Synthesis and reactions of metallo-diethynylbenzenes: building blocks for redox-active poly(phenyleneethynylene)s†

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The metallo-diethynylbenzene complex W($\equiv$CC$_6$H$_4$C$\equiv$CH-4)(dmpe)$_2$Cl, a precursor to metal-containing poly(phenyleneethynylene)s, has been prepared using alkyne-metathesis methodology and can be coupled into unsaturated organic frameworks at both the ethynyl moiety and the tungsten center and one-electron oxidized to the open-shell cation.

The unsaturation and limited conformational flexibility of phenylacetylenes (and, more generally, arylacetylenes) imparts to the polymeric materials derived from them extended π-electron systems and well defined lengths and shapes, respectively. These attributes have made poly(aryleneethynylene)s[1] the subjects of intensive research as regards their potential applications to molecular electronics,[2] photonics[3] and chemical sensing.[4] Control over the properties of poly-(aryleneethynylene)s is achieved typically by changing the polymer terminating groups and the nature and connectivity of the aryl hubs. Here, we describe a different approach to functionalizing poly(aryleneethynylene)s: the replacement of triply bonded carbon atoms in the backbone with triply bonded metal centers of metal–alkylidyne complexes.[5]

Covalent alkylidyne-containing polymers analogous to poly-(aryleneethynylene)s have not yet been prepared, although metal–alkylidyne coordination polymers[6] and poly(arylene-ethynylene)s to which metal centers are externally coordinated[7] have been reported. Recently, Mayr *et al.* reported an important advance toward this objective with their synthesis of Fischer-type alkylidyne compounds of the form W($\equiv$CC$_6$H$_4$I-4)(CO)$_2$(LL)X (LL = tmeda, dppe; X = Cl, Br, I),[8] which undergo cross-coupling reactions with phenylacetylenes to give compounds with phenyleneethynylene alkylidyne ligands. Simultaneously, we have been seeking to develop routes to related compounds based on Schrock's alkyne-metathesis reaction[9] because of the ease with which this methodology allows the synthesis of complexes with unsaturated alkylidyne ligands and the fact that the W($\equiv$CR)(OR′)$_3$ metathesis products allow access[10] to carbonyl-free derivatives of the type W($\equiv$CR)L$_4$X. This latter point is important because W(CR)(CO)$_n$L$_{4-n}$X compounds typically exhibit electrochemically irreversible oxidative processes,[11] which could limit their use as building blocks for redox-active polymers. Herein we report the synthesis, *via* an alkyne-metathesis route, of W($\equiv$CC$_6$H$_4$C$\equiv$CH-4)(dmpe)$_2$Cl **4** (dmpe = Me$_2$PCH$_2$CH$_2$PMe), some reactions that lead to its incorporation into unsaturated organic frameworks, and its redox chemistry.

Our general strategy for synthesizing compounds of the type W($\equiv$CArC$\equiv$CH)L$_4$X is to begin with readily prepared unsymmetrical diynylarenes (RC$\equiv$CArC$\equiv$CR′) into which the organic functionality of importance to the properties of the final compound is preincorporated, thus minimizing the number of reaction procedures necessary once the metal center is present. The terminal C$\equiv$CH unit of the target compound is masked in the starting diynylarene by a protecting R group that is sufficiently sterically demanding to prevent alkyne metathesis at the adjacent C$\equiv$C bond. The synthetic procedure for **4** using

this approach is outlined in Scheme 1. For this compound the unsymmetrical diynylarene is *p*-Pr^{n}C$\equiv$CC$_6$H$_4$C$\equiv$CSiPr$^i_3$, which undergoes metathesis with W$_2$(OBu^t)$_6$[12] exclusively at the propynyl C$\equiv$C bond to give W($\equiv$CC$_6$H$_4$C$\equiv$CSiPr$^i_3$-4)(OBu^t)$_3$ **1**.‡ Reaction of **1** with BCl$_3$ and dme,[10] provides W($\equiv$CC$_6$H$_4$C$\equiv$CSiPr$^i_3$-4)Cl$_3$(dme) **2**,‡ which undergoes two-electron reduction by Na/Hg amalgam in the presence of dmpe to give W($\equiv$CC$_6$H$_4$C$\equiv$CSiPr$^i_3$-4)(dmpe)$_2$Cl **3**.‡ The target terminal ethynyl derivative **4** is then obtained by protodesilylation of **3** with [NBu$^n_4$]F•xH$_2$O.‡
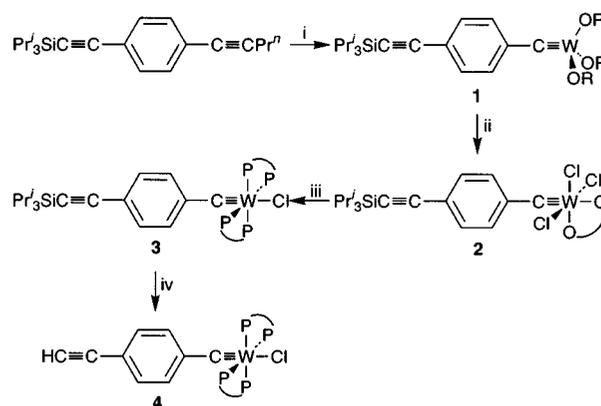
Scheme 1 *Reagents:*‡ i, 0.5 W$_2$(OBu^t)$_6$; ii, 3 BCl$_3$, dme (excess); iii, 2 dmpe, 2 Na/Hg; iv, [NBu$^n_4$]F•xH$_2$O (excess).

Compound **4** can be incorporated into extended unsaturated organic frameworks by functionalization at both the metal center and the terminal ethynyl moiety. A survey of representative reactions at these loci is presented in Scheme 2. Crucially, the fingerprint spectroscopic parameters of the ethynyl moiety (^{1}H NMR δ 2.92, $\nu_{C\equiv C}$ 2099 cm^{-1}) indicate that it is not strongly electronically perturbed relative to phenylacetylene (δ 2.93,
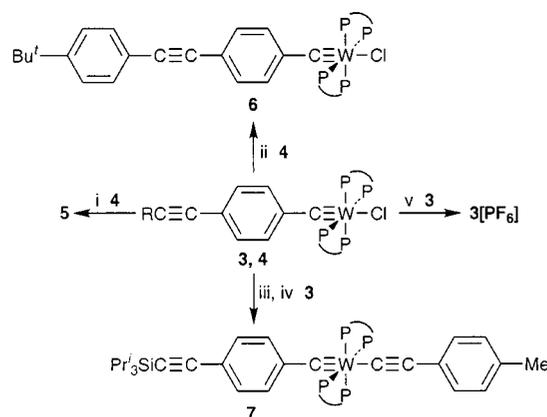
Scheme 2 *Reagents and conditions*: i, Li[N(SiMe$_3$)$_2$] (1 equiv.), THF, –78 °C (10 min), MeI (excess), 0 °C (2 h); ii, *p*-IC$_6$H$_4$Bu^t (1 equiv.), PdCl$_2$(PPh$_3$)$_2$/CuI (cat.), NEt$_2$H, 25 °C (5 h); iii, SiMe$_3$(OTf) (1 equiv.), toluene, 25 °C (1 h); iv, LiC$\equiv$CC$_6$H$_4$Me-4 (1 equiv.), DME, 0 °C (1 h), 25 °C (1 h); v, [C$_7$H$_7$][PF$_6$] (1 equiv.), CH$_2$Cl$_2$–MeCN (2:1), 0 °C (1 h).
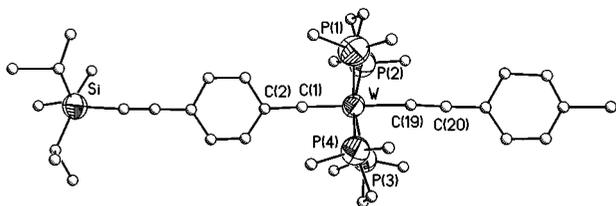
Fig. 1 Structure of W(≡CC₆H₄C≡CSiPrⁱ₃-4)(dmpe)₂(C≡CC₆H₄Me-4) **7**. Atoms are represented by spheres of arbitrary size (C) or thermal ellipsoids drawn at the 50% probability level (W, P, Si). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W–C(1) 1.93(3), W–C(19) 2.11(3), W–P$_{av}$ 2.42[1]; C(1)–W–C(19) 179.3(12), C(20)–C(19)–W 174(3), C(1)–W–P$_{av}$ 95.0(9), C(2)–C(1)–W 175(2).

2109 cm⁻¹) by the p-C≡W(dmpe)₂Cl group, and, thus, that its characteristic reactivity should be preserved. Consistent with this hypothesis, the ethynyl group of **4** can be deprotonated with Li[N(SiMe₃)₂] and subsequently methylated with MeI to give W(≡CC₆H₄C≡CMe-4)(dmpe)₂Cl **5**.‡ More importantly, the ethynyl group participates in Pd-catalyzed cross-coupling reactions with aryl halides: the reaction between **4** and p-IC₆H₄Buᵗ under standard conditions produces W[≡CC₆H₄(C≡CC₆H₄Buᵗ-4)-4](dmpe)₂Cl **6**‡ in nearly quantitative yield. At the tungsten center, substitution of the chloride ligand by unsaturated hydrocarbyl ligands can also be readily achieved. Treatment of **3** with Me₃Si(OTf) to yield W(≡CC₆H₄C≡CSiPrⁱ₃-4)(dmpe)₂(OTf) followed by reaction with LiC≡C–C₆H₄Me-4 provides W(≡CC₆H₄C≡CSiPrⁱ₃-4)(dmpe)₂(C≡CC₆H₄Me-4) **7**.‡ The structure of **7** (Fig. 1) is not of sufficient quality to provide quantitative insights but is interesting for the fact that it reveals that the phenyl rings are nearly coplanar, consistent with extended π conjugation in this compound.

In addition to the reaction chemistry of **3** and **4** that allows extension of their unsaturated frameworks, these compounds can be cleanly oxidized by one electron ($E_{1/2} \cong -0.8$ V vs. FeCp₂⁰⁄⁺ in THF);[11b] accordingly, the reaction between **3** and [C₇H₇][PF₆] provides orange [W(≡CC₆H₄C≡CSiPrⁱ₃-4)(dmpe)₂Cl][PF₆] (**3**[PF₆], Scheme 2).‡ The molecular structure of **3** (unpublished results) is very similar to that of closely related [W(≡CPh)(dmpe)₂Br]⁺[13] and we presume that it, too, possesses a (d$_{xy}$)¹ electron configuration.

The electronic spectra of **3**–**7** indicate that their π-electron systems are extensively delocalized. These spectra exhibit characteristic bands attributable to the (d$_{xy}$)²→(d$_{xy}$)¹(d$_{xz}$,d$_{yz}$)¹ [n→π*(W≡CR)] transition[13,14] as the lowest-energy features. This band strongly red shifts as unsaturated moieties are added to the alkylidyne ligand or to the axial site of the metal. Specifically, as the para-substituent on the alkylidyne ligand is changed from H [W(≡CPh)(dmpe)₂Cl] to C≡CSiPrⁱ₃ (**3**) to C≡CC₆H₄Buᵗ-4 (**6**) the n→π* band shifts progressively to lower energy (19230, 16780 and 16500 cm⁻¹, respectively). Similarly, replacing the axial chloride ligand of **3** with C≡CC₆H₄Me-4 (**7**) results in a red shift of the n→π* band from 16780 to 15870 cm⁻¹. These red shifts must be attributed to a lowering of the energy of the π* LUMO as a result of extending the π-system, since the d$_{xy}$ orbital is nonbonding (δ symmetry) with respect to the σ and π frameworks of the backbone.

The reactivity and physical properties of **4** suggest that this compound and its relatives should be important building blocks for new classes of poly(aryleneethynylene)s with expanded optical and redox functionality. There are no obvious reasons why the metathesis-based synthetic procedure reported here should not also yield building blocks with other aryl hubs (which are incorporated at the alkyne-metathesis step) or equatorial ligands [which are added in the course of the reduction of W(≡CArCCR)Cl₃(dme)], thus providing a high level of control over their physical properties. We are presently exploring the syntheses of such compounds.

Notes and references

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