

Syntheses and Structures of Diplatinum Hexatriynediyl Complexes, in Which the sp Carbon Chains Are Shielded by sp^3 Carbon Chains

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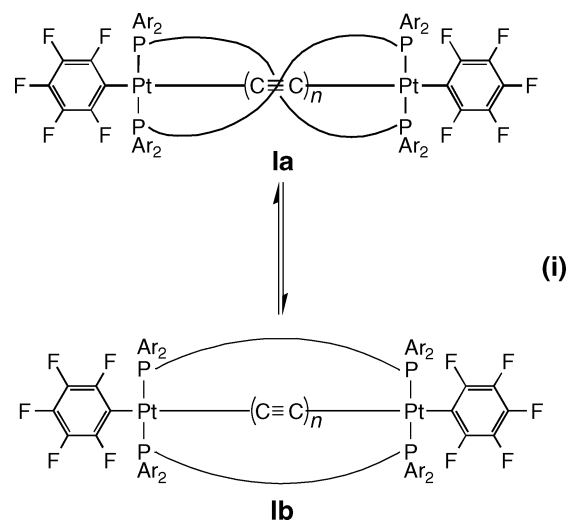
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Summary: When *trans,trans*-(C_6F_5)₂(*p*-tol₃P)₂Pt(C≡C)₃Pt-(*P*-*p*-tol₃)₂(C_6F_5) and $Ar_2P(CH_2)_mPAR_2$ ($m/Ar = 8/p$ -tol, 10/Ph, 11/Ph, 12/Ph, 14/*p*-tol) are reacted, *p*-tol₃P is displaced to give products in which the diphosphines span the platinum end groups. One crystal structure ($m = 14$) shows a double-helical conformation in which the sp^3 carbon chains twist around the sp chain, and others ($m = 10, 11$) show nonhelical conformations with lateral shielding of the sp chain.

Over the past decade, molecules in which sp carbon chains span two transition metals have attracted great attention, from both the standpoint of fundamental properties and possible applications in molecular devices.¹ The C_x linkages more efficiently delocalize the odd electrons of radical ions between the metal end groups, as compared to most other types of unsaturated bridging ligands.^{1b} We have described several series of complexes with Pt(C≡C)_{*n*}Pt units ($n = 3, 4, 6, 8$).^{2–6} For the octatetraynediyl complex *trans,trans*-(C_6F_5)₂(*p*-tol₃P)₂Pt(C≡C)₄Pt-(*P*-*p*-tol₃)₂(C_6F_5) (**PtC₈Pt**), reactions with diphosphines $Ar_2P(CH_2)_mPAR_2$ ($m = 10–14$) yield substitution products of the formula *trans,trans*-(C_6F_5)-($Ar_2P(CH_2)_mPAR_2$)Pt(C≡C)_{*n*}Pt($Ar_2P(CH_2)_mPAR_2$)(C_6F_5) (**PtC₈Pt-*m*/Ar**). These feature sterically shielded sp carbon chains. In the case with $m = 14$, the sp^3 chains wrap around the sp chain in a striking chiral double-helical conformation in the solid state (**Ia**; eq i). The corresponding radical cations become longer lived, inviting analogies to “insulated molecular wires”.

We sought to extend this chemistry to lower homologues with shorter (C≡C)_{*n*} bridges. It was thought that end group–end group steric interactions might lead to intrinsically dissymmetric structures, analogous to the twisted ground states of biaryls.⁷ This might increase



the barrier for converting one enantiomer of **Ia** to the other, a process that requires a conformation with coplanar end groups such as **Ib** and is fast on the NMR time scale for all complexes of the type **PtC₈Pt-14/Ar**. In this communication, we report (1) an improved synthesis of the hexatriynediyl complex *trans,trans*-(C_6F_5)₂(*p*-tol₃P)₂Pt(C≡C)₃Pt-(*P*-*p*-tol₃)₂(C_6F_5) (**PtC₆Pt**)³ that makes multigram quantities available, (2) substitutions with longer-chain diphosphines leading to assemblies of the type **Ia**, (3) substitutions with medium-chain diphosphines leading to assemblies of the type **Ib**, and (4) attendant crystallographic, VT NMR, and cyclic voltammetry data. In the following communication, reactions involving short-chain diphosphines that afford tetraplatinum complexes with “bundled” polyene chains are described.⁸

As shown in Scheme 1, **PtC₆Pt** was prepared from the same two precursors, **PtC₆SiEt₃** and **PtCl**, as reported earlier.³ In the first step, **PtC₆SiEt₃** and the fluoride salt n -Bu₄N⁺F⁻ were combined in protic media to generate the labile complex **PtC₆H**. Interestingly, when the subsequent CuCl-catalyzed cross-coupling was conducted in the presence of stoichiometric amounts of KPF₆ and *t*-BuOK, the yield of **PtC₆Pt** increased from 34% to 94%.⁹ Quantities exceeding 2 g were easily prepared.

(1) (a) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179. (b) Paul, F.; Lapinte, C. In *Unusual Structures and Physical Properties in Organometallic Chemistry*; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley: New York, 2002; pp 220–291. (c) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175.

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(3) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2003**, *9*, 3324.

(4) Computational study: Zhuravlev, F.; Gladysz, J. A. *Chem. Eur. J.*, in press.

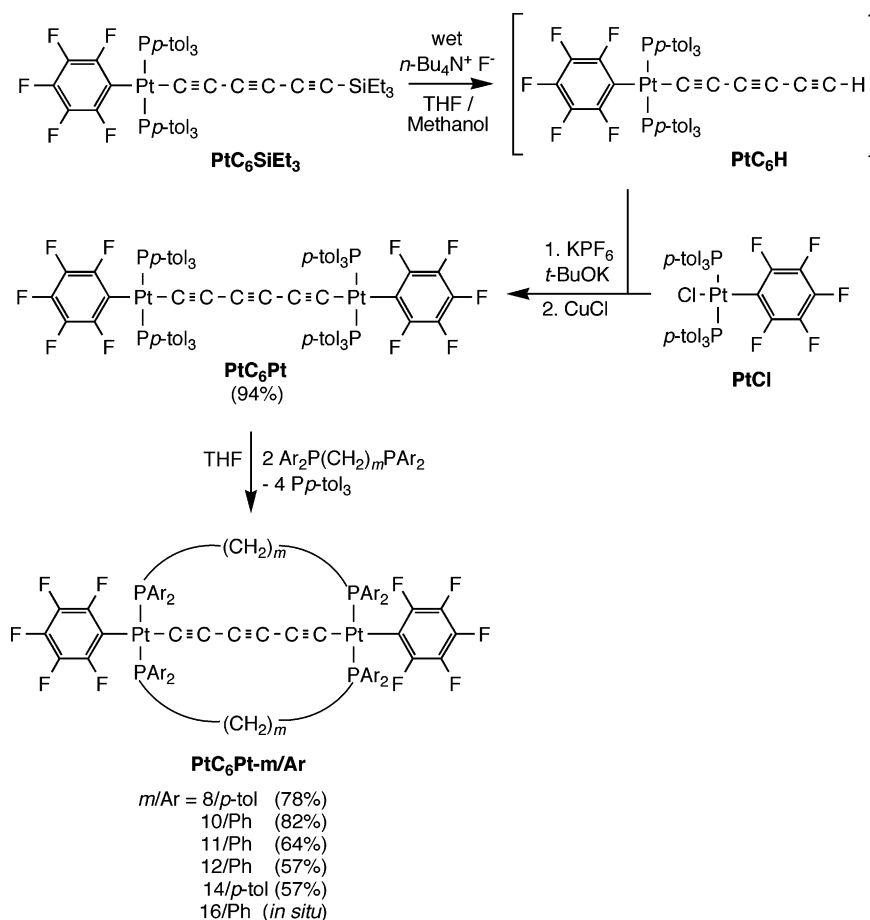
(5) Stahl, J.; Bohling, J. C.; Bauer, E. B.; Peters, T. B.; Mohr, W.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1871; *Angew. Chem.* **2002**, *114*, 1951.

(6) For other complexes with Pt(C≡C)₃Pt and Pt(C≡C)₄Pt linkages, see: (a) Wong, W.-Y.; Wong, C.-K.; Lu, G.-L.; Cheah, K.-W.; Shi, J.-X.; Lin, Z. *Dalton* **2002**, 4587. (b) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1400; *Angew. Chem.* **2003**, *115*, 1438.

(7) (a) Arulmozhiraja, S.; Fujii, T. *J. Chem. Phys.* **2001**, *115*, 10589 and references therein. (b) Müllen, K.; Heinz, W.; Klärner, F.-G.; Roth, W. R.; Kindermann, I.; Adamczak, O.; Wette, M.; Lex, J. *Chem. Ber.* **1990**, *123*, 2349.

(8) Owen, G. R.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5893.

Scheme 1. Syntheses of Diplatinum Hexatrienediyl Complexes



The crystal structure of a solvate was determined as described in the Supporting Information. As shown in Figure 1A,B, it exhibited an inversion center at the chain midpoint and the C₆H₄R/C₆F₅/C₆H₄R π -stacking interaction commonly seen in this series of compounds.^{3,5,10,11} To our surprise, the end groups were coplanar, with no van der Waals contacts (shortest hydrogen–hydrogen distance 2.71 Å). DFT calculations indicate no electronic conformational preference.⁴ Since this motif is observed with other platinum substituents and longer *sp* chain lengths,^{2,3,12} it must reflect a crystal-packing effect of considerable generality. Substitutions with diphosphines were nonetheless investigated, with the hope that steric interactions might still ensue between the modified end groups.

THF solutions of **PtC₆Pt** were treated with Ar₂P-(CH₂)_{*m*}PAR₂ (*m*/*Ar* = 8/*p*-tol, 10/Ph, 11/Ph, 12/Ph, 14/*p*-

(9) (a) Many Fe(C≡C)_{*n*}H and FeCl complexes undergo efficient cross-coupling when treated with KPF₆/*t*-BuOK: Coat, F.; Guillemot, M.; Paul, F.; Lapinte, C. *J. Organomet. Chem.* **1999**, 578, 76 and references therein. (b) No **PtC₆Pt** forms in the absence of CuCl.

(10) (a) Bauer, E. B.; Szafert, S.; Hampel, F.; Gladysz, J. A. *Organometallics* **2003**, 22, 2184. (b) Shima, T.; Bauer, E. B.; Hampel, F.; Gladysz, J. A. *Dalton* **2004**, 1012.

(11) (a) The bond lengths and angles for all compounds are typical and are given in the Supporting Information. (b) The least-squares planes [(P_A-Pt_A-P_A) + Pt_B] and [Pt_A + (P_B-Pt_B-P_B)] are used to calculate the angles defined by the end groups. The inclusion of a platinum from each terminus minimizes nonidealities arising from chain curvature. (c) Average C₆H₄R-C₆F₅ centroid-centroid distances (Å): **PtC₆Pt**, 3.665; **PtC₆Pt-10/Ph**, 3.631; **PtC₆Pt-11/Ph**, 3.705; **PtC₆Pt-14/p-tol**, 4.197. In the last compound, the nonstacked aryl groups nest close to the *sp*³ chains.

(12) Zheng, Q.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, 23, 5896.

tol, 16/Ph).¹³ In each case, the desired bis(diphosphine) complexes *trans,trans*-(C₆F₅)(Ar₂P(CH₂)_{*m*}PAR₂)Pt(C≡C)₃Pt(Ar₂P(CH₂)_{*m*}PAR₂)(C₆F₅) (**PtC₆Pt-*m*/Ar**) formed.

For the first five reactions, workups gave **PtC₆Pt-*m*/Ar** in 57–82% yields.¹⁴ In the last case, a ³¹P NMR spectrum of the reaction mixture suggested complete conversion to **PtC₆Pt-16/Ph**. However, the powder isolated (64%) could not again be dissolved. This is characteristic of oligomers that sometimes form upon sample concentration. Similar behavior is seen when **PtC₈Pt** and **PtC₁₂Pt** are combined with longer-chain diphosphines.¹⁵ The mass spectra of **PtC₆Pt-*m*/Ar** exhibited strong molecular ions, and IR spectra showed a single weak $\nu_{C\equiv C}$ band at 2104–2123 cm⁻¹. The PtC≡CC ¹³C NMR signals were essentially identical with those of **PtC₆Pt** (PtC≡C, 95.7–95.2 ppm; PtC≡CC, 61.7–60.3 ppm; in CDCl₃).

The crystal structures of **PtC₆Pt-10/Ph**, **PtC₆Pt-11/Ph**, and **PtC₆Pt-14/p-tol**, or solvates thereof, were determined as described in the Supporting Information.

(13) Mohr, W.; Horn, C. R.; Stahl, J.; Gladysz, J. A. *Synthesis* **2003**, 1279. Preparations for the diphosphines not found in this paper are given in the Supporting Information.

(14) All new compounds have been characterized by microanalysis, IR and NMR (¹H, ¹³C, ³¹P) spectroscopy, and mass spectrometry, as described in the Supporting Information.

(15) (a) Mohr, W. Doctoral Thesis, Universität Erlangen-Nürnberg, 2002. (b) The general structures of these oligomers can be proved by adding an excess of the more basic phosphine PEt₃. Substitution occurs to give the independently synthesized diplatinum complexes *trans,trans*-(C₆F₅)(Et₃P)₂Pt(C≡C)_{*n*}Pt(PEt₃)₂(C₆F₅).³

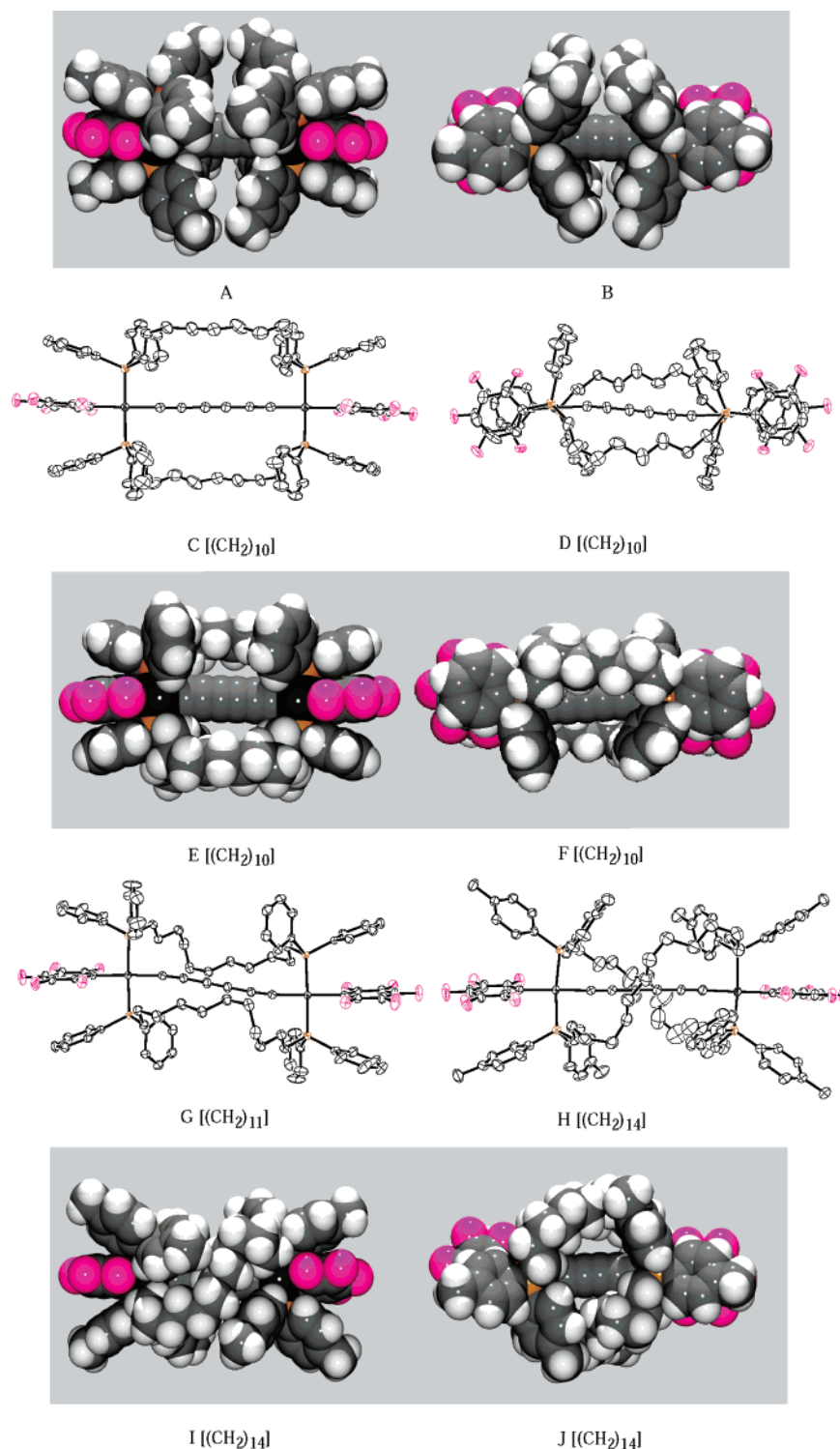


Figure 1. Space-filling and ORTEP representations of the molecular structures of (A, B) PtC_6Pt , (C–F) $\text{PtC}_6\text{Pt-10/Ph}$, (G) $\text{PtC}_6\text{Pt-11/Ph}$, and (H–J) $\text{PtC}_6\text{Pt-14/p-tol}$.

The molecular structure of $\text{PtC}_6\text{Pt-10/Ph}$, which features an inversion center at the chain midpoint and coplanar end groups, is depicted in Figures 1C–E. The methylene chain is not long enough to twist by 180° as in **1a**. Rather, the central $(\text{CH}_2)_6$ segments run roughly parallel to the sp chain in an “all-anti” conformation, laterally shielding two “sides”. The average distance from the methylene carbons to the Pt–Pt vector is 4.86 Å. The van der Waals radii of sp carbon, sp^3 carbon, and hydrogen atoms are 1.78, 1.70, and 1.20 Å, respectively.¹⁶

The structure of $\text{PtC}_6\text{Pt-11/Ph}$, which also features an inversion center at the chain midpoint and coplanar end groups, is depicted in Figure 1G. The extra methylene group leads to a sp^3 chain that is more “curved”, or richer in gauche conformational units, and that nearly crosses from the “top” to “bottom” half of the molecule at the midpoint. Nonetheless, each sp^3 chain returns to its hemisphere of origin, avoiding a helical conformation. Interestingly, the average distance from

(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

the methylene carbons to the Pt–Pt vector decreases to 4.03 Å, the lowest of all complexes in this study.

The structure of **PtC₆Pt-14/p-tol** contains two disordered methylene groups, and the dominant conformer is depicted in Figures 1H–J. The longer methylene chains are now able to wrap around the sp chain in a double-helical motif. The end groups define an angle of 189.3°—more than a half twist.^{11b} Both enantiomers are present in the unit cell. The sp chain is highly shielded, visible only through the bowl-like cavity highlighted in Figure 1J. However, the C₆H₄R/C₆F₅/C₆H₄R stacking interaction is weaker than in the other complexes,^{11c} and the sp and sp³ chains are not in van der Waals contact. The average distance from the methylene carbons to the Pt–Pt vector is 4.42 Å. In the three previously reported double-helical complexes of the formula **PtC₈Pt-14/Ar**, the average distances are only 3.93–3.97 Å, indicating tighter winding. Given the lower van der Waals surface of the C₆ vs C₈ bridge, it is not surprising that the methylene groups in **PtC₆Pt-14/p-tol** spiral with a greater average radius.

We sought to probe the structure of **PtC₆Pt-14/p-tol** in solution. The aryl groups and PCH₂ protons are diastereotopic in chiral helical conformations as in Figures 1H–J. However, when NMR spectra were recorded in CDCl₃ at –135 °C, separate aryl ¹³C or PCH₂ ¹H signals could not be observed. This indicates that the helical conformation, if maintained in solution, rapidly untwists and retwists to the opposite enantiomer via a formally achiral conformation such as **Ib**. Analogous results were obtained earlier with the higher homologues **PtC₈Pt-14/Ar**.⁵ Hence, there is no dramatic increase in the racemization barrier for complexes with shorter C₆ chains.

Finally, cyclic voltammograms of representative complexes were recorded. In each case, partially reversible one-electron oxidations were observed. The unshielded complex **PtC₆Pt** exhibited, as expected, $E_{p,a}$, $E_{p,c}$, E° , ΔE , and i_c/i_a values (1.156, 1.066, and 1.111 V, 90 mV,

and 0.71) intermediate between those of **PtC₄Pt** and **PtC₈Pt** (*n*-Bu₄N⁺BF₄[–]/CH₂Cl₂, 100 mV/s).³ The sterically shielded complexes **PtC₆Pt-10/Ph** and **PtC₆Pt-12/Ph** gave somewhat more reversible couples ($\Delta E = 85$, 75 mV; $i_c/i_a = 0.82$, 0.84). Unexpectedly, **PtC₆Pt-14/p-tol** showed a much less reversible couple ($\Delta E = 117$ mV; $i_c/i_a = 0.45$). This is the first time such a trend has been observed for a complex of the type **PtC_xPt-m/Ar** that is capable of a double-helical conformation. The basis for the attenuated stability of the corresponding radical cation remains under investigation.

In summary, we have been able to extend the novel structural motifs **Ia** and **Ib** to diplatinum hexatrienediyl complexes using methodology developed earlier for the higher octatetraynediyl homologues.⁵ However, although **PtC₆Pt-14/p-tol** exhibits a double-helical conformation in the solid state, this does not translate into an enhanced barrier to racemization in solution or longer lived radical cations. Future reports will describe lower butadienediyl homologues, in which end group–end group interactions cannot be avoided. Dissymmetric structures are indeed realized, but additional unusual conformational phenomena involving the sp³ carbon chains are encountered.¹⁷ Further types of novel structures based upon polyynediyl building blocks are described in the following communications.^{8,12}

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG, SFB Grant 583), the Humboldt Foundation (Fellowship to G.R.O.), and Johnson Matthey PMC (platinum loans) for support.

Supporting Information Available: Text and tables giving experimental procedures, characterization data¹⁴ for all new compounds, and crystallographic data; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Stahl, J. Doctoral Thesis, Universität Erlangen-Nürnberg, 2003.