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A new type of insulated molecular wire: a rotaxane derived from a metal-capped conjugated tetrayne†

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The platinum butadiynyl complex *trans*-$(C_6F_5)(p\text{-tol}_3P)_2Pt(C\equiv C)_2H$ and a CuI adduct of a 1,10-phenanthroline based 33-membered macrocycle react in the presence of K_2CO_3 and I_2 or O_2 to give a rotaxane (*ca.* 9%) in which the macrocycle is threaded by the sp carbon chain of *trans,trans*-$(C_6F_5)(p\text{-tol}_3P)_2Pt(C\equiv C)_4Pt(Pp\text{-tol}_3)_2(C_6F_5)$. The crystal structure and macrocycle/axle electronic interactions are analyzed in detail.

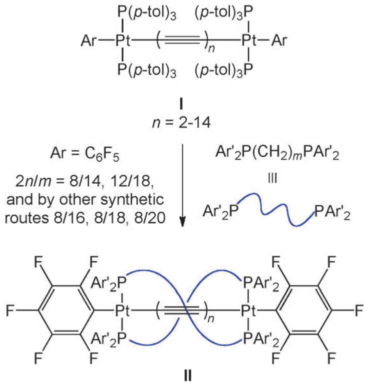
There has been much interest in the synthesis and redox chemistry of complexes in which two metals are separated by an unsaturated linker, especially with respect to the electronic properties associated with each accessible redox state.[1,2] Many phenomena involving electron delocalization or transfer between the termini have been documented, and such systems have often been referred to as molecular wires.[3] However, there have been fewer studies directed at the "insulation" of the unsaturated linkers in these assemblies.[4,5] In one limit, this would have the potential of suppressing linker/solvent and linker/linker reactions, leading to longer-lived species, and diminishing the solvent or counter-ion reorganization energy associated with mixed valence states.[6] In the opposite limit, the insulation could respond to a redox or charge transfer event in a defined chemical or mechanical manner.[7]

We[8] and others[2] have had an ongoing interest in dimetallic polyynediyl complexes, $L_mM(C\equiv C)_nML_m$, which feature the most fundamental unsaturated carbon linker. In previous efforts, we have synthesized a series of diplatinum adducts **I** (Scheme 1),[8b] and analogs in which the phosphine ligands on opposite termini are linked by sp^3 methylene chains (**II**).[5] In the solid state, the sp^3 chains adopt chiral double helical conformations about the sp chains, and oxidations to mixed valence Pt(II)/Pt(III) species become more reversible. However, the two enantiomers rapidly interconvert in solution, the mechanism of which involves the uncoiling of the protective helices.

We have therefore sought to sterically protect the sp carbon chains in ways that would not be compromised by dynamic processes. Our attention was drawn to a report of the oxidative homocoupling of an organic terminal alkyne with bulky endgroups, $(p\text{-PhC}_6H_4)_3C(CH_2)_6\text{-}p\text{-OC}_6H_4C\equiv CH$, by copper complexes of 1,10-phenanthroline containing macrocycles.[9] In what has been termed an "active template synthesis",[10] rotaxanes featuring 1,3-butadiyne based axles could be isolated. Other 1,3-butadiyne containing rotaxanes have been similarly prepared since.[11,12] Given the many terminal polyynes with bulky organometallic endgroups that have been prepared in our laboratory,[8] we were naturally curious whether this method could be extended to rotaxanes with dimetallic polyynediyl axles.

The platinum butadiynyl complex *trans*-$(C_6F_5)(p\text{-tol}_3P)_2Pt(C\equiv C)_2H$ (**1**) undergoes ready oxidative homocoupling to the diplatinum octatetraynediyl complex *trans,trans*-$(C_6F_5)(p\text{-tol}_3P)_2Pt(C\equiv C)_4Pt(Pp\text{-tol}_3)_2(C_6F_5)$ (**2**) under Hay conditions (O_2, cat. CuCl/TMEDA, acetone).[8b] However, for this study the recipe used to access rotaxanes from the alkyne $(p\text{-PhC}_6H_4)_3C(CH_2)_6\text{-}p\text{-OC}_6H_4C\equiv CH$ was applied. Thus, **1**, K_2CO_3, and the copper iodide complex of the 1,10-phenanthroline based macrocycle **3** shown in Scheme 2 (**3**·CuI)[9a] were combined in THF (2.5 : 4.0 : 1.0 mol ratio) at 55 °C (Conditions A). Then a THF solution of I_2 (2.0 equiv) was added dropwise. A silica gel column gave a mixture of the target rotaxane **2·3** accompanied by free **3**.

The yields of **2·3** in replicate reactions were low, and little or no homocoupling product **2** was detected. Interestingly, NMR



Scheme 1 Previously synthesized diplatinum polyynediyl complexes.

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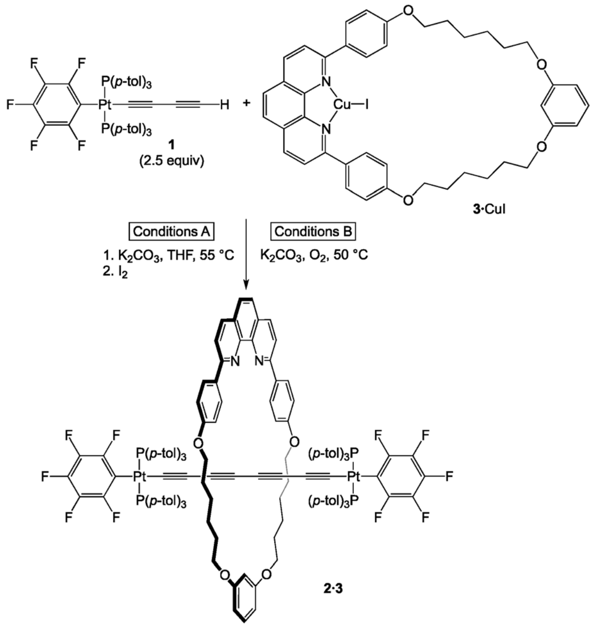
† Electronic supplementary information (ESI) available: Experimental procedures, crystallographic data, and additional figures. CCDC 881310. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33321j



Scheme 2 A rotaxane derived from a diplatinum polyynediyl complex.

data suggested the dominant formation of an iodinated PtC≡CCHI=CHI species, which could be independently generated from **1** and I_2. Hence, an alternative procedure involving **3**·CuI, O_2, and the base K_2CO_3 (50 °C) was investigated (Conditions B). Comparable quantities of **2**·**3** were obtained. An alumina column separated the **2**·**3**/ **3** mixtures, affording the former as a light yellow air stable solid in an average yield of 9%.

The structure of the rotaxane **2**·**3** was supported by a variety of data. The ^{1}H NMR spectra showed distinctive changes in chemical shifts, as exemplified in Fig. 1. The $OC\underline{H_2}C\underline{H_2}C\underline{H_2}$ signals of the macrocycle **3** shifted 0.65–0.82 ppm upfield, consistent with the modern interpretation of the magnetic shielding anisotropy of a polyyne.[13] As depicted in Fig. S1 (ESI†), the signal for the p-C_6H_4 protons closest to the OCH_2 substituent also shifted upfield (0.21 ppm), as did that for the m-C_6H_4 proton *ortho* to the two OCH_2 groups (0.34 ppm). However, the other m-C_6H_4 signals shifted slightly downfield, consistent with an *exo* orientation with respect to the polyyne chain. The methyl signals of the p-tol$_3$P ligands also shifted upfield (0.24 ppm, Fig. 1), perhaps due to shielding by the arene rings of the macrocycle. Analogous but often less pronounced upfield ^{1}H NMR shifts can be observed with diyne-based rotaxanes and catenanes.[9,11,12]

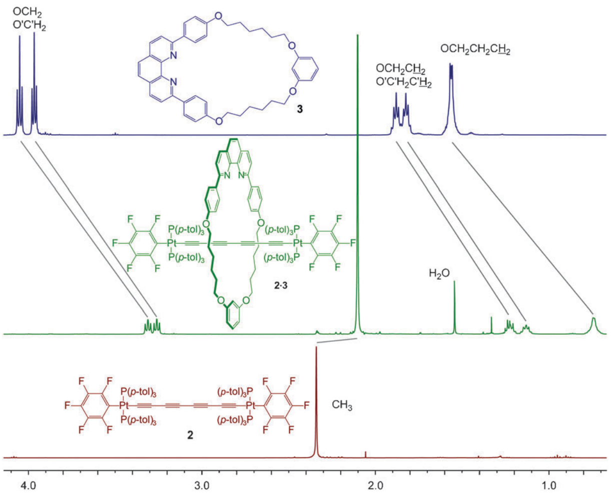


Fig. 1 Shifts in ^{1}H NMR signals upon rotaxane formation.

Crystals of a solvate of **2**·**3** could be grown from CH_2Cl_2/ hexanes. The crystal structure was solved as described in the supporting information, and two views are provided in Fig. 2. The former illustrates the close proximity of the sp carbon chain to the macrocycle atoms whose NMR chemical shifts become more shielded (average C(sp)/C(sp^3) distance 4.21 Å). The latter shows that the sp chain is substantially shielded by the macrocycle, with the closest contacts (C138, 3.403 Å; C139, 3.320 Å) slightly less than the sum of the van der Waals radii of sp^3 and sp hybridized carbon atoms (1.70 + 1.78 Å).[14] Only a few crystal structures have been reported for rotaxanes with diyne-based axles.[11c,12c,d]

The platinum diphosphine endgroups are clearly sufficiently bulky to block dethreading of the sp chain. In fact, the van der Waals contacts between the endgroups and the macrocycle suggest that the sp chain does not have much translational freedom to "slip" within the rotaxane, in contrast to the diynes in some previously prepared systems.[9,11] The bond lengths and angles associated with the PtC_8Pt linkage are close to those previously reported for **2** (Table S2, ESI†).[8b]

The IR $\nu_{C\equiv C}$ bands of **2**·**3** are at slightly higher frequencies than those of **2** (2149 *vs.* 2139 cm^{-1} (m/m) and 2008 *vs.* 1996 cm^{-1} (w/w) under side-by-side conditions). However, UV-visible

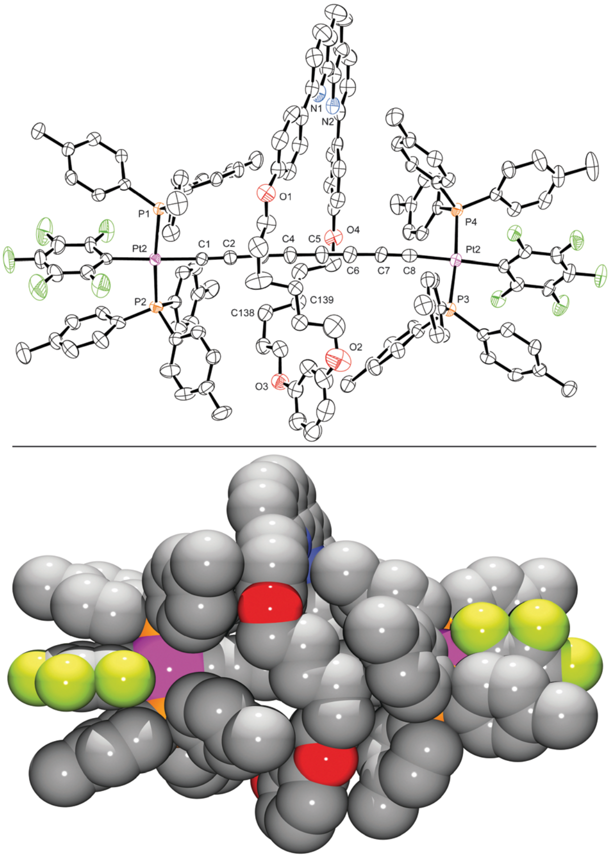


Fig. 2 Structure of **2**·**3**: top, thermal ellipsoid plot (55% probability contour); bottom, space filling representation.

spectra do not show any evidence for a significant electronic interaction between the rotaxane components. The spectrum of **2·3** (nm, 4.37 × 10^{-6} M in CH_2Cl_2 (ε, M^{-1} cm^{-1}) 267 (69 000), 293 (120 000), 325 (129 000), 355 (27 000), 381 (9000), 414 (5000); see Fig. S3†) is essentially identical to that of a 1 : 1 mixture of **2** and **3**. Only the absorption at 293 nm appeared slightly enhanced (*ca.* 15% relative to the mixture).

The redox properties of **2** as well as lower and higher homologs and derivatives of the type **II** (Scheme 1) have been studied in detail.[5,8b,15] Cyclic voltammograms (7–9 × 10^{-4} M, CH_2Cl_2, n-Bu_4N^+ PF_6^- or n-Bu_4N^+ BF_4^-, 23.0 ± 1 °C, Pt working and auxiliary electrodes, Ag wire or Ag/AgCl reference electrode; 100 mV s^{-1}; ferrocene, E° = 0.46 V) show that oxidations become less reversible as the sp chains become longer. Those of **2** exhibit an oxidation (E° 1.20–1.18 V, ΔE 118–91 mV) with a cathodic current comparable to the anodic current (Fig. S4;† $i_{c/a}$ = 0.48–0.94 depending upon conditions), indicating significant chemical reversibility. The cyclic voltammogram of macrocycle **3** shows oxidations ($E_{p,a}$ 1.40, 1.71 V) that are entirely irreversible, as evidenced by the absence of any cathodic current. The cyclic voltammogram of a 1 : 1 mixture of **2** and **3** exhibits oxidations at potentials close to those of the components ($E_{p,a}$ 1.27, 1.40 V), but no cathodic current, indicating some type of redox process involving both species.[16] That of **2·3** is, outside of a gradually increasing anodic current, featureless.

In summary, the availability of a new type of rotaxane featuring dimetal polyynediyl axles has been established. To our knowledge, this is the first rotaxane based upon a conjugated polyyne longer than butadiyne.[17] Furthermore, higher homologs should be readily accessible, as oxidative homocouplings become more facile as the sp chain in **1** is lengthened,[8b] and endgroup/macrocycle steric interactions should diminish. Efforts towards this end,[16b] will be reported in due course.

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