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π-Conjugated Metallabutadiyne Complexes: Synthesis, Structure, and Bonding

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Butadiyne and its derivatives are currently the subjects of extensive study, in large measure because they are valuable building blocks for electronic and photonic materials. Butadiynes are precursors to polydiacetylenes,[1] which are important because of their nonlinear optical and electrical conduction properties[1,2] and because they are the only conjugated polymers available for study in defect-free, crystalline environments,[3] while the C$\equiv$C—C$\equiv$C unit is widely used as a "molecular wire" in donor–acceptor and related compounds.[4] We have recently begun to prepare and study a new type of conjugated compound in which unsaturated carbon centers are replaced by multiply bonded metal atoms, with the aim of understanding the relationships among the structures, bonding, and properties of these species and those of the parent organic materials.[5] These interests led us to investigate the possibility that metal–alkylidyne complexes[6] might be useful building blocks for the preparation of internally substituted metallabutadiynes (RC$\equiv$M—C$\equiv$CR′). Such derivatives are attractive targets because the presence of a metal atom within the butadiyne backbone should provide a significant electronic, optical, and redox perturbation and because they retain the carbon termini necessary for preparing polydiacetylenes and other derivatives arising from C–C coupling reactions.[7] Although metal–alkylidyne compounds have been used in the syntheses of metal clusters,[8] they have not been previously employed as subunits in low-dimensional materials. Herein we report the preparation of a series of alkynyl-substituted methylidyne compounds of the type HC$\equiv$W(dmpe)$_2$(C$\equiv$CR) (dmpe = 1,2-bis(dimethylphosphino)ethane), as well as structural and spectroscopic evidence that these metallabutadiynes possess π-conjugated C$\equiv$W—C$\equiv$C backbones.

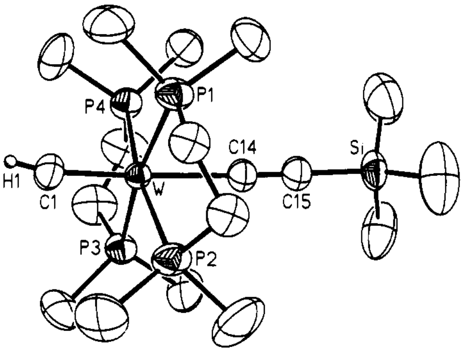
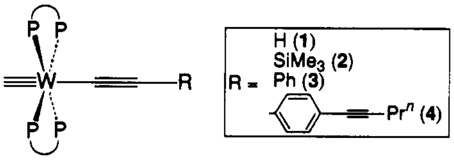


Figure 1. Molecular structure of W(CH)(dmpe)$_2$(CCSiMe$_3$) (**2**), drawn by ORTEP. For clarity, all hydrogen atoms except H(1) have been omitted. Thermal ellipsoids are drawn at the 50% probability level; H(1) is represented by an arbitrarily sized sphere. Selected bond distances (Å) and bond angles (deg), with esd's, are as follows: H–C(1) = 0.822 (89), W–C(1) = 1.801 (7), W–C(14) = 2.246 (6), W–P(1) = 2.440 (2), W–P(2) = 2.433 (2), W–P(3) = 2.429 (2), W–P(4) = 2.434 (2), C(14)–C(15) = 1.228 (9), C(15)–Si = 1.814 (7); H–C(1)–W = 164.4 (55), C(1)–W–C(14) = 177.0 (3), C(1)–W–P(1) = 94.2 (2), C(1)–W–P(2) = 96.4 (2), C(1)–W–P(3) = 93.4 (2); C(1)–W–P(4) = 93.0 (2), P(1)–W–P(2) = 80.5 (1), P(2)–W–P(3) = 97.8 (1), P(3)–W–P(4) = 80.8 (1), P(4)–W–P(1) = 99.6 (1), W–C(14)–C(15) = 178.2 (5), C(14)–C(15)–Si = 179.8 (7).

The compounds W(CH)(dmpe)$_2$(CCR) (R = H (**1**), SiMe$_3$ (**2**), Ph (**3**), 4-C$_6$H$_4$CCPr^n (**4**)) can be prepared in 25–60% yield via reaction of the corresponding alkynyllithium reagent with W(CH)(dmpe)$_2$(O$_3$SCF$_3$)[9,10] in ether solution. Compounds **1–4** were characterized by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.[11] Consistent with their alkynyl–methylidyne formulation, the ^{1}H and ^{13}C NMR spectra of **1–4** display single resonances in the ranges δ 6.65–6.85 and δ 251–255, respectively, arising from nuclei that are magnetically coupled to each other ($^1J_{CH}$ = 123 Hz), to tungsten ($^1J_{CW}$ = 184, $^2J_{HW}$ = 72 Hz), and to phosphorus.[11] These data indicate that the terminal CH ligand is present in each compound.[10,12,13] In addition, the ^{13}C NMR spectra of **1–4** each display two resonances in the range δ 100–160, characteristic of an η^1-alkynyl ligand.[5a,c,14] Importantly, the ^{1}H



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(11) Selected NMR data for **1–4** (C$_6$D$_6$ solution; J in hertz) are as follows: (**1**) ^{1}H δ 6.65 (d quin, $^2J_{HW}$ 73, $^3J_{HP}$ 3.5, $^5J_{HH}$ 0.8, W$\equiv$C*H*), 1.76 (d quin, $^4J_{HP}$ 3.7, $^5J_{HH}$ 0.8, C$\equiv$C*H*), ^{13}C δ 251 (d quin, $^1J_{CW}$ 185, $^1J_{CH}$ 122, $^2J_{CP}$ 12.3, W$\equiv$*C*H), 121 (quin, $^2J_{CP}$ 14.5, W*C*CH), 102 (d, $^1J_{CH}$ 214, WC*C*H), ^{31}P{^{1}H} δ 22.9 (s); (**2**) ^{1}H δ 6.77 (quin, $^2J_{HW}$ 72, $^3J_{HP}$ 3.5, W$\equiv$C*H*), ^{13}C δ 254 (d quin, $^1J_{CW}$ 184, $^1J_{CH}$ 122, $^2J_{CP}$ 12.4 W$\equiv$*C*H), 156 (quin, $^2J_{CP}$ 14.0, W*C*C), 122 (s, $^1J_{CSi}$ 85, C*C*Si), ^{31}P{^{1}H} δ 21.3 (s); (**3**) ^{1}H δ 6.85 (quin, $^2J_{HW}$ 73, $^3J_{HP}$ 3.5, W$\equiv$C*H*), ^{13}C δ 254 (m, $^1J_{CH}$ 122, W$\equiv$*C*H), 130 (m, W*C*CPh), 118 (br WC*C*Ph), ^{31}P{^{1}H} δ 22.3 (s); (**4**) ^{1}H δ 6.84 (quin, $^2J_{HW}$ 72.6, $^3J_{HP}$ 3.5, W$\equiv$C*H*), ^{13}C δ 255 (d quin, $^1J_{CW}$ 183, $^1J_{CH}$ 124, $^2J_{CP}$ 12.2, W$\equiv$*C*H), 133 (quin, $^2J_{CP}$ 14.5, W*C*C), 118 (s, WC*C*), ^{31}P{^{1}H} δ 23.4 (s). Satisfactory C and H analyses were obtained for each compound.

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NMR spectrum of the parent metallabutadiyne, **1**, exhibits 0.8 Hz splittings of the $H{-}C{\equiv}W{-}C{\equiv}C{-}H$ resonances, arising from the coupling of these two nuclei over five bonds; by comparison, $^5J_{HH} = 2.2$ Hz for butadiyne.[15] This result is indicative of π-electron delocalization within the $C{\equiv}W{-}C{\equiv}C$ backbone of **1**.[16]

The molecular structure of **2** was determined by a single-crystal X-ray diffraction study,[17] which revealed methylidyne and (trimethylsilyl)ethynyl ligands arranged trans to each other about a pseudooctahedral tungsten center (Figure 1). Along the backbone, the C—W—C—C—Si assemblage is nearly linear, with only the methylidyne hydrogen lying off this axis; the reasons for the bending of the methylidyne ligand have been discussed previously for $W(CH)(dmpe)_2(n\text{-}Bu)$.[13] The bond distances within the backbone indicate that the bond order alternates along the chain according to $H{-}C{\equiv}W{-}C{\equiv}C{-}Si$: the $W{\equiv}C$ (1.801 (7) Å) and $C{\equiv}C$ (1.228 (9) Å) distances are within the normal ranges for those of triply bonded $W(CH)(dmpe)_2X$ ($X = n\text{-}Bu$, 1.826 (5) Å;[13] X = Cl, 1.797 (10) Å[18]) and metal–alkynyl complexes,[5c,19,20] respectively, while the HCW—CCR bond is significantly longer (2.246 (6) Å) than either of the bonds flanking it. This latter distance is less than that expected for a W—C single bond in this environment, however, as evidenced by the fact that it is 0.16 Å shorter than that for the nonconjugated compound $W(CH)(dmpe)_2(n\text{-}Bu)$ (2.402 (7) Å);[13] based on the single-bond covalent radii of sp- and sp^3-hybridized carbons, a difference of only 0.08 Å between the W—C bond distances is expected. This contraction of the W—C bond for **2** suggests the presence of a π-bonding interaction between the $C{\equiv}W$ and $C{\equiv}C$ fragments.

The $\pi(C{\equiv}W{-}C{\equiv}C)$ conjugation suggested by the NMR data for **1** and the structural data for **2** is strongly manifested by the electronic spectra of metallabutadiynes **1–4**. These compounds, and other derivatives of the type $W(CH)(dmpe)_2X$ (X = Cl, I, n-Bu),[21] display a weak ($\epsilon \cong 400$) band as the lowest energy feature. It has been suggested previously that the orbital character of this electronic transition in molecules of the type $W(CPh)L_4X$ (X = halide) is $d_{xy} \rightarrow \pi^*(W{\equiv}CPh)$, the terminating orbital of which possesses metal d_{xz} or d_{yz} parentage (these levels are nondegenerate under C_{2v} symmetry);[22,23] by analogy, we suggest that the $d_{xy} \rightarrow \pi^*(W{\equiv}C)$ assignment is also appropriate here. For nonconjugated $W(CH)(dmpe)_2X$ complexes, the energy of this transition is largely insensitive to the nature of the trans ligand (X = Cl, $\bar{\nu}_{max}$ 24 810 cm^{-1}; X = I, $\bar{\nu}_{max}$ 24 210; X = n-Bu, $\bar{\nu}_{max}$ 23 470).[21] In contrast, this absorption band lies to distinctly lower energy for **1–4** (**1**, $\bar{\nu}_{max}$ 22 270 cm^{-1}; **2**, 21 830; **3**, 21 280; **4**, 20 240) and, impressively, spans a broader energy range as a function of the alkynyl R group (2000 cm^{-1}) than do the corresponding bands of the halide and alkyl derivatives (1300 cm^{-1}).

The structural and spectroscopic data for **1–4** indicate that the $C{\equiv}W{-}C{\equiv}C$ backbones of these metallabutadiynes are π-conjugated. We advance the following molecular orbital interpretation for these results. The energy and orbital interactions of the tungsten d_{xy} orbital are independent of the nature of the axial ligand, to first order, since this orbital is nonbonding (δ-symmetry) with respect to the $HC{\equiv}W{-}C{\equiv}CR$ axis. In contrast, mixings among the $\pi^*(C{\equiv}CR)$ and $\pi^*(W{\equiv}C)$ orbitals are symmetry allowed; these should stabilize $\pi^*(W{\equiv}C)$ and destabilize $\pi^*(C{\equiv}CR)$, resulting in a red shift of the $d_{xy} \rightarrow \pi^*(W{\equiv}C)$ transition of metallabutadiynes **1–4** relative to $W(CH)(dmpe)_2X$ derivatives with σ or, more so, σ/π-donor X ligands. The overall trend in spectroscopic energies (halide > alkyl > alkynyl) is consistent with this, as is the red shift within the metallabutadiyne series (**1** > **2** > **3** > **4**) with increasing π-conjugation of the alkynyl R group. Since the $\pi^*(C{\equiv}CR){-}\pi^*(W{\equiv}C)$ interactions occur among virtual orbitals, however, they cannot be responsible for the shortened HCW—CCR bond. This must arise from interactions between occupied and virtual orbitals, of which $\pi(C{\equiv}CR){-}\pi^*(W{\equiv}C)$ and $\pi(W{\equiv}C){-}\pi^*(C{\equiv}CR)$ are the most likely candidates. We are not able to distinguish between these possibilities with our current data, although we note that the latter is consistent with the observation of a relatively long $C{\equiv}C$ bond in **2**.

In conclusion, we have discovered a class of $\pi(C{\equiv}W{-}C{\equiv}C)$-conjugated metallabutadiynes. The synthesis of these internally substituted butadiynes opens a wide range of possibilities as regards the perturbation of the properties and electronic structures of polydiacetylenes and related oligomers; such compounds, and long-chain metallabutadiynes, are currently under investigation.

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Registry No. 1, 143493-89-4; **2**, 143493-90-7; **3**, 143493-91-8; **4**, 143493-92-9; $W(CH)(dmpe)_2(O_3SCF_3)$, 143493-93-0.

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[17] X-ray crystallographic data for **2**: $P2_1/n$; $a = 9.840$ (2) Å, $b = 16.569$ (3) Å, $c = 17.391$ (3) Å, $\beta = 100.21$ (1)°, $V = 2790.5$ (10) Å^3, $Z = 4$, $D_c = 1.415$ g cm^{-3}, μ(Mo Kα) = 44.13 cm^{-1}, $T = 225$ K. Of 4387 reflections collected ($4° \leq 2\theta \leq 48°$), 3339 with $F_o > 4.0\sigma(F_o)$ were used in the refinement of the structure. Data were corrected for absorption (XABS) and extinction effects. The structure was solved by direct methods. All non-hydrogen atoms were located and refined anisotropically, except for the C–C backbone of one of the dmpe ligands, which is disordered and was refined isotropically into two configurations. The methylidyne hydrogen was located, and refined isotropically ($U = 0.089$ (29) Å^2). All other hydrogen atom positions were calculated (d(C–H) = 0.96 Å). The structure was refined to $R_F = 2.68\%$, $R_{wF} = 3.25\%$, GOF = 0.99; $\Delta/\rho = 0.94$ e Å^{-3} (near W).

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Specific Abstraction of the 5′(*S*)- and 4′-Deoxyribosyl Hydrogen Atoms from DNA by Calicheamicin γ_1[1]

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The 1,4-diyl (**2**) generated from calicheamicin $\gamma_1{}^1$ (**1**, CLM) by reductive activation[1,2] and rearrangement[3,4] is believed to initiate DNA cleavage by hydrogen atom abstraction from both strands of the helix to give the reduced form of the drug, CLM ϵ (**3**).

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