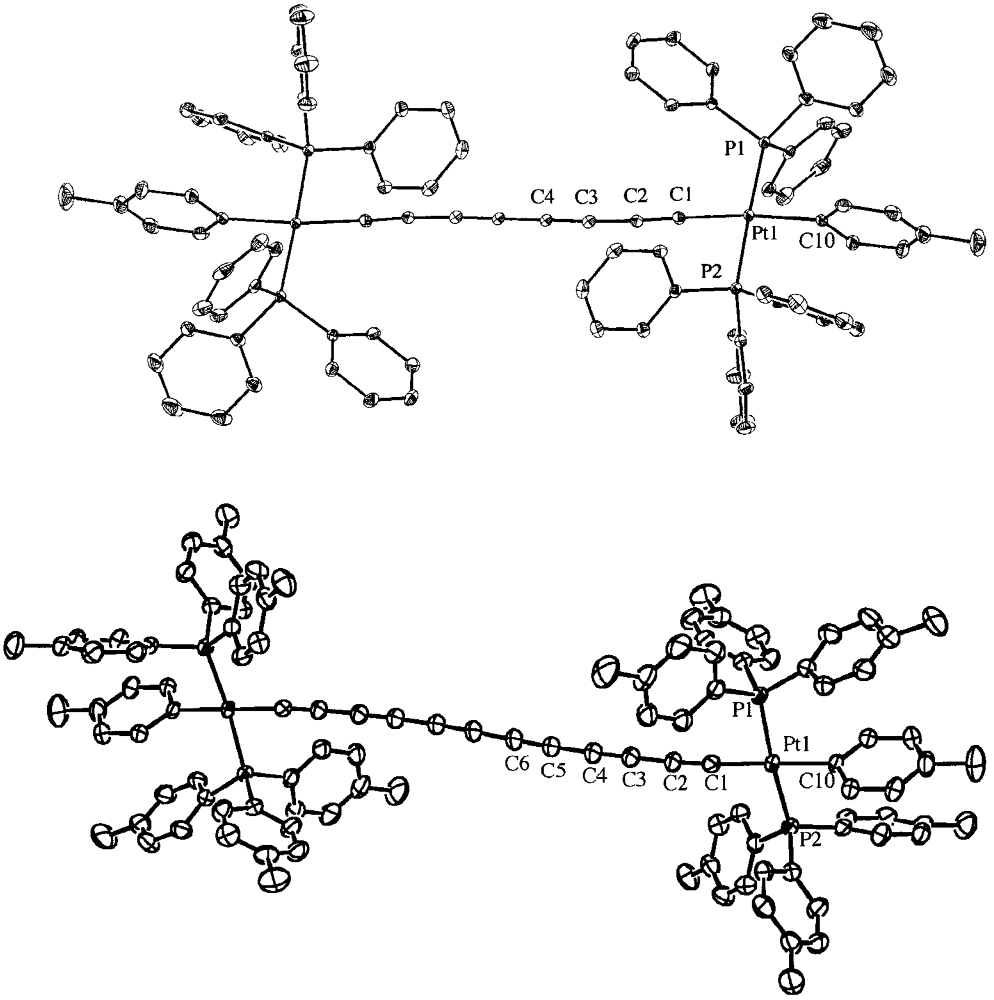

Figure 1. Molecular structures of **4′** (top) and **7** (bottom). Key distances (in Å; **4′**/**7**): Pt1−C1, 2.011(4)/1.990(3); Pt1−C10, 2.064(4)/2.060(3); Pt1−P1, 2.3073(11)/2.3055(8); Pt1−P2, 2.3002(11)/2.3164(8); C1−C2, 1.218(6)/1.233(4); C2−C3, 1.368(6)/1.358(4); C3−C4, 1.223(6)/1.210(5); C4−C4, 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 Pt*CCC* 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 Pt***C*** 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 polyynediyl complexes can easily be constructed with platinum end groups of the formula Ar(Ar$_3$P)$_2$Pt. 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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[13] Crystal structures of other *trans*-(X)(R$_3$P)$_2$PtC≡CR complexes: (a) Furlani, A.; Licoccia, S.; Russo, M. V.; Villa, A. C.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1984**, 2197. (b) Lewis, J.; Long, N. J.; Raithby, P. R.; Sheilds, G. P.; Wong, W.-Y.; Younus, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4283. (c) Bohling, J. C.; Peters, T. B.; Arif, A. M.; Hampel, F.; Gladysz, J. A. In *Coordination Chemistry at the Turn of the Century*; Ondrejoviç, G., Sirota, A., Eds.; Slovak Technical University Press: Bratislava, Slovakia, 1999; p 47.