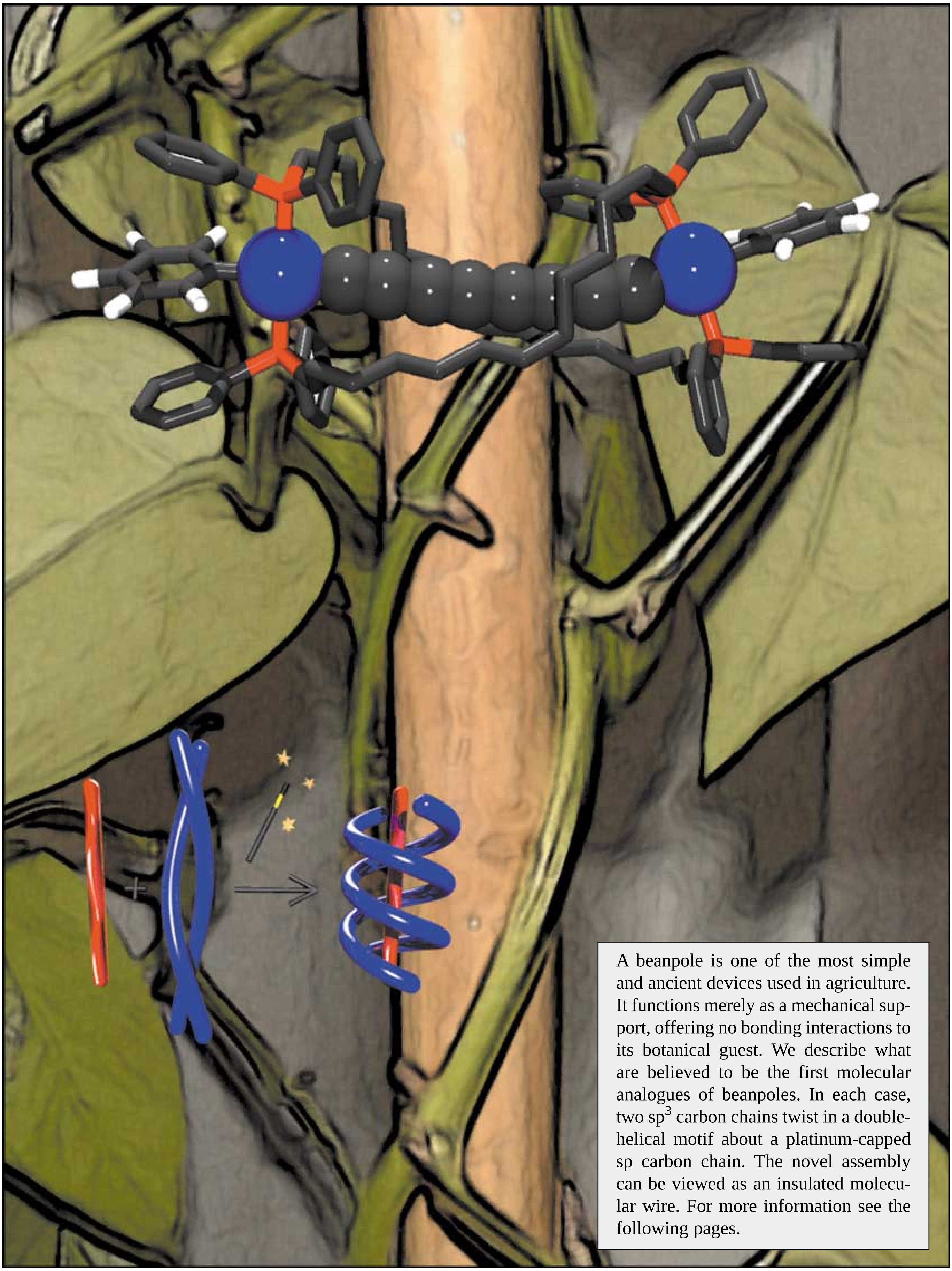

A beanpole is one of the most simple and ancient devices used in agriculture. It functions merely as a mechanical support, offering no bonding interactions to its botanical guest. We describe what are believed to be the first molecular analogues of beanpoles. In each case, two sp^3 carbon chains twist in a double-helical motif about a platinum-capped sp carbon chain. The novel assembly can be viewed as an insulated molecular wire. For more information see the following pages.

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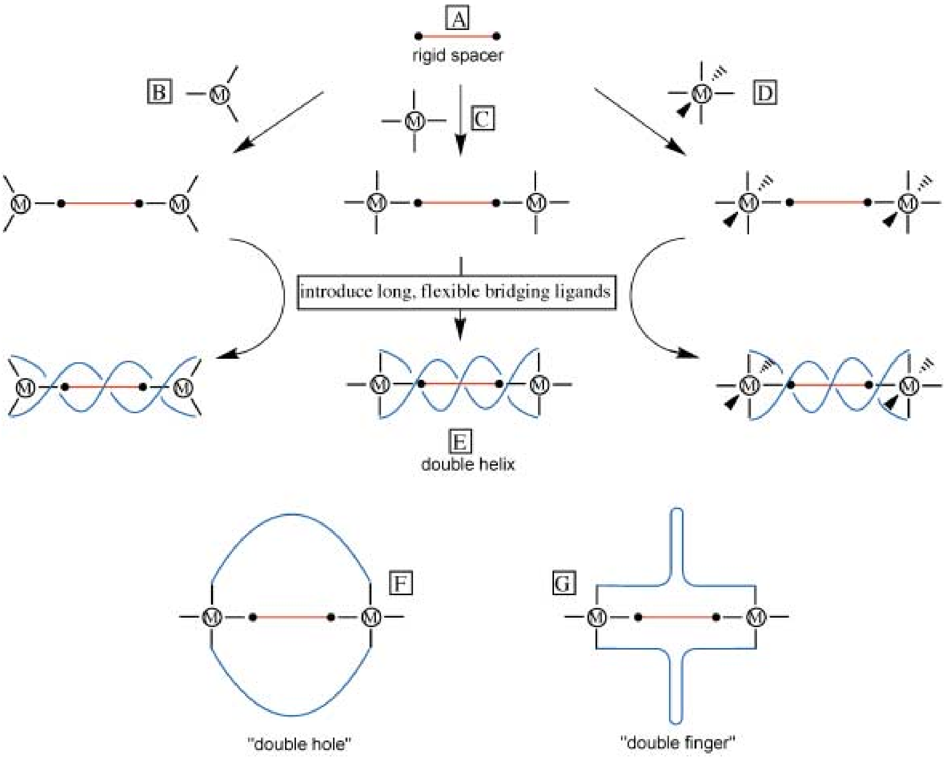
sp Carbon Chains Surrounded by sp^3 Carbon Double Helices: A Class of Molecules that are Accessible by Self-Assembly and Models for "Insulated" Molecular-Scale Devices**

Jürgen Stahl, James C. Bohling, Eike B. Bauer, Thomas B. Peters, Wolfgang Mohr, José M. Martín-Alvarez, Frank Hampel, and John A. Gladysz*

DNA was the first chemical substance to be recognized as a double helix. This structural motif, which is capable both of carrying information (e.g., the genetic code) and protecting interior functional domains, has since been engineered into a variety of nonnatural molecules.[1–6] Many of these are coordination compounds, often referred to as "helicates".[3, 4] To our knowledge, all double-helical molecules feature bonding interactions between the helix strands (e.g., hydrogen bonds), or covalent bonds to metal templates dispersed throughout the strands. Factors that promote or enforce complementarity—that is, the programming[1] or "encoding of specific structural and conformational information"[7]—are thought to be required. We wondered whether it might be possible to design double-helical molecules that lack these conventional binding elements or driving forces—in an extreme sense, species that would form double helices because "they felt like it".



Scheme 1. Geometrical analysis: representative endgroups (**B**, **C**, **D**) that can support double-helical motifs of flexible bridging ligands about rigid spacer ligands (**A**).

Our strategy was as follows. Start with a rigid, linear connecting rod, as represented by **A** in Scheme 1. Such building blocks are playing leading roles in the development of molecular-scale devices and nanochemistry.[8, 9] One of the most fundamental and svelte of such blocks would be a chain of sp-hybridized carbon atoms.[10, 11] Attach to each terminus an atom that supports at least two additional bonds, symmetrically disposed with respect to the rod. Transition metals would be obvious candidates, as exemplified by **B**–**D** (Scheme 1). The endgroups could anchor two (and sometimes more) long flexible chains incapable of bonding interactions—for example polymethylene $(CH_2)_n$ or polydifluoromethylene segments $(CF_2)_n$.

Once all covalent bonds are in place, there is the obvious question of conformation. Will the flexible chains twist about the rigid rod to give double helices as in **E** (Scheme 1), or preferentially adopt conformations with "holes" (**F**) or "fingers" (**G**)? Since monocyclic crown ethers and related macrocycles seldom exhibit conformations with holes,[12] we discounted possibility **F**. Space filling molecular models of various target molecules allowed the number of twists in the helical conformer **E** to be estimated. When the flexible chains were too short, twists or finger protrusions became impossible.

Such target structures have potential practical applications that merit note at the outset. Molecules in which unsaturated ligands span two transition metals can often be generated in more than one oxidation state, each of which is capable of exhibiting a variety of charge transfer phenomena, ranging from optical transitions to photoinduced electron transfer, and from hyperpolarizability to electron delocalization in radical ions.[13] Such properties are being exploited in nonlinear optics, various light-harvesting protocols, and many types of molecular-scale devices. With sp carbon bridges, chains as long as 20 carbon atoms, corresponding to metal–metal separations of 3 nm, have been realized.[11e] However, the stabilities of charged and/or radical oxidation states drastically decrease with chain length, precluding many applications of these wirelike assemblies. We thought that

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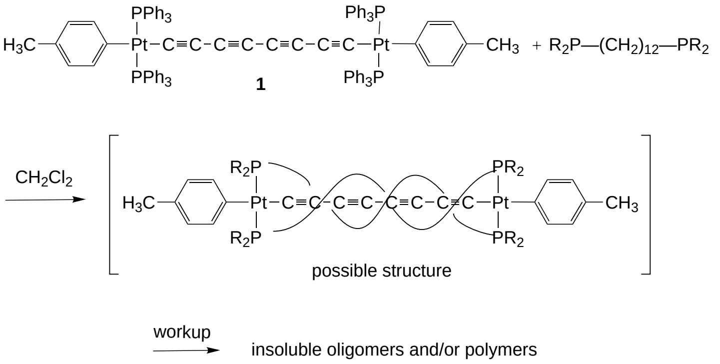
the double helix of **E** would shield and protect the often sensitive bridge, analogous to the insulation about household electrical wire.[14]

Here we describe successful syntheses of a family of diplatinum sp carbon chain complexes [Pt(C≡C)$_m$Pt] with the double-helical structure **E**. Two routes are presented. The first involves an unprecedented sequence of high-risk reactions that significantly advances the art of organometallic chemistry with respect to rational, directed syntheses of new materials. The second can be viewed as a coordination-driven "self-assembly" process with potential for operationally simple nanodevice syntheses.

We first utilized the [Pt(C≡C)$_4$Pt] complex **1** (Scheme 2),[15] which features an eight-carbon tetrayne bridge and square-planar endgroups. A related [PtC≡CPt] complex had been shown to undergo facile phosphane substitution.[16] Reactions of **1** with diphosphanes, in which the phosphorus atoms were separated by flexible bridges of twelve sp^3 carbon atoms, proceeded rapidly below room temperature. One product formed, as assayed by ^{31}P NMR spectroscopy and thin layer chromatography. However, when the solution was concentrated, an insoluble, presumably oligomeric or polymeric material formed. Only small portions could be induced to redissolve. Several monoplatinum complexes of macrocyclic diphosphanes have also been observed to oligomerize.[17]

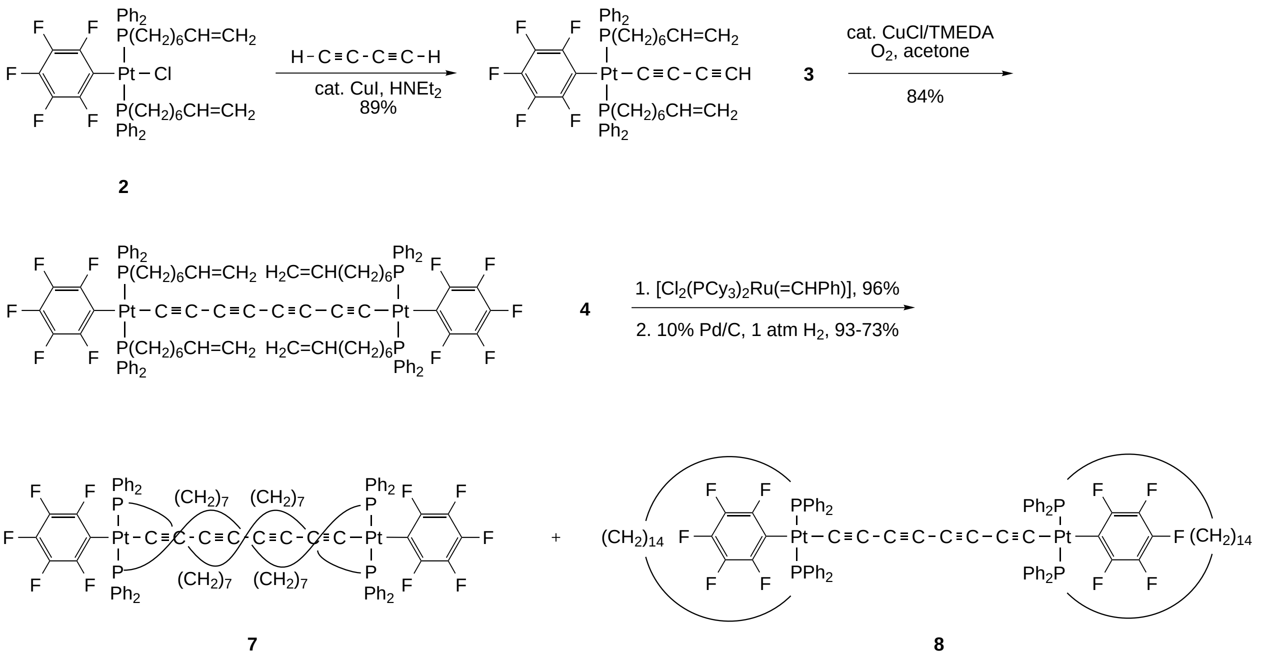


Scheme 2. First synthetic approach to double-helical complexes. R = Ph, *c*-C_6H_9.

A second-generation approach with two new design elements was investigated. First, the *p*-tolyl ligands on platinum were replaced with pentafluorophenyl (C_6F_5) ligands. This was intended to increase the Lewis acidity of platinum and retard phosphane dissociation, the suspected key step in oligomerization. Second, the diphosphane bridges would not be introduced by substitution, but generated within the coordination sphere by linking *functionalized mono*phosphane ligands. Accordingly, the monoplatinum complex **2** (Scheme 3), in which each phosphane ligand contains a hexamethylenevinyl group $(CH_2)_6CH{=}CH_2$, was prepared as previously described.[18]

As shown in Scheme 3, **2** was elaborated to the [Pt(C≡C)$_4$Pt] complex **4**. We were concerned that the first step (conditions as used en route to **1**) might be compromised by the vinyl groups in the phosphane ligands. This proved not to be a problem, and the 1,3-butadiynyl complex **3** was isolated in 89 % yield. An oxidative coupling was attempted under standard Hay conditions for terminal alkynes. Competing reactions involving vinyl groups were viewed as even more probable here, but **4** was isolated in 84 % yield.

We thought that it might be possible to connect the vinyl groups utilizing alkene metathesis, which we have shown can be effected in a variety of metal coordination spheres.[18] However, the mechanism involves a catalyst-bound alkylidene (RCH=M) that is also reactive towards alkynes—as evidenced by the wide use of ene/yne metathesis in organic synthesis.[19] Addition to either the $P(CH_2)_6CH{=}CH_2$ (desired) or [Pt(C≡C)$_4$Pt] (undesired) moieties might occur. Furthermore, two isomeric products would be possible: one in which phosphane ligands on opposite platinum atoms are joined (**5**, desired; similar to **7**), and one in which phosphane



Scheme 3. Synthesis of a double-helical complex through C=C metathesis. TMEDA = tetramethylethylenediamine.

ligands on the same platinum atom are joined to give an unusual *trans*-spanning diphosphane (**6**, undesired; similar to **8**). Statistically, the former is twice as probable, but the viability of the latter has been explicitly demonstrated.[18]

The reaction of **4** with Grubbs's ruthenium metathesis catalyst[20] gave a mixture (96 %) of *cis*/*trans* C=C isomers of **5** and/or **6** according to physical data. To simplify analysis, we sought to hydrogenate the C=C bonds without affecting the C≡C bonds. We were unaware of precedents for such selectivity, but a standard method gave exclusively C=C hydrogenation (Scheme 3; 93 %), as assayed by mass spectrometric and NMR spectroscopic analysis. We view this as evidence for the shielding of the sp carbon chain by the sp^3 carbon chains. As many as five ^{31}P NMR signals were observed, suggesting the presence of higher-order metathesis products not detected in the mass spectrum. Chromatography gave a highly crystalline species, shown below to have the desired structure **7**, in 32 % yield. An authentic sample of **8** (Scheme 3), which has *trans*-spanning diphosphane ligands, was independently prepared.[21] NMR analyses of product mixtures showed comparable amounts of **7** and **8**.

The crystal structures of both benzene and toluene sesquisolvates of **7** were determined.[22] Figure 1 offers five views (**H**–**L**) of the striking double-helical motif found in each. The planes of the platinum termini (P-Pt-P/Pt) define angles of 196.5°—more than a half twist. The sp and sp^3 carbon chains entwine with a spacing slightly greater than their van der Waals radii. The shielding of the sp carbon chain is extensive in **K**, but less in **L**, where a line of sight through a protecting rim of peripheral groups remains. The bond lengths and angles, and the slight sp carbon chain curvature in **7**, are unexceptional. They are very close to those of $[(C_6F_5)(p\text{-tol}_3P)_2Pt(C{\equiv}C)_4Pt(Pp\text{-tol}_3)_2(C_6F_5)]$ (**9**),[23] which lacks bridging diphosphanes, and other model compounds.[24]

Double-helical **7** is chiral, and both enantiomers are present in the unit cell. Stereogenesis can be analyzed as follows. One sp^3 carbon chain exhibits four *gauche* $CH_2CH_2CH_2X$ segments ($X = CH_2$, P) with torsion angles of ca. 60° (see C11′-C12′, C17′-C18′, C21′-C22′, C22′-C23′ in **H**), and the other three. Such segments are inherently chiral. In order for enantiomers of **7** to interconvert, each *gauche* segment must "untwist" to an *anti* conformation (torsion angle 180°), and then continue to a *gauche* segment of the opposite chirality. These motions need not occur in concert. However, each will be coupled to other conformational changes. Together, these provide the bulk of the energy barrier for enantiomer interconversion, a subject we return to below.

With the accessibility and double-helical structure of **7** confirmed, we checked whether detectable quantities might be generated by substitution reactions of the type in Scheme 2. As shown in Scheme 4, the $[Pt(C{\equiv}C)_4Pt]$ complex **9** was treated with the diphosphane $Ph_2P(CH_2)_{14}PPh_2$ under moderately dilute conditions. To our great surprise, **7** could be isolated in 87 % yield (Table 1); none of the isomer **8** was detected. Reactions with analogous diphosphanes bearing

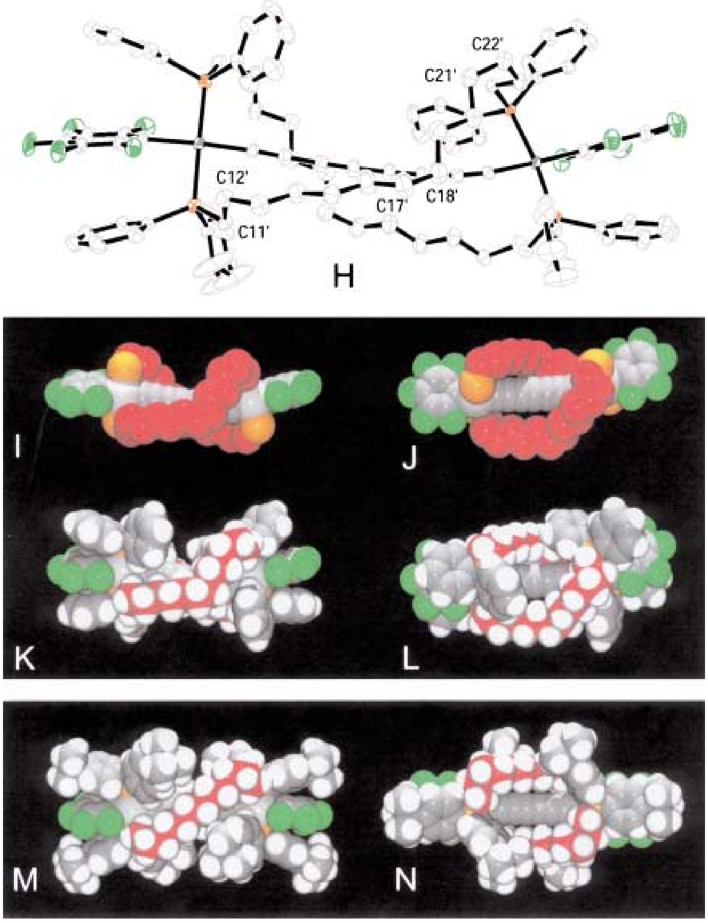
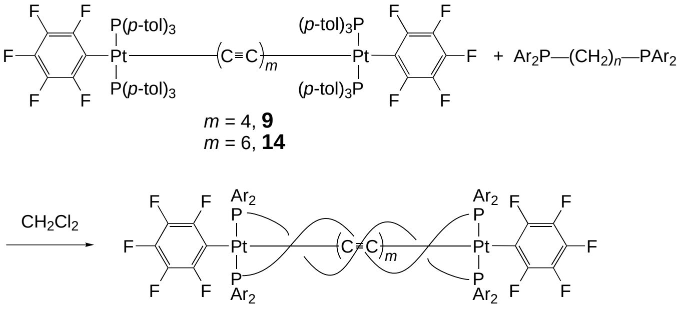


Figure 1. Structures of double-helical $[Pt(C{\equiv}C)_4Pt]$ complexes. **H**: ORTEP diagram of **7**; **I**, **J**: views of **7** parallel and perpendicular, respectively, to the planes of the C_6F_5 ligands with phenyl rings and hydrogen atoms omitted and the other atoms at van der Waals radii; **K**, **L**: analogous views of **7** but with phenyl rings and hydrogen atoms; **M**, **N**: analogous views of **11**.



Scheme 4. Syntheses of double-helical and nonhelical complexes by substitution at high dilution. For preparative details see Table 1.

Table 1. Experimental details of the reactions shown in Scheme 4.

m	*n*/Ar	*c*(**9**) or *c*(**14**) [mM]	Product	Yield [%]	sp^3/sp ratio	Structure
4	14/Ph	2.5	**7**	87	1.75	helical
4	14/*p*-tol	1.9	**10**	91	1.75	helical
4	14/*p*-C_6H_4tBu	1.5	**11**	77	1.75	helical
4	10/Ph	1.0	**12**	80	1.25	nonhelical[a]
4	11/Ph	1.0	**13**	80	1.38	–[b]
6	18/Ph	0.025	**15**	27	1.50	helical and nonhelical

[a] Helical structure impossible. [b] No crystal structure.

para-substituted phenyl rings gave the corresponding complexes **10** (*p*-Me) and **11** (*p*-*tert*-butyl) in 91 and 77% yields, respectively. These also crystallized in double-helical motifs (189.8 and 193.3° twisted). The structure of the latter is shown as **M** and **N** in Figure 1. The sp^3 carbon chains are more symmetrically arrayed than in **7**, with two four-carbon *gauche* segments in every $P(CH_2)_5$ moiety. The *tert*-butyl groups enhance the overall steric protection.

Next we expanded the range of sp^3 and sp carbon chain lengths investigated. As shown in Scheme 4 and Table 1, **9** and the shorter-chain diphosphanes $Ph_2P(CH_2)_nPPh_2$ ($n = 10, 11$) were reacted at higher dilution. Workup gave the corresponding complexes **12** and **13** (80%), respectively, with sp^3:sp carbon ratios (1.25, 1.38) appreciably lower than for **7**, **10**, and **11** (1.75). Two polymorphs of **12** crystallized (**O**, **P**; Figure 2), which, as expected, showed nonhelical motifs. The sp^3 carbon chains of the first were slightly disordered and laterally shielded the sp carbon chain. The sp^3 carbon chains of the second bowed in similar directions, exposing more of the sp carbon chain. The $[Pt(C{\equiv}C)_6Pt]$ complex **14**[23] was treated at very high dilution with the longer-chain diphosphane $Ph_2P(CH_2)_{18}PPh_2$ (Scheme 4, Table 1). Workup gave the corresponding complex **15** (27%), with an sp^3:sp carbon ratio of 1.50, as well as oligomeric material. In crystalline **15** two independent molecules are present in the unit cell (**Q**, **R**; Figure 2). The first exhibits a double-helical motif, but less twisted than the others (163.2°). The second is nonhelical. Hence, we currently consider an sp^3:sp carbon ratio of 1.50 as the minimum required for helicity.

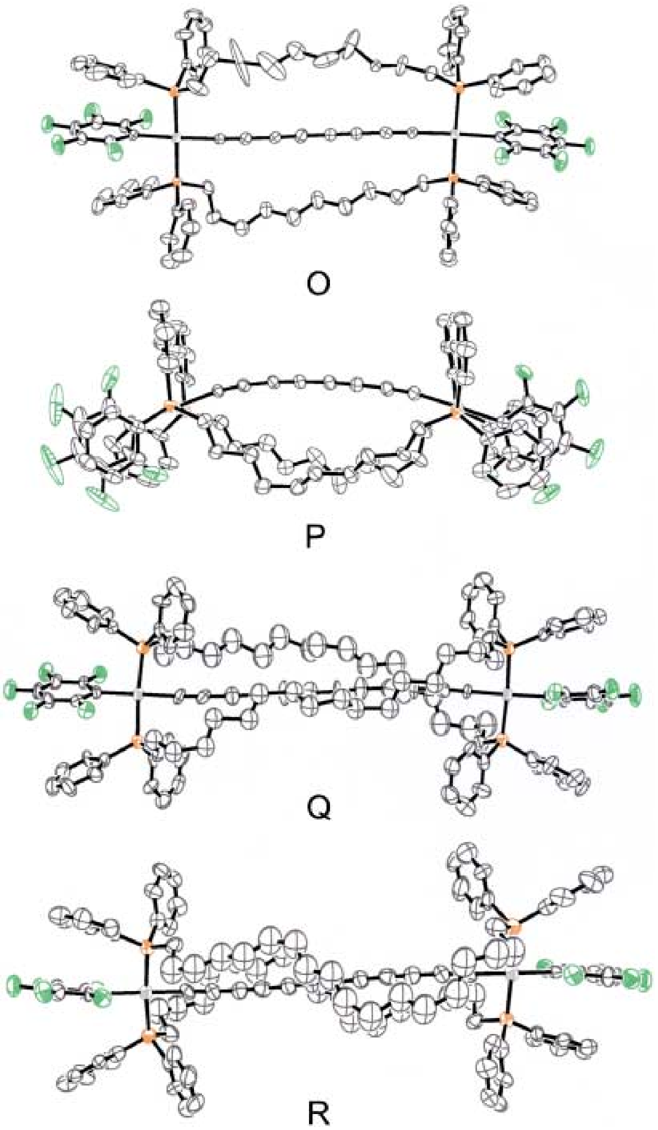


Figure 2. Molecular structures of other complexes (ORTEP diagrams). **O**, **P**: polymorphs of **12**; **Q**, **R**: the helical and nonhelical conformers of **15**.

Each of the synthesized molecules that could reasonably be expected to adopt a double-helical structure crystallizes in this structure. The phenomenon is no isolated occurrence. Thus, it is likely that similar motifs are favored in solution, and not imposed solely by crystal lattices. Helical molecules usually contain diastereotopic groups, such as the *tert*-butyl substituents in **11**. In solution, separate NMR signals are often observed.[7] However, when the helix can "untwist" and invert configuration, exchange occurs, giving a single signal. At the lowest feasible NMR temperatures, we see only one signal for the various diastereotopic groups in **7**, **10**, and **11**.[25] We interpret this as indicating a low barrier, on the order of 12 kcal mol^{-1}, for interconverting enantiomeric double helices. This would involve torsional motions about *gauche* segments as analyzed above, and the possible intermediacy of achiral conformers such as **F** and **G** (see Scheme 1).

The estimated barrier of 12 kcal mol^{-1} represents a measure of sp carbon chain protection—just as electrical wire coatings can be graded for durability under various conditions. We expect such barriers to correlate to the extra activation energy required for attack upon the sp carbon chains in **7**, **10**, and **11**, versus model compounds such as **9** lacking double-helical sheathing. In this regard, the $[Pt(C{\equiv}C)_mPt]$ complexes undergo electrochemical oxidation to labile radical cations. The cyclic voltammogram of **10** indicates a much more reversible oxidation than for **9**, and thus a kinetically more stable radical cation (ratio of cathodic to anodic currents, 0.71 and 0.49, respectively).[26] We are presently attempting to synthesize analogs of **7** with higher barriers. However, from the standpoint of device engineering, the ultimate goal is a portfolio of flexible bridges with a gradation of barriers.

Dynamic issues aside, our molecules are unique in the *absence* of bonding interactions or complementarity along the two helical chains. The sp carbon chain provides a mechanical support, without which the helical motif would not be an energetically competitive conformation. This represents the first molecular analog of a beanpole, an implement known to the most ancient agrarian societies.[27] The double-helical conformation is volumetrically compact, and crystal packing forces may play a role in the solid state. However, van der Waals attractions between the sp^3 and sp carbon chains should also be significant, as evidenced by studies showing that the affinities of single-helical foldamers for rodlike guests depend upon their lengths.[28]

In conclusion, we have discovered a surprising new class of double-helical molecules that can be accessed by directed syntheses (Scheme 3) and simple substitution processes (Scheme 4). The latter holds promise for the self-assembly of molecular-scale devices, whereas the alkene metathesis/hydrogenation sequence in the former can be viewed as an annealing protocol that cements a target structure in place. It can be expected that these wirelike assemblies, insulated similarly to shrink-wrapped electrical cord, can be extended to a variety of redox-active endgroups with various coordination geometries. This novel family of building blocks is certain to have applications in nanotechnology.

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[26] CH_2Cl_2, 100 mV s^{-1}, E° vs SCE (ferrocene = 0.46 V), **10**/**9**: $E_{p,a}$ 1.259/1.261 V; $E_{p,c}$ 1.168/1.143 V; E° 1.214/1.202 V; ΔE 91/118 mV.

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cis–trans Selectivity of Enzyme-Catalyzed Additions to 4-Substituted Cyclohexanones—Correlation with the Prelog/Ringold Model of Enzymatic Hydrogenation[**]

Franz Effenberger,[*] Jürgen Roos, and
Christoph Kobler

Dedicated to Professor Lutz F. Tietze
on the occasion of his 60th birthday

V. Prelog and co-workers were the first to use the conformational stability of cyclic ketones and alcohols to make a statement about the topography of the active site of an enzyme.[1] The enzymatic hydrogenation of 4-substituted cyclohexanones using NADH-dependent horse-liver alcohol dehydrogenase (LADH; NADH = nicotinamide adenine dinucleotide, reduced form) was particularly suitable for this

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