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A phase based approach to insulated molecular wires: Diplatinum octatetraynediyl complexes bearing fluorous trialkylphosphine ligands

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ABSTRACT

Reactions of [(tetrahydrothiophene)Pt(C_6F_5)μ-Cl]$_2$ and fluorous phosphines $P((CH_2)_mR_{fn})_3$ (R_{fn} = $(CF_2)_{n-1}CF_3$; m/n = **a**, 2/8; **b**, 3/8; **c**, 3/10) afford the chloride complexes *trans*-$(C_6F_5)((R_{fn}(CH_2)_m)_3P)_2PtCl$ (**8a**-**c**, 40–74%), which upon treatment with butadiyne and CuI (cat.) in $HNEt_2/CF_3C_6H_5$ give *trans*-$(C_6F_5)((R_{fn}(CH_2)_m)_3P)_2Pt(C{\equiv}C)_2H$ (**9a**-**c**, 44–64%). Subsequent reactions with oxygen and CuCl/TMEDA in acetone yield the title complexes *trans,trans*-$(C_6F_5)((R_{fn}(CH_2)_m)_3P)_2Pt(C{\equiv}C)_4Pt(P((CH_2)_mR_{fn})_3)_2(C_6F_5)$ (**10a**-**c**, 35–52%). All platinum complexes exhibit $CF_3C_6F_{11}$/toluene partition coefficients of >99:<1. The crystal structure of **8b** shows that the perfluoroalkyl groups segregate into fluorous domains. It was therefore thought that the perfluoroalkyl groups in **10a**-**c** would aggregate about the polyynediyl chain. However, these adducts could not be crystallized. Electrochemical oxidations of **10a**-**c** give radical cations that are much less stable than trialkyl and triarylphosphine analogs.

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1. Introduction

There has been intense ongoing interest in complexes in which two metals are linked by a π conjugated, alkyne-containing bridge [1], including a singular body of work by Jack Lewis, to whom this special issue is dedicated [2]. Such species are often viewed as prototypes for molecular wires. However, the "all alkyne" versions, polyynediyl complexes [1a,3], gradually diminish in stabilities as the carbon chains are lengthened [4]. This trend is much more pronounced for paramagnetic analogs resulting from one electron oxidations or reductions [4]. To address these problems and other issues, attention has been given to developing what are sometimes termed "insulated molecular wires" [5].

We have taken two distinct approaches to insulating or sterically protecting the sp carbon chains of polyynediyl complexes. One features termini spanning diphosphine ligands of the formula $Ar_2P(CH_2)_zPAr_2$, which can be introduced by substitution or metathesis reactions as illustrated in Scheme 1 for diplatinum complexes (**I**) [6,7]. The sp^3 chains adopt double helical conformations in the solid state. The other involves shielding the sp chain with a macrocycle, in the form of a rotaxane assembled by an "active template" strategy [8] as exemplified by **II** in Scheme 2 [9].

We wondered whether a third, architecturally simpler approach to sp carbon chain protection might complement those in Schemes 1 and 2. Specifically, a variety of fluorous trialkylphosphines are now readily available [10–12]. Most of these feature substituents of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$, abbreviated $(CH_2)_mR_{fn}$. The $(CH_2)_m$ unit or "methylene spacer" dampens the electron withdrawing effect of the perfluoroalkyl segment, although far from completely when m = 2 or 3 [13]. Molecules or domains that are rich in perfluoroalkyl groups tend to phase separate from their non-fluorous counterparts, as evidenced by many types of phenomena in solution [14] and seen in a variety of crystal structures [15,16].

Given that the families of diplatinum polyynediyl complexes depicted above carry two phosphine ligands on each terminus, it should be possible to introduce four fluorous phosphines with a total of twelve extended perfluoroalkyl groups. Although these could be arranged in a variety of motifs, contact between the fluorous domains would be maximized if as many as sterically feasible would adopt conformations that roughly parallel the sp carbon chain, as shown in **IV** in Scheme 3. Hence, there seemed to be a distinct possibility of "spontaneous self assembly" of insulating perfluorocarbon tubules.

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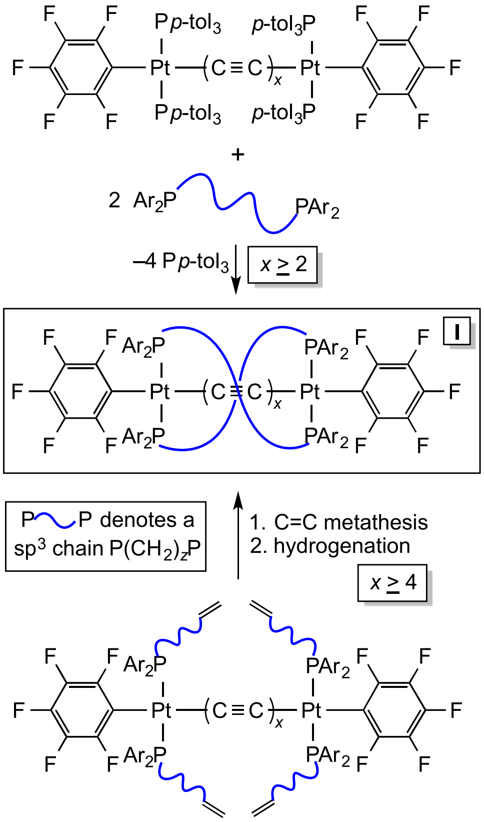
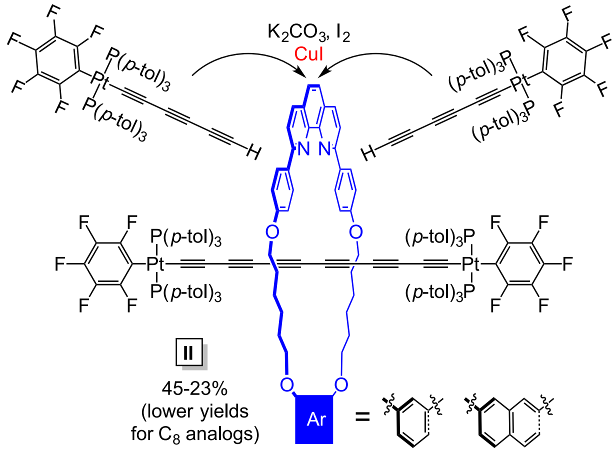


Scheme 1. Syntheses of helically protected polyynediyl complexes by coordination driven self assembly (top) and olefin metathesis followed by hydrogenation (bottom).



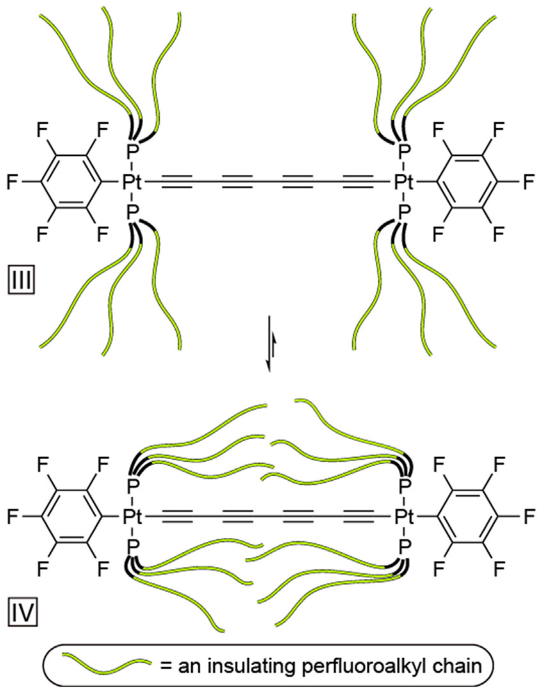
Scheme 2. Syntheses of polyynediyl complex rotaxanes by an "active template" strategy.

In this paper, practical syntheses of a series of fluorous phosphine substituted diplatinum octatetraynediyl complexes are presented. A crystal structure of a precursor exhibits a high degree of perfluoroalkyl group segregation in the lattice. Their extremely high fluorophilicities and the effect of the fluorous phosphine ligands upon redox properties are quantified [17].

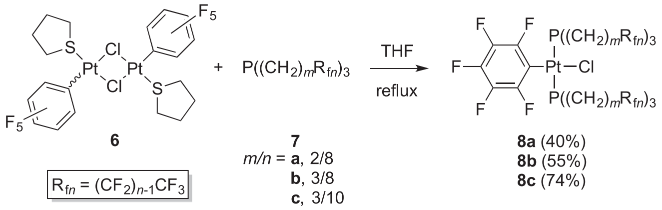
2. Results

2.1. Platinum chloride complexes

The fluorous phosphines $P((CH_2)_mR_{fn})_3$ (**7**) in Scheme 4 [10],



Scheme 3. Proposed phase separation (right, **IV**) of perfluoroalkyl groups in diplatinum octatetraynediyl complexes with fluorous aliphatic phosphine ligands.



Scheme 4. Syntheses of the fluorous platinum chloride complexes **8a-c**.

which feature two or three methylene spacers and either perfluorooctyl or perfluorodecyl groups, are soluble in fluorous solvents and insoluble in most organic solvents with the exception of THF. They are stable in air as solids but readily oxidize in solution. As shown in Scheme 4, the phosphines were combined with the known diplatinum bis(tetrahydrothiophene) complex **6** [18] in a ca. four to one molar ratio (i.e., two phosphines per platinum atom) in refluxing THF under an inert atmosphere. Workups afforded the platinum fluorous phosphine chloride complexes **8a-c** as air stable white powders in 40–74% yields.

Complexes **8a-c** were insoluble in organic solvents such as CH_2Cl_2 and acetone. Thus, NMR spectra were recorded in perfluorobenzene (C_6F_6), using a small amount of $CDCl_3$ cosolvent for a deuterium lock. However, it should be emphasized in passing that perfluoroarenes are much more polar than perfluoroalkanes and are not considered fluorous [14]. These and all new complexes below were characterized by NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) and IR spectroscopies and microanalyses, as summarized in the experimental section. The $^{31}P\{^1H\}$ NMR signals (Table 1) show $^1J_{PPt}$ values that are diagnostic of *trans* geometries at platinum [19].

Single crystals of **8b** were grown from C_6F_6, and the X-ray structure determined as detailed in Table 2 and the experimental section. The molecular structure is shown in Fig. 1. Three of the six $(CH_2)_3R_{f8}$ groups showed disorder (chains 2, 3, 6 as labeled in Fig. 1); the dominant conformations were used for all analyses. Key

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