## Wire-like PtC=CC=CC=CC=CPt moieties surrounded by double-helical "insulation": new motifs featuring $P(CH_2)_{20}P$ and $P(CH_2)_4O(CH_2)_2O(CH_2)_4P$ linkages<sup>†</sup>

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Ring-closing alkene metatheses of *trans*,*trans*-( $C_6F_5$ )(Ph<sub>2</sub>P– Z-CH=CH<sub>2</sub>)<sub>2</sub>Pt(C=C)<sub>4</sub>Pt(Ph<sub>2</sub>P-Z-CH=CH<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>) (Z = (CH<sub>2</sub>)<sub>9</sub>, (CH<sub>2</sub>)<sub>4</sub>O(CH<sub>2</sub>)<sub>2</sub>), followed by hydrogenation, give the title compounds; the former exhibits an exceptionally twisted conformation, and the latter establishes that functional groups can be incorporated into the flexible sp<sup>3</sup> chain.

There are many types of unsaturated ligands that can link two metal or other redox-active centers and mediate various chargeand electron-transfer processes.<sup>1</sup> In the macroscopic world, electron transporting materials such as household electrical wire are commonly insulated from their environments. Accordingly, several research groups have endeavoured to "insulate" such molecular assemblies, and a variety of clever strategies have been applied.<sup>2-5</sup>

In previous reports, we have described numerous diplatinum polyynediyl or  $Pt(C\equiv C)_nPt$  complexes (n = 3-14).<sup>6-11</sup> These feature the most fundamental type of unsaturated bridging ligand, a wire-like sp carbon chain.<sup>12</sup> As shown in Scheme 1, the hexatriynediyl and octatetraynediyl complexes *trans*,*trans*- $(C_6F_5)(p-tol_3P)_2Pt(C\equiv C)_nPt(Pp-tol_3)_2(C_6F_5)$  (I; n = 3, 4) and the  $a,\omega$ -diphosphines  $Ar_2P(CH_2)_mPAr_2$  (II; m = 8, 10-12, 14) react to give the substitution products *trans*,*trans*- $(C_6F_5)(Ar_2$ 

 $P(CH_2)_m PAr_2$ )  $Pt(C \equiv C)_n Pt(Ar_2P(CH_2)_m PAr_2)(C_6F_5)$  (III).<sup>9</sup> In all cases, the termini-spanning diphosphine ligands sterically shield the sp carbon chains. Crystal structures show that the flexible sp<sup>3</sup> chains can, when sufficiently long (m = 14), wrap around the sp chains in a striking chiral double-helical motif (IIIb). In all four examples characterized to date, the endgroups define angles of 189.3–196.5°, slightly more than a half twist.<sup>13</sup>

We sought to further define the accessibility of such "insulated" bimetallic systems with respect to various parameters. First, can the sp<sup>3</sup> chains be lengthened, and if so do more highly twisted helices result? Second, can functional groups be incorporated into the sp<sup>3</sup> chains? These might provide control elements for self-assembly processes. Third, can isomeric species with *trans*-spanning diphosphine ligands also form (**IV**, Scheme 1), and if so to what degree do they shield the sp chain? Unfortunately, reactions of diplatinum complexes **I** and diphosphines **II** with  $m \ge 16$  afforded only oligomers.<sup>9a,14</sup> Hence, we turned to an alternative synthesis involving alkene metathesis described in our original study.<sup>9a</sup> Although this route is somewhat longer, it does not require phosphine substitution and delivers the target molecules reliably.

An octatetraynediyl complex analogous to I but with the alkenecontaining phosphine  $Ph_2P(CH_2)_9CH=CH_2$  (a) was prepared similarly to a lower homolog<sup>9a</sup> as summarized in Scheme 2 and detailed in the ESI<sup>†</sup>. First, a diplatinum di(tetrahydrothiophene) complex and a were reacted to give the monoplatinum bis(phosphine) chloride complex 1a (95%).<sup>15</sup> This was treated with butadiyne/HNEt<sub>2</sub> in the presence of a catalytic amount of



Scheme 1 Limiting structures for complexes derived from  $C_6F_5Pt(C\equiv C)_nPtC_6F_5$  units and diphosphines  $Ar_2P(CH_2)_mPAr$  (II).

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Scheme 2 Syntheses of precursors to double helical complexes. Conditions: (a)  $CH_2Cl_2$ ; (b)  $H(C\equiv C)_2H$ , cat. CuCl,  $HNEt_2$ ; (c)  $O_2$ , cat. CuCl/TMEDA, acetone.

CuI to yield the butadiynyl complex **2a** (80%). Subsequent Hay oxidative coupling afforded the desired diplatinum complex **3a** (77%). All complexes were characterized by microanalysis, mass spectrometry, and IR and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) spectroscopy, as summarized in the ESI<sup>†</sup>.

As shown in Scheme 3 (top), **3a** was treated with Grubbs' catalyst. Subsequent hydrogenation and column chromatography gave three fractions. The first contained the title complex **4** (17%), and the third the other possible intramolecular metathesis product **5** (15%). These correspond to **III** and **IV** with  $n/m/Ar = 4/20/C_6H_5$ . An intermediate fraction contained a 2 : 1 4/5 mixture (31%). The spectroscopic properties of **4** and **5** were rather similar.

However, the most intense ion in the mass spectrum of 4 was the molecular ion, whereas 5 gave extensive fragmentation to monoplatinum ions.

The crystal structures of **4** and **5** were determined as described in the ESI<sup>†</sup> (including details of how nine disordered sp<sup>3</sup> carbon atoms in the former were modeled).<sup>16</sup> As depicted in Fig. 1, **4** exhibited a markedly helical conformation, with the endgroups defining an angle of 294.8°—more than three-quarters of a twist. As illustrated by the space-filling representations C and D, the sp carbon chain is nearly completely shielded. Curiously, all other Pt(C=C)<sub>n</sub>Pt complexes with n > 2 crystallize with the endgroups within ±18.4° of coplanarity.<sup>17</sup> DFT calculations show that



Fig. 1 ORTEP (A, B, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity) and space-filling (C, D) representations of 4.



Scheme 3 Syntheses of double helical complexes. Conditions: (a) 7 mol%  $Ru(=CHPh)(PCy_3)_2(Cl)_2$ ; (b) 10 mol% Pd/C, 1 atm, 14 d; (c) 6 mol%  $Ru(=CHPh)(PCy_3)(H_2IMes)(Cl)_2$ .

endgroup rotation is essentially barrierless, with no electronically preferred conformation.<sup>8</sup> Like all similar double helical diplatinum complexes,<sup>9</sup> both enantiomers are present in the unit cell.

As depicted in Fig. 2, the isomer **5** crystallizes in a "double half-clamshell" conformation, with the macrocycles directed on opposite sides of the  $P_2Pt-PtP_2$  plane and an inversion center between C4 and C4a. Views G and H show that the sp chain is still extensively shielded, although not to the extent as in **4**. Two distinct gaps remain above and below the  $P_2Pt-PtP_2$  plane. Homologs of **5** with shorter sp<sup>3</sup> chains crystallize in analogous conformations.<sup>18</sup>

Next, the oxygenated alkene-containing phosphine  $Ph_2P(CH_2)_4O(CH_2)_2CH=CH_2$  (b) was synthesized (ESI<sup>†</sup>). As illustrated in Scheme 2, it was converted to the corresponding diplatinum octatetraynediyl complex 3b by a sequence parallel to 3a. Complex 3b reacted sluggishly with Grubbs' catalyst, but

Grubbs' second generation catalyst was much more effective. As shown in Scheme 3, subsequent hydrogenation gave the title complex 6 in 27% overall yield after chromatography. Later fractions contained only small amounts of non-oligomeric products. Although no complex analogous to 5 was noted, a yield of <5% would not have been detected.

The crystal structure of **6** was determined.<sup>16</sup> As depicted in Fig. 3, a double-helical conformation was again found. The number of atoms in each flexible sp<sup>3</sup> chain (sixteen) is intermediate between those of **IIIb** (fourteen) and **4** (twenty). However, the endgroups define an angle of  $164.1^{\circ}$ —somewhat less than a half twist, and less than the range of values for **IIIb** (189.3–196.5°). Thus, the degree of twisting is not a simple function of the number of atoms in the flexible chains. View L shows that a region of the sp chain remains exposed (the opposite side is more shielded).

A cylindrical helix is characterized by a radius, which for **6**, **4**, and **IIIb** can be approximated by calculating the average distance from every atom in the sp<sup>3</sup> chain to the Pt–Pt vector. The value for **6** (4.28 Å) is greater than those of other octatetraynediyl complexes of the type **IIIb** (3.76–4.04 Å). This logically follows from the combination of (a) the lower degree of twisting, and (b) the two extra atoms in each sp<sup>3</sup> chain. Perhaps there is an underlying electronic effect of the oxygen atoms, the lone pairs of which point conspicuously away from the sp chain. The value for the more highly twisted complex **4** (4.13 Å) is intermediate. Note that as the sp<sup>3</sup> chains become longer and longer, the contact surface of the sp chain will eventually be saturated, requiring helices of greater radii, and/or alternative conformations.

Finally, cyclic voltammograms of **4–6** were recorded. In each case, partially reversible oxidations were observed ( $E_{p,a}$ ,  $E_{p,c}$ ,  $E^{\circ}$ ,  $\Delta E$ ,  $i_{c/a}$ : 1.300/1.305/1.304 V, 1.236/1.208/1.231 V, 1.268/1.256/1.268 V, 64/97/73 mV, 0.82/0.53/0.75), which are presumed to represent one-electron processes.<sup>19</sup> These data can be compared to those for the unshielded complexes **3a** and **3b**, and an analogous species with the saturated phosphine Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub><sup>20</sup> (1.408/1.310/1.301 V, 1.226/1.239/1.214 V, 1.317/1.274/1.258 V, 182/71/87 mV, 0.15/0.72/0.68). The  $\Delta E$  and  $i_{c/a}$  values show that the double helical complex **4** (but not **5**) undergoes somewhat more reversible oxidations than the unshielded complexes, consistent with a longer lived radical cation; however, oxygen-containing **6** is not significantly better than **3b**.

Complexes **4** and **6** add considerable diversity to the growing number of artificial double-stranded helices.<sup>21</sup> As noted earlier,<sup>9a</sup> species of the type **IIIb** are distinguished by a lack of bonding interactions or complementarity between the two flexible strands. Thus, they should be more predisposed to dynamic behavior than classical helicates. Accordingly, the NMR properties of **4** and **6** indicate that the enantiomers are rapidly interconverting in solution, even at low temperatures, presumably by an untwisting/retwisting process. Naturally, other conformations must be populated, and experiments to probe this point are in progress. In summary, this study has established that alkene metathesis can be used to access complexes **IIIb** with sp<sup>3</sup> chains that are considerably longer than those hitherto available, as well as functionalized. Further extensions of the methodology in Scheme 3 will be reported in due course.

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Fig. 2 ORTEP (E, F with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity) and space-filling (G, H) representations of 5.



Fig. 3 ORTEP (I, J with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity) and space-filling (K, L) representations of 6.

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