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# Longitudinally extended molecular wires based upon $\text{PtC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C}$ repeat units: Iterative syntheses of functionalized linear $\text{PtC}_8\text{Pt}$ , $\text{PtC}_8\text{PtC}_8\text{Pt}$ , and $\text{PtC}_8\text{PtC}_8\text{PtC}_8\text{Pt}$ assemblies

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# Longitudinally Extended Molecular Wires Based upon $\text{PtC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C}$ Repeat Units: Iterative Syntheses of Functionalized Linear $\text{PtC}_8\text{Pt}$ , $\text{PtC}_8\text{PtC}_8\text{Pt}$ , and $\text{PtC}_8\text{PtC}_8\text{PtC}_8\text{Pt}$ Assemblies

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**Summary:** Condensations of  $(p\text{-tol}_3\text{P})_2\text{PtCl}_2$  with  $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CSiMe}_3$  and  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  give mono- or bis((trimethylsilyl)butadiynyl) complexes that are desilylated and elaborated by oxidative cross-couplings and homocouplings to give the title compounds  $\text{trans-Cl}[(p\text{-tol}_3\text{P})_2\text{PtC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C}]_m\text{Pt}(P\text{-}p\text{-tol}_3)_2\text{Cl}$  ( $m = 1\text{--}3$ ).

Molecules in which sp carbon chains span two transition metals have attracted great attention from both fundamental and applied perspectives.<sup>1</sup> Many such wire-like compounds are now available, and researchers are attempting to construct multidimensional arrays that model more complex types of devices.<sup>2</sup> Efforts in our laboratory have focused on the elaboration of  $\text{Re}(\text{C}\equiv\text{C})_n\text{Re}^3$  and  $\text{Pt}(\text{C}\equiv\text{C})_n\text{Pt}^{4-6}$  systems. These building blocks are available with chain lengths of up to 20 carbons.

In the previous communication, we described “bundles” of  $\text{Pt}(\text{C}\equiv\text{C})_n\text{Pt}$  moieties ( $n = 3, 4$ ) in which the sp chains were laterally arrayed.<sup>7</sup> In this communication, we report efficient syntheses of longitudinal arrays based upon  $\text{PtC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C}$  repeat units that contain as many as four platinum atoms. Several polymers derived from  $\text{PtC}\equiv\text{CC}\equiv\text{C}$ ,  $\text{PdC}\equiv\text{CC}\equiv\text{C}$ , or  $\text{NiC}\equiv\text{CC}\equiv\text{C}$  units have been described,<sup>8</sup> as well as many that involve bis-(alkynyl) arenes,  $\text{MC}\equiv\text{C}\text{--Ar}\text{--C}\equiv\text{C}$ .<sup>9</sup> However, to our knowledge iterative synthetic methodologies that yield families of  $[\text{M}(\text{C}\equiv\text{C})_n]_m$  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  $\text{Pt}(\text{C}\equiv\text{C})_n\text{Pt}$  assemblies,<sup>4-7</sup> we began with the monofunctional platinum building blocks  $\text{trans-Ar}'(\text{Ar}_3\text{P})_2\text{PtCl}$ . 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  $(\text{Ar}_3\text{P})_2\text{PtCl}_2$ . 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  $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CSiMe}_3$  and  $(p\text{-tol}_3\text{P})_2\text{PtCl}_2$  (1:1 mol ratio) spontaneously condensed in refluxing THF (Scheme 1).<sup>10</sup> Workup gave the monosubstituted product  $\text{trans-Cl}(p\text{-tol}_3\text{P})_2\text{PtC}\equiv\text{CC}\equiv\text{CSiMe}_3$  (**1**),<sup>11</sup> derived from  $\text{Me}_3\text{SnCl}$  elimination, in 63% yield.<sup>12</sup> The diyne was in turn easily isolated from the sequential reaction of  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  with  $n\text{-BuLi}$  and  $\text{Me}_3\text{SnCl}$ .<sup>13</sup> 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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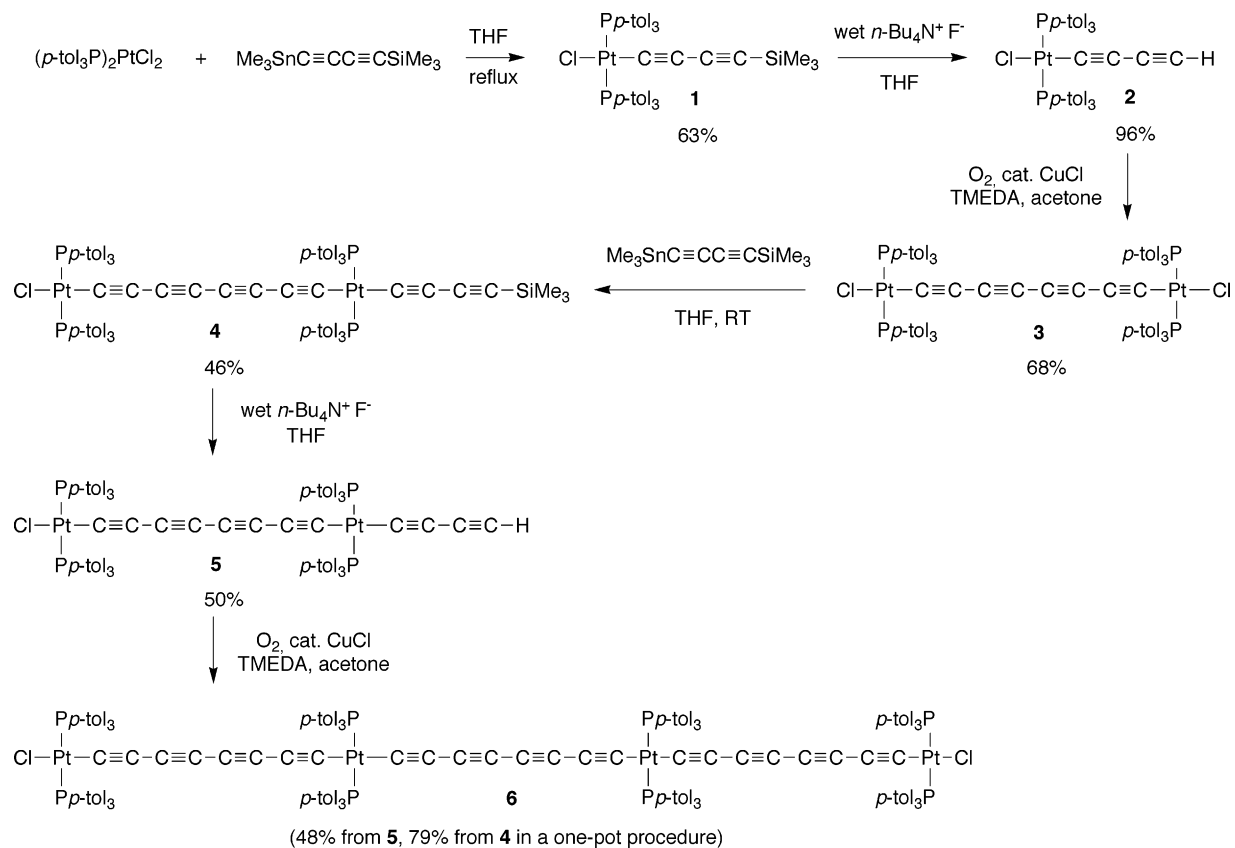
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(10) Both the *cis*- and *trans*-dichloride complexes give *trans* substitution products. The yields given are for reactions with the *cis* isomer, which is the kinetic product from  $\text{K}_2\text{PtCl}_4$  and  $p\text{-tol}_3\text{P}$ : (a) Alt, H. G.; Baumgärtner, R.; Brune, H. A. *Chem. Ber.* **1986**, *119*, 1694. (b) Matern, E.; Pikies, J.; Fritz, G. Z. *Anorg. Allg. Chem.* **2000**, *626*, 2136.

(11) All new compounds have been characterized by microanalysis, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) and IR spectroscopy, and mass spectrometry, as described in the Supporting Information.

(12) (a) Reactions of other  $\text{L}_2\text{PtCl}_2$  complexes and  $\text{Me}_3\text{SnC}\equiv\text{CPh}$  give the monosubstitution product  $\text{trans-ClL}_2\text{PtC}\equiv\text{CPh}$  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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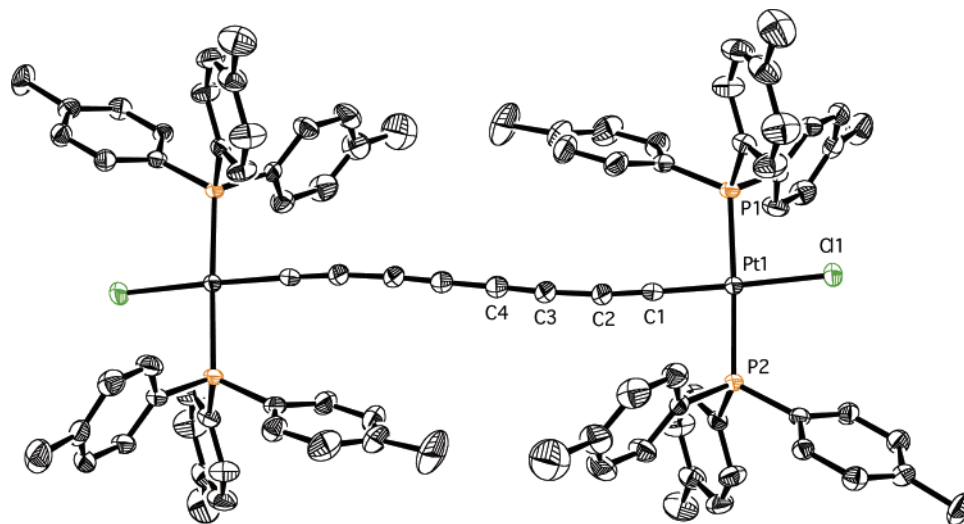
Scheme 1. Syntheses of the Diplatinum and Tetraplatinum Complexes **3** and **6**

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

Complex **1** was elaborated to a diplatinum octatetraynediyl complex, similarly to other (trialkylsilyl)-butadiynyl adducts described earlier. First, reaction with wet  $n\text{-Bu}_4\text{N}^+\text{F}^-$  gave the desilylated species *trans*- $\text{Cl}(p\text{-tol}_3\text{P})_2\text{PtC}\equiv\text{CC}\equiv\text{CH}$  (**2**) in 96% yield. An oxidative homocoupling under Hay conditions ( $\text{O}_2$ , catalyst CuCl, TMEDA) afforded *trans,trans*- $\text{Cl}(p\text{-tol}_3\text{P})_2\text{PtC}\equiv\text{CC}\equiv$

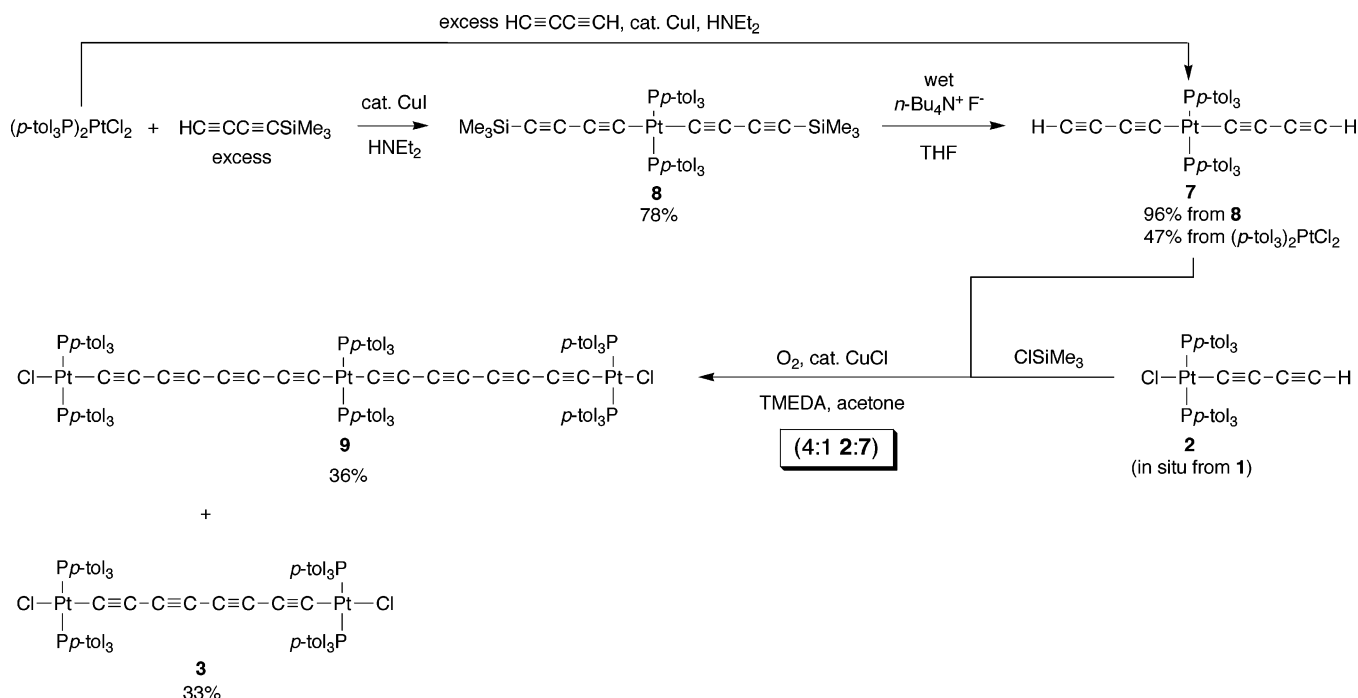
$\text{CC}\equiv\text{CC}\equiv\text{C}(\text{P}p\text{-tol}_3)_2\text{Cl}$  (**3**) in 68% yield. A crystal structure of a solvate was determined as described in the Supporting Information, and the result is depicted in Figure 1. The sp carbon chain adopts an S-shaped conformation, a feature seen in other tetraynes.<sup>1b</sup> All bond lengths and angles are well within the ranges found in related diplatinum complexes.<sup>1b,4-7</sup>

Reactions of **3** were studied next. As shown in Scheme 1, treatment with 1.0 equiv of  $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CSiMe}_3$  gave the monosubstituted complex *trans,trans*- $\text{Cl}(p\text{-$



**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**

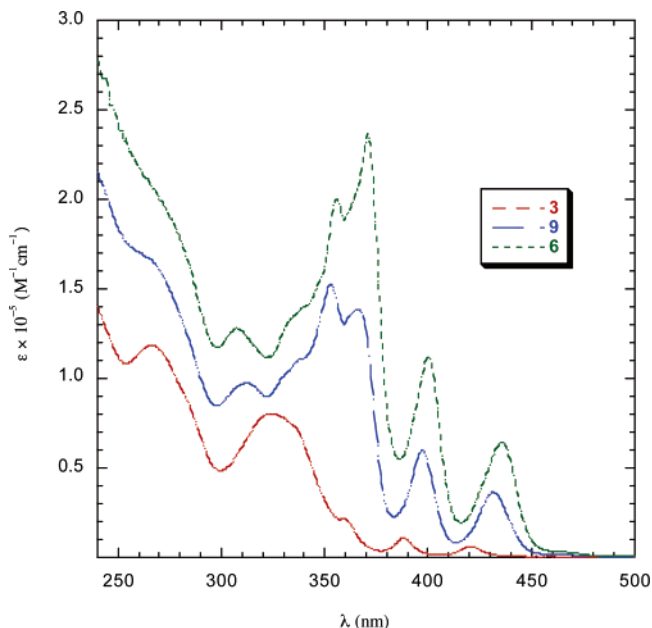


tol<sub>3</sub>P)<sub>2</sub>PtC≡CC≡CC≡CC≡CPt(P-*p*-tol<sub>3</sub>)<sub>2</sub>C≡CC≡CSiMe<sub>3</sub> (**4**) in 46% yield after chromatography. We were surprised by the degree of selectivity, as we have always found symmetrical tetraynes very difficult to desymmetrize. A desilylation/homocoupling sequence analogous to that used to convert **2** to **3** afforded first *trans,trans*-Cl(*p*-tol<sub>3</sub>P)<sub>2</sub>PtC≡CC≡CC≡CC≡CPt(P-*p*-tol<sub>3</sub>)<sub>2</sub>C≡CC≡CH (**5**; 50%) and then the tetraplatinum tris(octatetraynediyl) target complex *trans,trans,trans,trans*-Cl(*p*-tol<sub>3</sub>P)<sub>2</sub>PtC≡CC≡CC≡CC≡CPt(P-*p*-tol<sub>3</sub>)<sub>2</sub>C≡CC≡CC≡CC≡CC≡C(*p*-tol<sub>3</sub>P)<sub>2</sub>PtC≡CC≡CC≡CC≡CC≡CPt(P-*p*-tol<sub>3</sub>)<sub>2</sub>Cl (**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**.

To access the triplatinum homologue of **6**, a 2-fold cross-coupling was envisioned. First, (*p*-tol-3P)<sub>2</sub>PtCl<sub>2</sub> was condensed with excess HC≡CC≡CH in HNEt<sub>2</sub> in the presence of CuI. As shown in Scheme 2, workup gave the bis(butadiynyl) complex *trans*-HC≡CC≡Cpt(P-*p*-tol-3)<sub>2</sub>C≡CC≡CH (**7**; 47%).<sup>14</sup> Alternatively, an analogous condensation of (*p*-tol-3P)<sub>2</sub>PtCl<sub>2</sub> and HC≡CC≡CSiMe<sub>3</sub> gave *trans*-Me<sub>3</sub>SiC≡CC≡Cpt(P-*p*-tol-3)<sub>2</sub>C≡CC≡CSiMe<sub>3</sub> (**8**; 78%), which could be desilylated to **7** (96%) by procedures analogous to those above. Next, in a one-pot sequence, **1** was desilylated to **2**, ClSiMe<sub>3</sub> was added to scavenge fluoride ion,<sup>5</sup> 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)<sub>2</sub>PtC≡CC≡CC≡CC≡CC≡CCpt(P-*p*-tol-3)<sub>2</sub>C≡CC≡CC≡CC≡CC≡CCpt(P-*p*-tol-3)<sub>2</sub>Cl (**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  $\geq 170$  °C in the solid state, and solutions showed no deterioration after several hours in air. The IR spectra were practically identical (2138–2142  $\text{cm}^{-1}$  m, 2008–1999  $\text{cm}^{-1}$  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  $^{13}\text{C}$  NMR chemical shifts of the  $\text{ClPtC}\equiv$  carbons (83.8–83.6 ppm,  $^2J_{\text{CP}} = 15.3\text{--}9.6$  Hz)



**Figure 2.** UV–visible spectra ( $\text{CH}_2\text{Cl}_2$ ,  $1.25 \times 10^{-5}$  M).

(14) The  $n\text{-Bu}_3\text{P}$  analogue of **7** and the  $\text{Ph}_3\text{P}$  analogue of **8** have been previously characterized: (a) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101. (b) Peters, T. B.; Zheng, Q.; Stahl, J.; Bohling, J. C.; Arif, A. M.; Hampel, F.; Gladysz, J. A. *J. Organomet. Chem.* **2002**, *641*, 53.

were upfield of those of the  $\equiv\text{C}\text{PtC}\equiv$  carbons (106.1–105.8 ppm,  $^2J_{\text{CP}} = 16.0\text{--}15.3$  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).<sup>3–7</sup> Cyclic voltammograms ( $n\text{-Bu}_4\text{N}^+\text{BF}_4^-/\text{CH}_2\text{Cl}_2$ , 100 mV/s) showed partially reversible one-electron oxidations, with the  $i_{\text{c}}/i_{\text{a}}$  values decreasing with chain length (**3/9/6**:  $E_{\text{p,a}} = 1.116/1.150/1.208$  V;  $E_{\text{p,c}} = 1.063/1.056/1.065$  V;  $\Delta E$  100/95/140 mV;  $i_{\text{c}}/i_{\text{a}} = 0.94/0.53/0.52$ ). Series of diplatinum polyynediyl complexes exhibit analogous  $i_{\text{c}}/i_{\text{a}}$  trends.<sup>4,5</sup>

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  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  or  $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CSiMe}_3$ . 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  $\text{PtC}\equiv\text{CC}\equiv\text{C}\text{PtC}\equiv\text{CC}\equiv\text{C}\text{Pt}$  linkages have been previously reported,<sup>8b</sup> as well as related species with other metals.<sup>8b,15</sup> but analogous assemblies involving four metal atoms are to our knowledge unknown.<sup>16</sup>

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.<sup>17,18</sup>

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft (DFG, SFB Grant 583) and Johnson Matthey PMC (platinum loans) for support.

**Supporting Information Available:** Text and tables giving experimental procedures, compound characterization data,<sup>11</sup> 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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