

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

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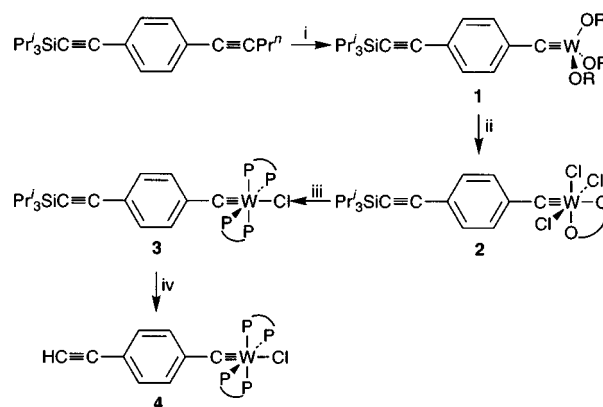
The metallo-diethynylbenzene complex $W(\equiv CC_6H_4C\equiv CH-4)(dmpe)_2Cl$, a precursor to metal-containing poly(phenyleneethynylene)s, has been prepared using alkyne-metathesis methodology and can be coupled into unsaturated organic frameworks at both the ethynyl moiety and the tungsten center and 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)s¹ the subjects of intensive research as regards their potential applications to molecular electronics,² photonics³ 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 polymers⁶ and poly(aryleneethynylene)s to which metal centers are externally coordinated⁷ 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 $W(\equiv CC_6H_4I-4)(CO)_2(LL)X$ ($LL = tmeda, dppe$; $X = Cl, Br, I$),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 reaction⁹ 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 access¹⁰ to carbonyl-free derivatives of the type $W(\equiv CR)L_4X$. This latter point is important because $W(CR)(CO)_nL_{4-n}X$ 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 $W(\equiv CC_6H_4C\equiv CH-4)(dmpe)_2Cl$ **4** ($dmpe = Me_2PCH_2CH_2PMe$), some reactions that lead to its incorporation into unsaturated organic frameworks, and its redox chemistry.

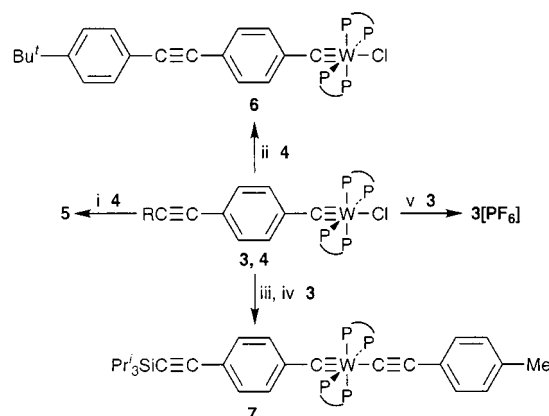
Our general strategy for synthesizing compounds of the type $W(\equiv CArC\equiv CH)L_4X$ is to begin with readily prepared unsymmetrical diynylarenes ($RC\equiv CArC\equiv CR'$) into which the organic functionality of importance to the properties of the final compound is preincorporated, thus minimizing 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 - $Pr^uC\equiv CC_6H_4C\equiv CSiPr^i_3$, which undergoes metathesis with $W_2(OBu^t)_6$ ¹² exclusively at the propynyl $C\equiv C$ bond to give $W(\equiv CC_6H_4C\equiv CSiPr^i_3-4)(OBu^t)_3$ **1**.[†] Reaction of **1** with BCl_3 and dme ,¹⁰ provides $W(\equiv CC_6H_4C\equiv CSiPr^i_3-4)Cl_3(dme)$ **2**,[‡] which undergoes two-electron reduction by Na/Hg amalgam in the presence of $dmpe$ to give $W(\equiv CC_6H_4C\equiv CSiPr^i_3-4)(dmpe)_2Cl$ **3**.[‡] The target terminal ethynyl derivative **4** is then obtained by protodesilylation of **3** with $[NBu^u_4]F\cdot xH_2O$.[‡]



Scheme 1 Reagents: † i, 0.5 $W_2(OBu^t)_6$; ii, 3 BCl_3 , dme (excess); iii, 2 $dmpe$, 2 Na/Hg ; iv, $[NBu^u_4]F\cdot xH_2O$ (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 (1H 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, $-78^\circ C$ (10 min), MeI (excess), $0^\circ C$ (2 h); ii, p - $IC_6H_4Bu^t$ (1 equiv.), $PdCl_2(PPh_3)_2/CuI$ (cat.), NEt_2H , $25^\circ C$ (5 h); iii, $SiMe_3(OTf)$ (1 equiv.), toluene, $25^\circ C$ (1 h); iv, $LiC\equiv CC_6H_4Me-4$ (1 equiv.), DME, $0^\circ C$ (1 h), $25^\circ C$ (1 h); v, $[C_7H_7][PF_6]$ (1 equiv.), CH_2Cl_2-MeCN (2:1), $0^\circ C$ (1 h).

† Dedicated to Professor Warren R. Roper on the occasion of his 60th birthday.

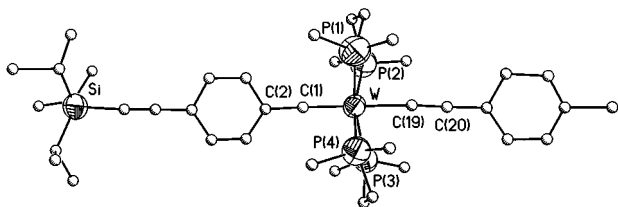


Fig. 1 Structure of $W(\equiv CC_6H_4C\equiv CSiPr_3-4)(dmpe)_2(C\equiv CC_6H_4Me-4)$ **7**. Atoms are represented by spheres of arbitrary size (C) or thermal ellipsoids drawn at the 50% probability level (W, P, Si). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): 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 $p-C\equiv W(dmpe)_2Cl$ group, and, thus, that its characteristic reactivity should be preserved. Consistent with this hypothesis, the ethynyl group of **4** can be deprotonated with $Li[N(SiMe_3)_2]$ and subsequently methylated with MeI to give $W(\equiv CC_6H_4C\equiv CMe-4)(dmpe)_2Cl$ **5**.[‡] More importantly, the ethynyl group participates in Pd-catalyzed cross-coupling reactions with aryl halides: the reaction between **4** and $p-IC_6H_4Bu^t$ under standard conditions produces $W(\equiv CC_6H_4(C\equiv CC_6H_4Bu^t-4)-4)(dmpe)_2Cl$ **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 $Me_3Si(OTf)$ to yield $W(\equiv CC_6H_4C\equiv CSiPr_3-4)(dmpe)_2(OTf)$ followed by reaction with $LiC\equiv C_6H_4Me-4$ provides $W(\equiv CC_6H_4C\equiv CSiPr_3-4)(dmpe)_2(C\equiv CC_6H_4Me-4)$ **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. $FeCp_2^{0/+}$ in THF);^{11b} accordingly, the reaction between **3** and $[C_7H_7][PF_6]$ provides orange $[W(\equiv CC_6H_4C\equiv CSiPr_3-4)(dmpe)_2Cl][PF_6]$ (**3** $[PF_6]$, Scheme 2).[‡] The molecular structure of **3** (unpublished results) is very similar to that of closely related $[W(\equiv CPh)(dmpe)_2Br]^+{}^{13}$ 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 $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz}, d_{yz})^1 [n \rightarrow \pi^*(W\equiv CR)]$ transition^{13,14} as the lowest-energy features. This band strongly red shifts as unsaturated moieties are added to the alkyldiene ligand or to the axial site of the metal. Specifically, as the *para*-substituent on the alkyldiene ligand is changed from H [$W(\equiv CPh)(dmpe)_2Cl$] to $C\equiv CSiPr_3$ (**3**) to $C\equiv CC_6H_4Bu^t-4$ (**6**) the $n \rightarrow \pi^*$ band shifts progressively to lower energy (19230, 16780 and 16500 cm^{-1} , respectively). Similarly, replacing the axial chloride ligand of **3** with $C\equiv CC_6H_4Me-4$ (**7**) results in a red shift of the $n \rightarrow \pi^*$ 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 $W(\equiv CArCCR)Cl_3(dme)_2$], thus providing a high level of control over their physical properties. We are presently exploring the syntheses of such compounds.

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Notes and references

[‡] Preparative details for **1–4** and selected NMR [CD_2Cl_2 , 25 $^\circ C$ (1H) or -10 $^\circ C$ ($^{13}C(W\equiv C)$, ^{31}P)] and IR ($\nu_{C\equiv C}$, cm^{-1}) data are as follows. **1**: $W_2(OBu^t)_6$ (0.25 g, 0.31 mmol) and $p-Pr^tC\equiv CC_6H_4C\equiv CSiPr_3$ (0.20 g, 0.62 mmol) in pentane (5 mL) were stirred together for 10 min at 25 $^\circ C$ and allowed to stand for 12 h at -35 $^\circ C$. Removal of solvent under vacuum at 25 $^\circ C$ gave **1** as a red-brown oil (0.31 g, 0.46 mmol, 74% yield). 1H , δ 7.37 (d, 2H), 7.00 (d, 2H), 1.44 (s, 27H), 1.05 (s, 21H); ^{13}C , δ 257; IR 2159. **2**: The reaction between **1** (0.30 g, 0.45 mmol), DME (excess), and BCl_3 (1.33 mL, 1 M in heptane, 1.33 mmol),¹⁰ gave **2** as a green powder (0.20 g, 0.31 mmol, 68% yield). 1H , δ 7.66 (d, 2H), 6.76 (d, 2H), 4.42 (s, 3H), 4.26 (m, 2H), 4.07 (m, 2H), 3.90 (s, 3H), 1.12 (s, 21H); IR 2152. **3**: To a stirred, 0 $^\circ C$ solution of **2** (1.20 g, 1.85 mmol) in THF (150 mL) was added dmpe (0.67 g, 4.46 mmol) and Na/Hg amalgam (0.4%, 194.91 g, 3.89 mmol Na). After 12 h at 25 $^\circ C$ the organic phase was decanted and reduced to dryness under vacuum. The remaining solid was extracted with pentane and the extract filtered, concentrated, and layered with acetonitrile, giving **3** as a green powder (1.21 g, 1.53 mmol, 83% yield). 1H , δ 7.20 (d, 2H), 6.62 (d, 2H), 1.55 (br, 8H), 1.49 (m, 12H), 1.46 (m, 12H), 1.20 (s, 21H); ^{13}C , δ 252; $^{31}P\{^1H\}$ 23.6; IR 2146. **4**: A stirred, -78 $^\circ C$ solution of **3** (0.20 g, 0.25 mmol) in THF (10 mL) was treated with $[NBu^t_4]F\cdot xH_2O$ (1.88 mL, 0.2 M in THF for $x = 0$, 0.38 mmol), warmed to 25 $^\circ C$ over 1 h, and then reduced to dryness under vacuum. The remaining solid was extracted with pentane and the extract filtered, concentrated, and cooled to -35 $^\circ C$, giving **4** as a green powder (0.09 g, 0.14 mmol, 56% yield). 1H , δ 7.23 (d, 2H), 6.64 (d, 2H), 2.92 (s, 1H), 1.52 (br, 8H), 1.49 (m, 12H), 1.45 (m, 12H); ^{13}C , δ 252; $^{31}P\{^1H\}$, δ 23.6; IR 2099. **5**: 1H , δ 7.18 (d, 2H), 6.63 (d, 2H), 1.83 (s, 3H), 1.73 (br, 8H), 1.64 (m, 12H), 1.45 (m, 12H); ^{13}C , δ 252; $^{31}P\{^1H\}$ 28.5; IR 2241, 2208 (Fermi resonance). **6**: 1H , δ 7.39 (d, 2H), 7.34 (d, 2H), 7.05 (d, 2H), 6.66 (d, 2H), 1.76 (br, 8H), 1.69 (m, 12H), 1.50 (m, 12H), 1.30 (s, 9H); ^{13}C , δ 253; $^{31}P\{^1H\}$ δ 26.8; IR 2210. **7**: 1H , δ 6.98 (d, 2H), 6.89 (d, 2H), 6.86 (d, 2H), 6.73 (d, 2H), 2.22 (s, 3H), 1.77 (br, 8H), 1.68 (m, 12H), 1.62 (m, 12H), 1.08 (s, 21H); ^{13}C , δ 255; $^{31}P\{^1H\}$, δ 21.3; IR 2145, 2060. **3** $[PF_6]$: IR 2149.

[§] Crystallographic data for **7**: $C_{37}H_{100}ClP_4SiW$, $M = 916.44$, monoclinic, space group $P2_1/n$, $a = 8.977(9)$, $b = 30.30(3)$, $c = 16.45(2)$ Å, $\beta = 95.23(9)^\circ$, $V = 4455(8)$ Å³, $Z = 4$, $\mu = 2.847$ mm⁻¹, $T = 213$ K, 5218 reflections measured, 4784 independent reflections, $R1 [I > 2\sigma(I)] = 0.1279$, $wR2 [I > 2\sigma(I)] = 0.2811$. Crystals of **7** diffracted weakly due to their small size; only the W, P and Si atoms could be successfully anisotropically refined. CCDC 182/1174. See <http://www.rsc.org/suppdata/cc/1999/589/> for crystallographic files in .cif format.

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