Longitudinally Extended Molecular Wires Based upon PtC=CC=CC=CC=C Repeat Units: Iterative Syntheses of Functionalized Linear PtC₈Pt, PtC₈PtC₈Pt, and PtC₈PtC₈PtC₈PtC₈Pt Assemblies

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Summary: Condensations of $(p\text{-}tol_3P)_2PtCl_2$ with Me_3 -SnC=CC=CSiMe_3 and HC=CC=CSiMe_3 give mono- or bis((trimethylsilyl)butadiynyl) complexes that are desilylated and elaborated by oxidative cross-couplings and homocouplings to give the title compounds trans-Cl[(ptol_3P)_2PtC=CC=CC=CC=C]_mPt(P-p-tol_3)_2Cl (m = 1-3).

Molecules in which sp carbon chains span two transition metals have attracted great attention from both fundamental and applied perspectives.¹ Many such wire-like compounds are now available, and researchers are attempting to construct multidimensional arrays that model more complex types of devices.² Efforts in our laboratory have focused on the elaboration of Re-(C=C)_nRe³ and Pt(C=C)_nPt⁴⁻⁶ systems. These building blocks are available with chain lengths of up to 20 carbons.

In the previous communication, we described "bundles" of $Pt(C=C)_nPt$ moieties (n = 3, 4) in which the sp chains were laterally arrayed.⁷ In this communication, we report efficient syntheses of longitudinal arrays based upon PtC=CC=CC=CC=C repeat units that contain as many as four platinum atoms. Several polymers derived from PtC=CC=C, PdC=CC=C, or NiC=CC=C units have been described,⁸ as well as many that involve bis-(alkynyl) arenes, $MC=C-Ar-C=C.^9$ However, to our knowledge iterative synthetic methodologies that yield families of $[M(C=C)_n]_m$ species remain unknown. When

such series are available, the gradual transition of physical and chemical properties to the macromolecular limit can be mapped.

In our earlier synthesis of $Pt(C \equiv C)_n Pt$ assemblies,^{4–7} we began with the monofunctional platinum building blocks *trans*-Ar'(Ar₃P)₂PtCl. The chloride ligands could easily be replaced by alkynyl ligands, and subsequent oxidative couplings led to the target molecules. However, for the stepwise synthesis of longitudinally extended homologues, difunctional platinum building blocks are required. One obvious choice would be the dichloride complex (Ar₃P)₂PtCl₂. However, at some stage in the sequence, monofunctionalization is required. Scouting reactions with terminal alkynes or diynes using conditions employed previously were not promising. In all cases, mixtures of monoalkynyl, bis(alkynyl), and unreacted complexes were obtained.

After some experimentation, it was found that the unsymmetrical diyne Me₃SnC=CC=CSiMe₃ and $(p-tol_3P)_2PtCl_2$ (1:1 mol ratio) spontaneously condensed in refluxing THF (Scheme 1).¹⁰ Workup gave the monosubstituted product *trans*-Cl(*p*-tol_3P)_2PtC=CC=CSiMe_3 (1),¹¹ derived from Me₃SnCl elimination, in 63% yield.¹² The diyne was in turn easily isolated from the sequential reaction of HC=CC=CSiMe_3 with *n*-BuLi and Me₃-SnCl.¹³ Perhaps this platinum-carbon bond-forming reaction has a steric requirement greater than that of the others investigated, giving a greater rate difference

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^{(12) (}a) Reactions of other L₂PtCl₂ complexes and Me₃SnC≡CPh give the monosubstitution product *trans*-ClL₂PtC≡CPh in good yield: Cardin, C. J.; Cardin, D. J.; Lappert, M. F. J. Chem. Soc., Dalton Trans. **1977**, 767. (b) Many related reactions are known that require a palladium catalyst: Lo Sterzo, C. Synlett **1999**, 1704.

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for the substitution of the first and second chlorine ligands and higher selectivity for monosubstituion at platinum.

Complex 1 was elaborated to a diplatinum octatetraynediyl complex, similarly to other (trialkylsilyl)butadiynyl adducts described earlier. First, reaction with wet n-Bu₄N⁺F⁻ gave the desilylated species *trans*-Cl(p-tol₃P)₂PtC=CC=CH (2) in 96% yield. An oxidative homocoupling under Hay conditions (O₂, catalyst CuCl, TMEDA) afforded *trans*,*trans*-Cl(p-tol₃P)₂PtC=CC= $CC \equiv CPt(P-p-tol_3)_2Cl$ (3) in 68% yield. A crystal structure of a solvate was determined as described in the Supporting Information, and the result is depicted in Figure 1. The sp carbon chain adopts an S-shaped conformation, a feature seen in other tetraynes.^{1b} All bond lengths and angles are well within the ranges found in related diplatinum complexes.^{1b,4-7}

Reactions of **3** were studied next. As shown in Scheme 1, treatment with 1.0 equiv of $Me_3SnC \equiv CC \equiv CSiMe_3$ gave the monosubstituted complex *trans.trans*-Cl(*p*-



Figure 1. Structure of the diplatinum moiety of **3**·2(acetone). Key distances (Å): Pt1-C1, 1.933(4); Pt1-P1, 2.3145(10); Pt1-P2, 2.3214(10); Pt1-Cl1, 2.3483(10); C1-C2, 1.210(6); C2-C3, 1.368(6); C3-C4, 1.199(6); C4-C4a, 1.376(9); Pt1-Pt1a, 12.7499(3). Key angles (deg): C1-Pt1-P1, 86.31(12); C1-Pt1-P2, 91.29(12); P1-Pt1-P2, 177.10(4); C1-Pt1-Cl1, 178.13(12); P1-Pt1-Cl1, 95.54(4); P2-Pt1-Cl1, 86.87(4); C2-C1-Pt1, 178.6(4); C1-C2-C3, 174.6(5); C4-C3-C2, 174.9-(6); C3-C4-C4a, 178.3(7).



Scheme 2. Synthesis of the Triplatinum Complex 9 excess HC=CC=CH, cat. Cul, HNEt₂

 $tol_3P)_2PtC \equiv CC \equiv CC \equiv CPt(P-p-tol_3)_2C \equiv CC \equiv CSi$ Me_3 (4) in 46% yield after chromatography. We were surprised by the degree of selectivity, as we have always found symmetrical tetraynes very difficult to desymmetrize. A desilylation/homocoupling sequence analogous to that used to convert 2 to 3 afforded first $trans, trans-Cl(p-tol_3P)_2PtC \equiv CC \equiv CC \equiv CC \equiv CPt$ - $(P-p-tol_3)_2C \equiv CC \equiv CH$ (5; 50%) and then the tetratris(octatetraynediyl) platinum target complex $trans, trans, trans, trans-Cl(p-tol_3P)_2PtC \equiv CC \equiv CC \equiv CC \equiv CC$ $CPt(P-p-tol_3)_2C \equiv CC \equiv CC \equiv C(p-tol_3P)_2PtC \equiv CC \equiv CC \equiv CC$ $CC \equiv CPt(P-p-tol_3)_2Cl$ (6; 48%). A one-pot variation gave 6 in 79% yield from 4. Interestingly, the desilylation of **4** was much slower than that of **1**.

33%

To access the triplatinum homologue of 6, a 2-fold cross-coupling was envisioned. First, (*p*-tol₃P)₂PtCl₂ was condensed with excess $HC \equiv CC \equiv CH$ in $HNEt_2$ in the presence of CuI. As shown in Scheme 2, workup gave the bis(butadiynyl) complex trans-HC=CC=CPt(P-ptol₃)₂C=CC=CH (7; 47%).¹⁴ Alternatively, an analogous condensation of $(p-tol_3P)_2PtCl_2$ and $HC \equiv CC \equiv CSiMe_3$ gave trans-Me₃SiC=CC=CPt(P-p-tol₃)₂C=CC=CSiMe₃ (8; 78%), which could be desilvated to 7 (96%) by procedures analogous to those above. Next, in a onepot sequence, 1 was desilylated to 2, ClSiMe₃ was added to scavenge fluoride ion,⁵ and **2** was cross-coupled with 0.25 equiv of 7 under Hay conditions. Chromatography gave the triplatinum bis(octatetraynediyl) target complex trans, trans, trans- $Cl(p-tol_3P)_2PtC \equiv CC \equiv CC \equiv CC \equiv CC$ $CPt(P-p-tol_3)_2C \equiv CC \equiv CC \equiv CC \equiv CPt(P-p-tol_3)_2Cl$ (9) in 36% yield based upon 7. As would be expected, some homocoupling product 3 also formed (33% based upon 1).

The physical properties of **3**, **9**, and **6** were compared. First, all samples were stable to ≥ 170 °C in the solid state, and solutions showed no deterioration after several hours in air. The IR spectra were practically identical (2138–2142 cm⁻¹ m, 2008–1999 cm⁻¹ w). As depicted in Figure 2, UV–visible spectra showed progressively more intense and red-shifted absorptions, indicative of electronic interactions between the tetrayne moieties. In the noninteractive limit, the molar extinction coefficients would only be proportional to the number of tetrayne moieties. Although single crystals of **9** and **6** have not yet been obtained, on the basis of the data for **3**, the chlorine–chlorine distances can be estimated as 30.3 and 43.1 Å, respectively.

Interestingly, the ¹³C NMR chemical shifts of the ClPtC= carbons (83.8-83.6 ppm, ${}^{2}J_{CP} = 15.3-9.6$ Hz)



Figure 2. UV-visible spectra (CH₂Cl₂, 1.25×10^{-5} M).

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were upfield of those of the \equiv CPtC \equiv carbons (106.1-105.8 ppm, ${}^{2}J_{CP} = 16.0-15.3$ Hz). As noted for many related complexes, the chemical shifts of the four innermost sp carbons fell in a narrow range (63.6–58.7 ppm).³⁻⁷ Cyclic voltammograms (n-Bu₄N⁺BF₄^{-/}CH₂Cl₂, 100 mV/s) showed partially reversible one-electron oxidations, with the i_c/i_a values decreasing with chain length (**3/9/6**: $E_{p,a} = 1.116/1.150/1.208$ V; $E_{p,c} = 1.063/$ $1.056/1.065 \text{ V}; \Delta E \ 100/95/140 \text{ mV}; i_c/i_a = 0.94/0.53/0.52).$ Series of diplatinum polyynediyl complexes exhibit analogous $i_{\rm c}/i_{\rm a}$ trends.^{4,5}

In summary, this study has provided the first series of longitudinally extended linear polymetallic/sp carbon arrays to be obtained by directed synthesis, as opposed to polymerization or oligomerization. The methodology developed can likely be further extended, such as by condensation of **9** with HC=CC=CSiMe₃ or Me₃SnC= CC≡CSiMe₃. The net result is a well-defined series of stable, easily handled functionalized building blocks that may be of use for molecular devices. Triplatinum complexes with PtC=CC=CPtC=CC=CPt linkages have been previously reported,^{8b} as well as related species with other metals.^{8b,15} but analogous assemblies involving four metal atoms are to our knowledge unknown.¹⁶ The properties of the preceding compounds remains under active investigation, and our next paper will report the introduction of a sulfur functionality, a frequently employed "alligator clip" for binding to surfaces.17,18

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Supporting Information Available: Text and tables giving experimental procedures, compound characterization data,¹¹ 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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