Organometallics **2004,** *23,* 5893−5895

Syntheses and Structures of Tetraplatinum Bis(polyynediyl) Complexes with Laterally Arrayed sp Carbon Chains

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Received August 19, 2004

Summary: Reactions of trans,trans-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_nPt(P\text{-}p\text{-}tol_3)_2(C_6F_5)$ *(*$n = 3, 4$*) and* $Ph_2P(CH_2)_3PPh_2$ *(2.5 equiv) give the tetraplatinum complexes trans,trans,trans,trans-*$(C_6F_5)Pt(C{\equiv}C)_nPt(C_6F_5)(PPh_2(CH_2)_3Ph_2P)_2(C_6F_5)Pt(C{\equiv}C)_nPt(C_6F_5)(PPh_2(CH_2)_3Ph_2P)_2$ *(95−81%), in which two sp carbon chains span two 12-membered-ring termini. Chain−chain interactions have been probed by crystallography, UV−visible spectroscopy, cyclic voltammetry, and thermolyses.*

There are now hundreds of molecules in which sp carbon chains span two transition metals, as summarized in a recent comprehensive review.[1] Much of this interest has been prompted by their rich redox chemistry, the unique and often unusual structural[2] and electronic[3] features of each redox state,[4] and the obvious connection to molecular wires. Chain length represents one of several fundamental structural variables. We[5−8] and others[9] have described several series of polyynediyl or $M(C{\equiv}C)_nM$ complexes that can be extended to 12−20 carbon atoms.

The linear bridges constitute versatile connectors that can in principle be patterned into a variety of architectures. We have sought to construct various arrays of polyynediyl linkages as models for more sophisticated types of molecular devices. These might include "bundles" that laterally juxtapose sp chains via a common end group assembly—a "multiply stranded" molecular wire—or, as reported in the following communication,[10] longitudinally extended systems. Youngs, Bruce, and Anderson have already synthesized elegant square-shaped complexes with metal corners and polyynediyl edges.[11]

In previous papers, we described reactions of the diplatinum complexes *trans,trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_nPt(P\text{-}p\text{-}tol_3)_2(C_6F_5)$ ($n = 3{-}6$; $\mathbf{PtC_{2n}Pt}$) and diphosphines $Ar_2P(CH_2)_mPAr_2$ ($m = 8{-}18$).[7,12] When the *m*/*n* values are appropriate, substitution products form in which the diphosphines span the platinum termini, *trans,trans*-$(C_6F_5)(Ar_2P(CH_2)_mPAr_2)Pt(C{\equiv}C)_nPt(Ar_2P(CH_2)_mPAr_2)(C_6F_5)$. The sp carbon chains are sterically protected, and when the *m*/*n* ratios are sufficiently high, the sp^3 chains wrap around the sp chain in striking chiral double-helical conformations. We wondered what would happen at much lower values of *m* (e.g., 2−3)—a fundamental question that constitutes the subject of this communication. Would dimeric or oligomeric complexes form that contain multiple sp carbon chains? Or would substitution be accompanied by geometric isomerism, giving termini with *cis*-diphosphine chelates?

As shown in Scheme 1, THF solutions of $\mathbf{PtC_6Pt}$[6,12] and $\mathbf{PtC_8Pt}$[6] (3.9−2.5 M) were treated with solid $Ph_2P(CH_2)_3PPh_2$ (dppp; 2.5 equiv). Workup gave homogeneous products, and ^1H NMR spectra clearly showed that dppp had displaced the P-*p*-tol$_3$ ligands (95% and 81% yields). Both complexes exhibited a single ^{31}P signal, indicating that the trans geometries at platinum were maintained.[13] The mass spectra showed strong ions consistent with *tetra*platinum products $[\mathbf{Pt'C_xPt'}]_2$ ($x = 6, 8$). The ^{13}C NMR and IR spectra resembled those of the precursors, suggesting the sp carbon chains to be intact.

Crystals of the solvate $[\mathbf{Pt'C_6Pt'}]_2{\cdot}4CH_2Cl_2$ were grown from CH_2Cl_2/methanol, and the X-ray structure

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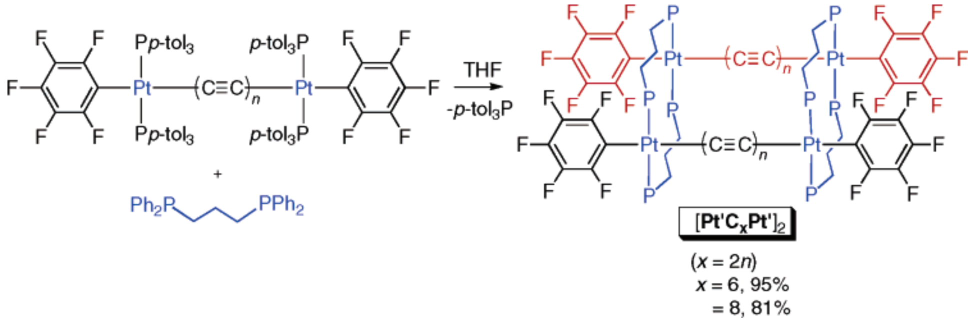
(13) All new compounds have been characterized by microanalysis, NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy, and mass spectrometry, as described in the Supporting Information.

10.1021/om049354f CCC: US 27.50

Publication on Web 11/10/2004

Scheme 1. Syntheses of Title Compounds



was determined as described in the Supporting Information. The result, depicted in Figure 1 (top and middle of the left-hand side), confirmed the provisional formulation. Each dppp ligand spans two platinum atoms that belong to different Pt(C$\equiv$C)$_3$Pt linkages. The net result is a “bundle” of two sp carbon chains with 12-membered-

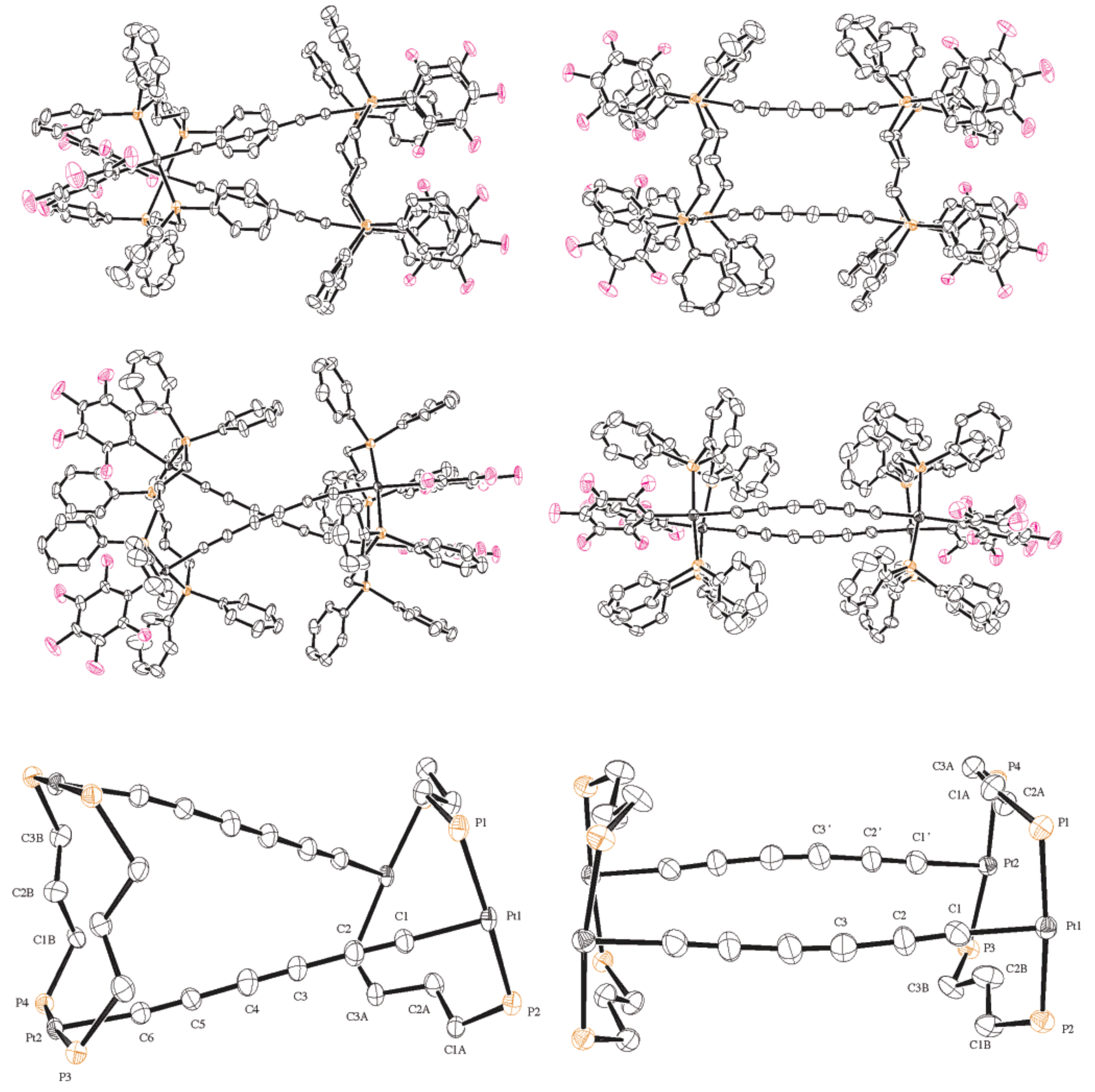


Figure 1. Crystal structures of [**Pt′C$_6$Pt′**]$_2$: (left column) representations of [**Pt′C$_6$Pt′**]$_2$·4CH$_2$Cl$_2$; (right column) representations of [**Pt′C$_6$Pt′**]$_2$·3CH$_2$Cl$_2$·C$_4$H$_8$O.

ring termini of the formula $PtPPh_2(CH_2)_3Ph_2PPtPPh_2(CH_2)_3Ph_2P$. As best visualized in the partial structure in Figure 1 (bottom of the left-hand side), a C_2 axis passes through the 12-membered rings.

The structure of $[\mathbf{Pt'C_6Pt'}]_2\cdot 4CH_2Cl_2$ exhibits several unusual twisting phenomena. First, the platinum square planes in $Pt(C{\equiv}C)_nPt$ complexes are normally coplanar. However, those in $[\mathbf{Pt'C_6Pt'}]_2\cdot 4CH_2Cl_2$ are nearly perpendicular, with angles of 96−101°.[14] Second, the sp carbon chains are not parallel but “crossed” by ca. 83.1°, as approximated by the angles of the $Pt_A{-}Pt_B{-}Pt_C$ and $Pt_B{-}Pt_C{-}Pt_D$ planes. Furthermore, the closest carbon−carbon contact between the chains, 3.60 Å, is only slightly greater than the sum of the van der Waals radii (2 × 1.78 Å).[2,15] This is well within the range required for solid-state reactions of polyynes, such as topochemical polymerization.[2,16] However, the closest analogous intermolecular contact is 10.80 Å.

Later in the course of this study, the crystalline solvate $[\mathbf{Pt'C_6Pt'}]_2\cdot 3CH_2Cl_2\cdot C_4H_8O$ was isolated from a reaction mixture, and the structure shown in Figure 1 (right-hand side) determined. In this pseudopolymorph,[17] the twisting phenomena noted above are absent. Now the platinum square planes of each $Pt(C{\equiv}C)_3Pt$ moiety are nearly coplanar, with angles of 0−25°.[14] The two $Pt(C{\equiv}C)_3Pt$ segments are also nearly coplanar; the average and maximum atomic deviations from the least-squares plane are 0.163 and 0.269 Å, respectively. The $Pt_A{-}Pt_B{-}Pt_C$ and $Pt_B{-}Pt_C{-}Pt_D$ planes define an angle of 0°. The closest carbon−carbon contact between the chains, 4.95 Å, is much greater than in the other structure. Accordingly, the crystal density, sometimes used to gauge relative stabilities of polymorphs,[17] is lower (1.622 vs 1.711 Mg/m^3).

The bond lengths and angles associated with the $Pt(C{\equiv}C)_3Pt$ segments are similar in both pseudopolymorphs and close to those of $\mathbf{PtC_6Pt}$ and related compounds in the previous paper.[12] Although $C_6H_5/C_6F_5/C_6H_5$ π stacking interactions are apparent in Figure 1, the average centroid−centroid distances (3.85 and 4.00 Å) are greater than those in related compounds ($\mathbf{PtC_6Pt}$, 3.66 Å). In any event, these structures indicate that $[\mathbf{Pt'C_xPt'}]_2$ should have a range of accessible conformations in solution. Interestingly, the UV−visible spectra of $[\mathbf{Pt'C_xPt'}]_2$ are quite similar to those of the diplatinum counterparts $\mathbf{PtC_xPt}$,[18] suggesting only minor chain−chain electronic interactions. The nature of the transitions is analyzed in detail elsewhere.[19]

The thermal properties of $[\mathbf{Pt'C_xPt'}]_2$ were studied. The complexes decomposed without melting at ca. 220 ($x = 6$) and 186 °C ($x = 8$), and TGA experiments showed the onset of mass loss at 266−269 °C. Between 200 and 250 °C, the IR bands of $[\mathbf{Pt'C_8Pt'}]_2$ at 2150 and 2007 cm^{-1} were replaced by that of a new C≡C-rich substance at 2077 cm^{-1}. Next, redox properties were probed by cyclic voltammetry. In contrast to the diplatinum complexes $\mathbf{PtC_xPt}$, which undergo partially reversible oxidations to radical cations,[6] the tetraplatinum complexes exhibit irreversible behavior characteristic of an ECE process. A plausible rationale for this difference would involve chain−chain coupling in the initially formed radical cation. We have previously suggested that such processes contribute to the progressively lower stabilities of bimetallic radical cations $[M(C{\equiv}C)_nM]^{\bullet+}$ as the chains lengthen and become sterically more accessible.[6,8]

To date, well-defined chain−chain coupling reactions of the tetraplatinum complexes have remained elusive. Crystallographic studies of air-oxidized samples have provided evidence for species with $R(C{=}O)C(R){=}C(R)(C{=}O)R$ junctures (R = $(C{\equiv}C)_nPt$ moiety), but the structures could not be fully refined (from $[\mathbf{Pt'C_6Pt'}]_2$: IR 2080/1636 cm^{-1}, br m/br m; FAB MS *m/z* 3274, MH$^+$). In other preliminary efforts, the shorter-chain tetraplatinum complex $[\mathbf{Pt'C_4Pt'}]_2$ has been similarly synthesized. However, attempts to prepare the longer-chain analogue $[\mathbf{Pt'C_{12}Pt'}]_2$ yield mainly poorly soluble oligomers or polymers. Interestingly, similar reactions of $\mathbf{PtC_xPt}$ and $Ph_2P(CH_2)_2PPh_2$ (dppe) give, at least in some cases, diplatinum complexes with *cis*-dppe chelates at each terminus. In all of the preceding substitution reactions, there are issues of kinetic and thermodynamic control, and experiments to probe these points are in progress.

In summary, we have shown that suitable diphosphine ligands can bundle $M(C{\equiv}C)_nM$ units into lateral arrays. In these first-generation systems, the sp carbon chains are capable of various interactions. However, geometrically rigid diphosphines could be employed to enforce greater spacings and modulate these phenomena. Other types of donor ligands might be used to template multiple sp chains or bring the metal termini—which are separated by $P(CH_2)_3P$ moieties in $[\mathbf{Pt'C_xPt'}]_2$—into conjugation. From a performance standpoint, molecular wires that are comprised of multiple unsaturated strands should have unique attributes and advantages.[20] Potential synthetic routes to all of these motifs are under active investigation.

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 and characterization data[13] for all compounds and crystallographic data for $[\mathbf{Pt'C_6Pt'}]_2$; crystal data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049354F

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[14] The exact value depends on the method of calculation: $(P_A{-}Pt_A{-}P_A){-}Pt_B$ vs $Pt_A{-}(P_B{-}Pt_B{-}P_B)$, 95.5°; $C_{ipsoA}{-}(P_A{-}Pt_A{-}P_A)$ vs $(P_B{-}Pt_B{-}P_B){-}C_{ipsoB}$, 101.1°; $C_{ipsoA}{-}(P_A{-}Pt_A{-}P_A){-}C_{\alpha A}$ vs $C_{\alpha B}{-}(P_B{-}Pt_B{-}P_B){-}C_{ipsoB}$, 99.9°. The corresponding values for $[\mathbf{Pt'C_6Pt'}]_2\cdot 3CH_2Cl_2\cdot C_4H_8O$ are 0, 25.0, and 20.5°.

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[18] Data for$[\mathbf{Pt'C_8Pt'}]_2/\mathbf{PtC_8Pt}$ (CH_2Cl_2, nm (ϵ, M^{-1} cm^{-1})): 310/294 (129 000/88 000), 322/326 (193 000/126 000), 352/356 (12 600/7000), 379/383 (9800/6000), 410/414 (6000/3000). In an idealized limit without chain−chain interactions, band broadening, etc., the ϵ values for the former complex should be twice those of the latter.

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