but several other propellane candidates were not successful.

**Acknowledgment**. We thank Mr. LunTeh Yuen and Mr. Louis D. Scampavia for their expertise in the synthesis of propellanes. Mr. Tom Finger carried out pore-filling experiments with 2,2-dimethylbutane using a system designed by Dr. A. Rainis. Dr. D. M. Wilson provided $^{13}C$ MAS–NMR spectra. Solution spectra were obtained by Dr. S. D. Toto. Dr. R. N. Reynolds, Jr., contributed useful considerations on the resolution of guest isomers. Some of the diffraction and computing equipment used in this study were purchased under NSF Grant CHE-8802721 to the University of California at Davis. We thank Chevron Research and Technology Company for continued support during these investigations.

**Supplementary Material Available:** Listing of crystal data, solution and refinement data, atomic coordinates, bond angles, bond lengths, and X-ray diffraction data (14 pages). Ordering information is given on any current masthead page.

---

# Preparation and Characterization of 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$. Structural and Spectroscopic Manifestations of $\delta$(MM)–$\pi$(CC) Conjugation

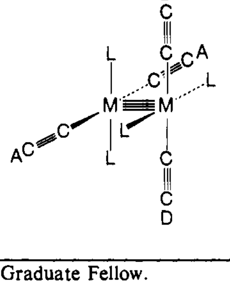
**Timothy C. Stoner,**[†] **Steven J. Geib, and Michael D. Hopkins***[,‡]

*Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.* *Received August 12, 1991*

**Abstract:** The compound $W_2$-1,1-$(CCMe)_2$-2,2-$Cl_2$-$(PMe_3)_4$ (denoted 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$, **1**) has been prepared from the reaction between $W_2Cl_4(PMe_3)_4$ and LiCCMe (2 equiv). The asymmetric substitution pattern has been confirmed by X-ray crystallography (space group $P2_1/c$; $a = 15.383$ (3) Å, $b = 10.417$ (2) Å, $c = 19.038$ (4) Å, $\beta = 103.15$ (3)°, $V = 2971$ Å$^3$, $Z = 4$, $D_c = 1.836$ g cm$^{-3}$, $T = -69$ °C). The most noteworthy structural parameters of **1** are the W–C distances (2.13 Å), which are 0.19 Å shorter than those of $W_2(CH_3)_8{}^{4-}$; these short distances are consistent with strong $\delta$(MM)–$\pi$(CC) conjugation, since only a 0.08-Å contraction is predicted from the difference between the covalent radii of sp- and sp$^3$-hybridized carbon. The CC$CH_3$ resonance in the $^1$H-NMR spectrum of **1** is a pseudoseptet; selective $^{31}$P-decoupling experiments indicate that this is the result of coupling, over five and six bonds, to the phosphorus nuclei on both metal centers, the six-bond coupling being facilitated by the $\delta$–$\pi$ orbital pathway. The energy and intensity of the $^1(\delta\rightarrow\delta^*)$ electronic-absorption band of **1** are also consistent with $\delta$–$\pi$ conjugation: the band red shifts and intensifies as the conjugated chain length increases across the series $W_2Cl_4(PMe_3)_4$ ($\delta$) < **1** ($\delta$–$\pi$) < $W_2(CCMe)_4(PMe_3)_4$ ($\pi$–$\delta$–$\pi$). These results indicate that there are strong similarities among the electronic structures of these conjugated transition-metal complexes and those of analogous organic compounds.

## Introduction

Conjugated molecules and polymers that contain transition metals as an integral part of their unsaturated backbones should possess electrical and optical properties that are enhanced relative to their numerous and extensively studied organic counterparts. Few such metal compounds are known,[1–3] however, and their physical properties are largely unexplored. As part of our studies directed at elucidating the electronic and structural analogies among conjugated organic and transition-metal systems,[2,3] we recently described the preparation and characterization of a series of symmetrically substituted dimetallapolyynes of the type $M_2(CCR)_4(PMe_3)_4$ (M = Mo, W; R = alkyl, aryl), for which we inferred the presence of $\pi$(CC)–$\delta$(MM)–$\pi$(CC) conjugation from resonance-Raman and electronic-spectroscopic data.[2] In light of these findings, an interesting question is whether this $\pi$–$\delta$–$\pi$ orbital pathway will facilitate donor–acceptor interactions in differentially substituted dimetallapolyynes of the type $M(CCD)_2L_2\overset{4}{-}M(CCA)_2L_2$, where CCD and CCA are $\eta^1$-alkynyl ligands that are capped by electron donating and accepting groups, respectively; such interactions have significant structural and electronic consequences for organic polyynes.[4] Unfortunately, asymmetrically substituted, quadruply bonded compounds are rare,[5] and general synthetic routes to them have not been developed. Herein we report the synthesis of $W_2$-1,1-$(CCMe)_2$-2,2-$Cl_2$-$(PMe_3)_4$ (hereafter denoted 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$, **1**), an important precursor to such species, as well as new structural and spectroscopic evidence for $\delta$–$\pi$ conjugation that independently substantiates and significantly strengthens our earlier conclusions[2] concerning the electronic structures of dimetallapolyynes.



---

[†] Andrew W. Mellon Graduate Fellow.

[‡] NSF Presidential Young Investigator (1987–1992); Dreyfus New Faculty Awardee (1987–1992); Packard Foundation Fellow (1990–1995).

(1) (a) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222–2236. (b) Wheeler, R. A.; Hoffmann, R.; Strähle, J. *J. Am. Chem. Soc.* **1986**, *108*, 5381–5387. (c) Critchlow, S. C.; Smith, R. C.; Doherty, N. M. In *Atomic and Molecular Processing of Electronic and Ceramic Materials: Preparation, Characterization, and Properties*; Aksay, I. A., McVay, G. L., Stoebe, T. G., Wager, J. F., Eds.; Materials Research Society: Pittsburgh, 1988; pp 153–158. (d) Roesky, H. W. *Polyhedron* **1989**, *8*, 1729–1731. (e) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118–4120. (f) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673–674. (g) Bartley, S. L.; Dunbar, K. R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 448–450. (h) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709–8724.

(2) Stoner, T. C.; Dallinger, R. F.; Hopkins, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 5651–5653.

(3) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703–704.

(4) (a) Stämpfli, U.; Neuenschwander, M. *Chimia* **1984**, *38*, 157–159. (b) Stiegman, A. E.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 5884–5886. (c) Fouquey, C.; Lehn, J.-M.; Malthête, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1424–1426. (d) Galli, R.; Neuenschwander, M.; Engel, P. *Helv. Chim. Acta* **1988**, *71*, 1914–1923. (e) Graham, E. M.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R.; Stiegman, A. E.; Schaefer, W. P.; Marsh, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 8771–8779. (f) Khundkar, L. R.; Stiegman, A. E.; Perry, J. W. *J. Phys. Chem.* **1990**, *94*, 1224–1226.

(5) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

0002-7863/92/1514-4201$03.00/0

**Table I.** Crystal, Data Collection, and Refinement Parameters for **1**

| (a) Crystal Parameters | | | |
|---|---|---|---|
| formula | $C_{18}H_{42}Cl_2P_4W_2$ | $V$, Å$^3$ | 2971 (1) |
| formula wt | 821.036 | $Z$ | 4 |
| cryst syst | monoclinic | $d_{calcd}$, g cm$^{-3}$ | 1.836 |
| space group | $P2_1/c$ | $\mu$, cm$^{-1}$ | 83.06 |
| $a$, Å | 15.383 (3) | temp, °C | −69 |
| $b$, Å | 10.417 (2) | cryst dimens, mm | 0.20 × 0.20 × 0.30 |
| $c$, Å | 19.038 (4) | | |
| $\beta$, deg | 103.15 (3) | | |
| **(b) Data Collection** | | | |
| diffractometer | Nicolet R3m/V | scan speed, deg min$^{-1}$ | variable, 5–20 |
| | | reflns collected | 5737 |
| radiation | Nb-filtered Mo K$\alpha$ | unique data | 5243 |
| | | $R$(int), % | 1.40 |
| scan technique | $\theta/2\theta$ | unique data obsvd | 3489 ($F_o > 5\sigma(R_o)$) |
| $2\theta$ scan range | 4° ≤ $2\theta$ ≤ 50° | std reflns | 3/197 |
| data collected | $\pm h,+k,+l$ | | |
| decay | ≤1% | | |
| **(c) Refinement** | | | |
| $R_F$, % | 3.70 | GOF | 1.01 |
| $R_{wF}$, % | 4.64 | data/parameter | 14.8 |
| $\Delta(\rho)$, e Å$^{-3}$ | 1.43 (near W(1)) | $g^a$ | 0.001 |
| mean $(\Delta/\sigma)_{max}$ | 0.008 | | |

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

## Experimental Section

**General Procedures.** All manipulations were carried out under inert-atmosphere conditions using standard glovebox and Schlenk techniques. Solvents were distilled from appropriate drying agents under either a nitrogen atmosphere or reduced pressure. NMR spectra were acquired of $C_6D_6$ solutions with Bruker AF300 ($^1H$) or AF500 ($^1H\{^{31}P\}$, $^{13}C$, $^{31}P\{^1H\}$) spectrometers.

**1,1-W$_2$(CCMe)$_2$Cl$_2$(PMe$_3$)$_4$ (1).** Propyne (excess, Farchan) was passed over a stirred solution of *n*-butyllithium (8.09 mL, 12.9 mmol, 1.6 M in hexanes, Aldrich) in diethyl ether (30 mL) at −78 °C, resulting in the immediate formation of a white precipitate. The suspension was stirred for 20 min following the completion of this addition, at which point it was warmed to room temperature and added to a stirred slurry of $W_2Cl_4(PMe_3)_4$[6] (5.27 g, 6.48 mmol) in dimethoxyethane (50 mL) at 0 °C. After the reaction mixture was stirred for 2 days at room temperature, the volatile components were removed in vacuo and the residue extracted with pentane. The resulting solution was filtered through Celite and then stripped to dryness under vacuum. The powdery violet product (yield 50–75%) is sufficiently pure for use in reactions. Dark-violet crystals of **1** were grown from a concentrated hexamethyldisiloxane solution at −78 °C, removed by filtration, and washed with cold acetonitrile (2 × 15 mL). Yield after recrystallization: 0.81 g (0.99 mmol, 15%). Anal. Calcd (found) for $C_{18}H_{42}Cl_2P_4W_2$: C, 26.33 (26.05); H, 5.16 (5.03); Cl, 8.63 (8.64). $^1H$ NMR (300 MHz): $\delta$ 2.95 (pseudo sep, 6 H, $2(^5J_{HP}) = 6.30$ or 11.30 Hz, $^6J_{HP} + {^{6'}J_{HP}} = 11.30$ or 6.30 Hz, CC*Me*); 1.72 (virtual (vir) t, 18 H, $^2J_{HP} + {^4J_{HP}} = 7.70$ Hz, P$_a$*Me*$_3$); 1.58 (vir t, 18 H, $^2J_{HP} + {^4J_{HP}} = 7.45$ Hz, P$_b$*Me*$_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz): $\delta$ 154 (C*C*Me); 126 (br, *C*CMe); 16.6 (vir t, $^1J_{CP} + {^3J_{CP}} = 30.42$ Hz, P*Me*$_3$); 14.3 (vir t, $^1J_{CP} + {^3J_{CP}} = 29.41$ Hz, P*Me*$_3$); 5.9 (CC*Me*). $^{31}P\{^1H\}$ NMR (202.4 MHz): $\delta$ 8.41 (t, P$_a$, $^3J_{P_aP_b} = 29.6$ Hz, satellites: $^1J_{WP_a} = 241$ Hz); −23.27 (t, P$_b$, satellites: $^1J_{WP_b} = 202$ Hz). $^1H\{^{31}P_a\}$ NMR (500 MHz): $\delta$ 2.95 (t or vir t, $2(^5J_{HP})$ or $^6J_{HP} + {^{6'}J_{HP}} = 11.30$ Hz, CC*Me*); 1.72 (s, P$_a$*Me*$_3$); 1.58 (vir t, P$_b$*Me*$_3$). $^1H\{^{31}P_b\}$ NMR (500 MHz): $\delta$ 2.95 (t or vir t, $2(^5J_{HP})$ or $^6J_{HP} + {^{6'}J_{HP}} = 6.30$ Hz, CC*Me*); 1.72 (vir t, P$_a$*Me*$_3$); 1.58 (s, P$_b$*Me*$_3$).

**Single-Crystal X-ray Diffraction Study of 1.** The parameters used during the collection of diffraction data for **1** are set out in Table I. A dark-violet crystal of **1** was coated in Fluorolube, which set the crystal to a fine glass fiber when placed under a stream of nitrogen at −69 °C. On the basis of systematic absences and photographic evidence, **1** was uniquely assignable to the monoclinic space group $P2_1/c$. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 18° ≤ $2\theta$ ≤ 25°. A profile-fitting procedure was applied to all data to improve the precision of the measurement of weak reflections. A semiempirical absorption correction (XABS) was applied to the diffraction data. Diffraction data were corrected for extinction effects.

The structure was solved using the direct-methods program TREF, which located the two tungsten atoms. Remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined anisotropically. Idealized atom positions were calculated for all hydrogen atoms ($d$(C–H) = 0.96 Å). There is one molecule of **1** per asymmetric unit. The final difference Fourier synthesis showed only a diffuse background. An inspection of $F_o$ vs $F_c$ values and trends based upon sin $\theta$, Miller index, or parity group failed to reveal any systematic errors in the X-ray data.

**Table II.** Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$ × 10$^3$) for **1**$^a$

| | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|
| W(1) | 7899.1 (3) | 1214.4 (5) | 6604.9 (2) | 27 (1) |
| W(2) | 6590.8 (3) | 2291.9 (4) | 6472.5 (2) | 26 (1) |
| Cl(1) | 5616 (2) | 1796 (3) | 5339 (2) | 41 (1) |
| Cl(2) | 6592 (2) | 3593 (3) | 7510 (2) | 38 (1) |
| P(1) | 7664 (2) | −36 (3) | 5464 (2) | 35 (1) |
| P(2) | 8712 (2) | 1989 (3) | 7807 (2) | 34 (1) |
| P(3) | 5673 (2) | 714 (3) | 6987 (2) | 34 (1) |
| P(4) | 6922 (2) | 4318 (3) | 5880 (2) | 35 (1) |
| C(1) | 8819 (8) | 2303 (11) | 6171 (6) | 35 (4) |
| C(2) | 9393 (8) | 2806 (14) | 5921 (7) | 46 (5) |
| C(3) | 7830 (7) | −563 (11) | 7154 (6) | 33 (4) |
| C(4) | 7872 (9) | −1547 (12) | 7500 (7) | 41 (5) |
| C(5) | 10078 (10) | 3464 (18) | 5638 (9) | 76 (7) |
| C(6) | 7869 (12) | −2649 (15) | 7957 (9) | 72 (7) |
| C(7) | 7516 (10) | 780 (13) | 4609 (7) | 56 (6) |
| C(8) | 6816 (9) | −1287 (13) | 5282 (7) | 51 (5) |
| C(9) | 8681 (9) | −928 (15) | 5495 (8) | 66 (6) |
| C(10) | 8987 (10) | 3670 (13) | 7972 (8) | 58 (6) |
| C(11) | 9806 (9) | 1276 (14) | 7990 (8) | 57 (5) |
| C(12) | 8316 (8) | 1513 (13) | 8589 (6) | 45 (5) |
| C(13) | 4560 (9) | 1418 (14) | 6871 (8) | 58 (6) |
| C(14) | 5420 (9) | −843 (11) | 6564 (7) | 40 (4) |
| C(15) | 5952 (9) | 390 (15) | 7938 (7) | 56 (6) |
| C(16) | 5960 (9) | 5395 (13) | 5825 (7) | 50 (5) |
| C(17) | 7024 (12) | 4246 (14) | 4949 (7) | 65 (7) |
| C(18) | 7867 (9) | 5326 (14) | 6281 (8) | 53 (5) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table III.** Selected Bond Distances (Å) and Bond Angles (deg) for **1**

| Distances | | | | | |
|---|---|---|---|---|---|
| W(1)–W(2) | 2.268 (1) | W(1)–C(3) | 2.141 (12) | C(1)–C(2) | 1.213 (19) |
| W(1)–P(1) | 2.488 (3) | W(2)–Cl(1) | 2.387 (3) | C(2)–C(5) | 1.459 (23) |
| W(1)–P(2) | 2.479 (3) | W(2)–Cl(2) | 2.395 (3) | C(3)–C(4) | 1.212 (17) |
| W(1)–C(1) | 2.122 (13) | W(2)–P(3) | 2.506 (3) | C(4)–C(6) | 1.441 (20) |
| | | W(2)–P(4) | 2.499 (3) | | |

| Angles | | | |
|---|---|---|---|
| W(2)–W(1)–P(1) | 102.3 (1) | Cl(1)–W(2)–Cl(2) | 138.6 (1) |
| W(2)–W(1)–P(2) | 100.9 (1) | W(1)–W(2)–P(3) | 101.3 (1) |
| P(1)–W(1)–P(2) | 156.8 (1) | Cl(1)–W(2)–P(3) | 85.2 (1) |
| W(2)–W(1)–C(1) | 110.2 (3) | Cl(2)–W(2)–P(3) | 86.8 (1) |
| P(1)–W(1)–C(1) | 85.2 (3) | W(1)–W(2)–P(4) | 101.6 (1) |
| P(2)–W(1)–C(1) | 86.8 (3) | Cl(1)–W(2)–P(4) | 85.7 (1) |
| W(2)–W(1)–C(3) | 109.9 (3) | Cl(2)–W(2)–P(4) | 86.1 (1) |
| P(1)–W(1)–C(3) | 87.7 (3) | P(3)–W(2)–P(4) | 157.0 (1) |
| P(2)–W(1)–C(3) | 84.4 (3) | W(1)–C(1)–C(2) | 173.1 (11) |
| C(1)–W(1)–C(3) | 139.8 (4) | C(1)–C(2)–C(5) | 177.4 (16) |
| W(1)–W(2)–Cl(1) | 110.6 (1) | W(1)–C(3)–C(4) | 173.8 (10) |
| W(1)–W(2)–Cl(2) | 110.7 (1) | C(3)–C(4)–C(6) | 174.1 (15) |

Atomic coordinates are set out in Table II, with bond distances and angles in Table III. All computer programs used in the collection, solution, and refinement of crystal data are contained in the Siemens program packages SHELXTL PLUS (VMS version 4.2).

## Results and Discussion

We have established (via spectroscopic studies) that the formation of $M_2(CCR)_4(PMe_3)_4$ from $M_2Cl_4(PMe_3)_4$ and LiCCR (4 equiv) occurs by stepwise replacement of Cl by CCR.[7] Assuming that the trans effect of the $\sigma$-alkynyl ligand is greater than that of chloride,[8] on the basis[9] that the alkynyl ligand is the

---

(6) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801–2806.

(7) Stoner, T. C.; Hopkins, M. D. Unpublished results.

(8) Although the trans effects of $\sigma$-alkynyl ligands have not been quantified, the strong trans influences of these ligands have been noted: (a) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46–50. (b) Manojlović-Muir, L.; Henderson, A. N.; Treurnicht, I.; Puddephatt, R. J. *Organometallics* **1989**, *8*, 2055–2061.

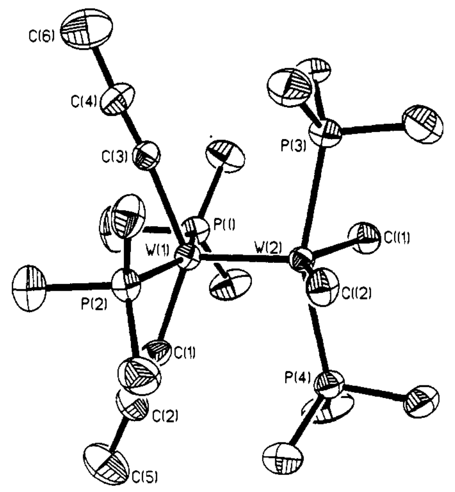
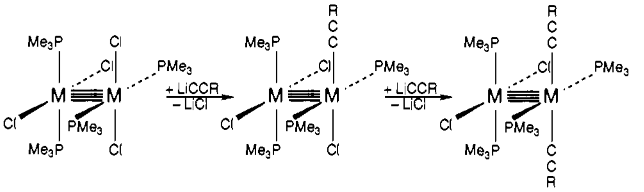


Figure 1. ORTEP drawing of 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$ (1). Atoms are represented by their thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme I



stronger σ base of the two and alone is capable of π backbonding, we reasoned that the chloride ligand trans to the alkynyl ligand in $M_2(\eta^1\text{-}CCR)Cl_3(PMe_3)_4$, the presumed initial intermediate in this reaction, should be more labile than those of the adjacent $MCl_2(PMe_3)_2$ center, and thus that differentially substituted complexes of the type 1,1-$M_2(CCR)_2Cl_2(PMe_3)_4$ might be formed selectively after the second equivalent of LiCCR is added (Scheme I).[10] Accordingly, the reaction between $W_2Cl_4(PMe_3)_4$ and 2 equiv of LiCCMe in dimethoxyethane cleanly (as judged by electronic-absorption spectroscopy) yields a product of composition $W_2(CCMe)_2Cl_2(PMe_3)_4$. The NMR data for this compound indicate that a single isomer is present in solution. Addition of 2 equiv of LiCCMe to $W_2(CCMe)_2Cl_2(PMe_3)_4$ results in the formation of $W_2(CCMe)_4(PMe_3)_4$, analogous to complexes previously reported by us.[2]

While prior X-ray crystallographic studies of $M_2(CCR)_4(PMe_3)_4$ complexes have been unsuccessful,[2,11] that of $W_2(CCMe)_2Cl_2(PMe_3)_4$ was straightforward and revealed (Figure 1) that substitution of propynyl ligands for chloride ligands has occurred at only one of the two metal centers. Few asymmetrically substituted, quadruply metal–metal bonded compounds have been isolated; this is the first example of such a complex derived from the important $M_2X_4L_4$ class.[5] The coupling of unsaturated metal and carbon fragments in 1 does not structurally distort either one to a significant extent: the propynyl ligands coordinate in a linear, end-on fashion, with C≡C bond distances (average $d$(CC) = 1.21 Å, Table III) comparable to those found in propyne (1.207 Å)[12] and metal–($\eta^1$-alkynyl) complexes (1.18–1.22 Å),[13] while the W–W, W–Cl, and W–P bond distances and their associated bond angles are very similar to those of $W_2Cl_4(PMe_3)_4$[14] (Table IV). The sole exceptions to this are the W–P bond lengths of the $W(CCMe)_2(PMe_3)_2$ fragment of 1, which are 0.02 Å shorter than those of the adjacent $WCl_2(PMe_3)_2$ center and of $W_2Cl_4(PMe_3)_4$. A similar result has been noted for $Mo_2(CH_3)_4(PMe_3)_4$, the Mo–P bond lengths of which are 0.04 Å shorter than those of $Mo_2Cl_4(PMe_3)_4$;[15] this difference has been attributed to stronger Mo→P π bonding in the comparatively electron-rich methyl complex.[15]

**Table IV.** Average Core Bond Distances (Å) and Bond Angles (deg) for 1 and $W_2Cl_4(PMe_3)_4$

| | 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$ (1) | | |
|---|---|---|---|
| | $W(CCMe)_2(PMe_3)_2$ | $WCl_2(PMe_3)_2$ | $W_2Cl_4(PMe_3)_4$[a] |
| distances | | | |
| W–W | 2.268 | | 2.262 |
| W–P | 2.484 | 2.503 | 2.507 |
| W–Cl | | 2.391 | 2.392 |
| angles | | | |
| WWP | 101.6 | 101.5 | 101.2 |
| WWCl | | 110.7 | 111.6 |

[a] Reference 14.

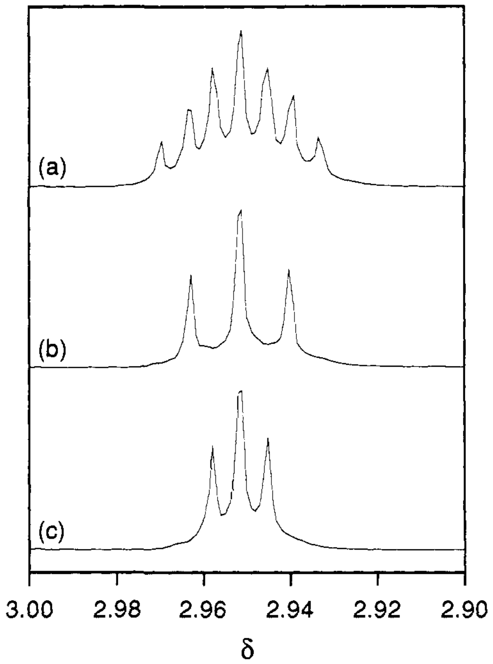


Figure 2. $^1$H-NMR spectra of 1,1-$W_2(CCMe)_2Cl_2(PMe_3)_4$ (1) in the region of the CCC$H_3$ resonance: (a) fully coupled spectrum; (b) $^1H\{^{31}P_a\}$ spectrum; (c) $^1H\{^{31}P_b\}$ spectrum.

The most striking structural parameters of 1, and those most relevant to the question of MM–CC conjugation, are the W–C distances (average $d$(W–C) = 2.13 Å, Table III), which are 0.19 Å shorter than those of $W_2Me_8^{4-}$ (the only alkyl-ligated, quadruply bonded tungsten dimer for which good structural data are available).[16] Since the difference between the single-bond covalent radii of sp- and sp$^3$-hybridized carbon is only 0.08 Å,[17] this anomalously large bond contraction suggests the presence of a significant W–C π-bonding interaction. On energetic grounds, the MM- and CC-based orbitals most likely to be involved in M–C π bonding are the frontier [δ,δ*] and [π,π*] sets, respectively, among which the combinations yielding 2-electron interactions are δ(MM)–π*(CC) and δ*(MM)–π(CC). An apparent contradiction to this picture is the absence of elongated CC and WW multiple bonds for 1, which one might expect to arise from these

---

(9) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: Reading, MA, 1966; pp 24–29.

(10) Discussions of the operation of ligand trans effects and influences in quadruply bonded complexes are given in the following: (a) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953–3955. (b) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 2041–2042.

(11) Stoner, T. C.; Hopkins, M. D.; Schaefer, W. P.; Marsh, R. E. Submitted to *Inorg. Chem.*

(12) Dubrulle, A.; Boucher, D.; Burie, J.; Demaison, J. *J. Mol. Spectrosc.* **1978**, *72*, 158–164.

(13) (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911–920 and references therein. (b) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89–124.

(14) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040–4045.

(15) Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1990**, *29*, 2594–2599.

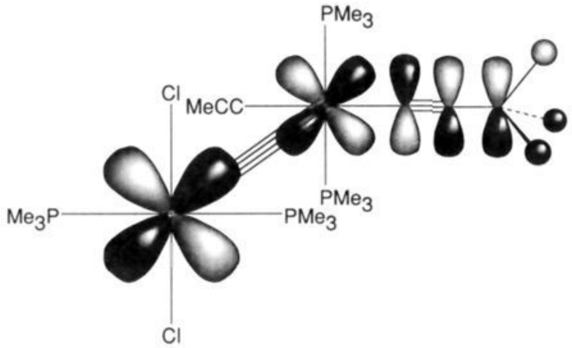
(16) Collins, D. M.; Cotton, F. A.; Koch, S. A.; Millar, M.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 2017–2020.

(17) Sutton, L. E., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1965; pp S14s–S15s.

orbital mixings. This observation is not inconsistent with the presence of $\delta$–$\pi$ conjugation, however, since C≡C bond lengths in conjugated organic polyynes do not differ significantly from those of simple alkynes—those for $H(C{\equiv}C)_2H$, $Me(C{\equiv}C)_3Me$, $(p\text{-}NO_2C_6H_4)(C{\equiv}C)_3(C_6H_4\text{-}p'\text{-}NH_2)$, $Me_3Si(C{\equiv}C)_4SiMe_3$, and $Ph(C{\equiv}C)_4Ph$ lie between 1.19 and 1.22 Å[4e,18]—and because the metal–metal distances of quadruply bonded $M_2X_4L_4$ complexes typically span a narrow range for a given metal,[5,15,19] from which only very strongly M–X $\pi$-bonded derivatives (e.g., $M_2(OR)_4L_4$)[20] deviate by as much as 0.05 Å.

Additional manifestations of $\delta(MM)$–$\pi(CC)$ conjugation are found in the $^1$H-NMR spectrum of **1**, which displays a pseudoseptet at 2.95 ppm as the resonance attributable to the propynyl ligand (Figure 2a), instead of the expected singlet. Selective $^{31}$P-decoupling experiments indicate that this fine structure arises from the coupling of these nuclei to the phosphorus nuclei both on the propynyl-bearing metal center (five bonds removed) and on the adjacent metal center (six bonds removed): individually irradiating the two $^{31}$P resonances yields apparent triplet resonances in the $^1$H-NMR spectrum that exhibit splittings of 11.3 and 6.3 Hz (Figure 2b,c).[21] We currently lack sufficient data to unambiguously assign the two $^{31}$P resonances to specific trimethylphosphine ligands, because both $^1H\{^{31}P\}$ propynyl resonances appear as triplets, as opposed to the triplet and doublet of doublets expected of an $A_3A'_3X_2YY'$ spin system.[22] As a result, we cannot determine which splitting (11.3 or 6.3 Hz) is attributable to the five-bond H–P coupling, and which to the six-bond coupling. Nonetheless, the observation of long-range spin–spin coupling in **1** is significant because such coupling is a spectroscopic hallmark of conjugation in organic compounds. The mechanism of long-range spin–spin coupling in organic species is based on $\sigma$–$\pi$ exchange coupling and delocalization through the $\pi$ system of the $\sigma$-electron spin polarization of the magnetically coupled nuclei;[23] the six-bond H–P coupling observed for **1** is presumably enhanced analogously by $\delta$–$\pi$ electron delocalization, and by the fact that there is a C–H bonding orbital of the appropriate symmetry to mix with this system. The alternative explanation that the spin–spin coupling arises from through-space as opposed to through-bond interactions is obviated by the fact that the corresponding $^1$H-NMR resonance for $W_2(CC\text{-}t\text{-}Bu)_4(PMe_3)_4$[2] is a singlet. This compound must possess closer P–H contacts between the eclipsed trimethylphosphine and alkynyl ligands than does **1** but lacks direct orbital overlap between the C–H and $\delta$–$\pi$ systems.

The energy and intensity of the $^1(\delta \rightarrow \delta^*)$ electronic-absorption band of **1** are fully consistent with this picture of $\delta$–$\pi$ conjugation.



We noted previously[2] that these $^1(\delta \rightarrow \delta^*)$ parameters are a sensitive indicator of $\pi$–$\delta$–$\pi$ conjugation in dimetallapolyynes, as demonstrated by the considerably lower energy and greater intensity of this formally metal–metal localized transition for $M_2(CCR)_4(PMe_3)_4$ complexes than for $M_2X_4(PMe_3)_4$ complexes with saturated ligands (X = Cl, Br, I, $CH_3$), and by their marked dependence upon the nature of the alkynyl R group. For **1**, the $^1(\delta \rightarrow \delta^*)$ band is observed at 13765 cm$^{-1}$ with an oscillator strength ($f$) of 0.031 ($n$-hexane solution); these values are intermediate between those for $W_2Cl_4(PMe_3)_4$ ($\bar{\nu}_{max} = 15175$ cm$^{-1}$, $f = 0.026$) and $W_2(CCMe)_4(PMe_3)_4$ ($\bar{\nu}_{max} = 12930$ cm$^{-1}$, $f = 0.039$). The key point to be drawn from these data, regarding the nature of the conjugation in **1**, is that the trend in $^1(\delta \rightarrow \delta^*)$ energy and intensity for $W_2Cl_4(PMe_3)_4$, **1**, and $W_2(CCMe)_4(PMe_3)_4$, namely, a decrease in energy and increase in intensity as the conjugated chain lengthens ($\delta < \delta\text{–}\pi < \pi\text{–}\delta\text{–}\pi$), exactly parallels that observed for organic polyenes, for which the red shift and intensification of the lowest-energy $\pi \rightarrow \pi^*$ band (relative to that of ethylene) roughly scales with the number of unsaturated moieties.[24]

These structural and spectroscopic results for **1** are significant in that they mirror the corresponding properties of analogous conjugated organic compounds. We conclude from this that there are strong similarities among the electronic structures of these conjugated transition-metal complexes and related organic compounds, and that the electronic properties of donor–acceptor dimetallapolyynes derived from precursors of the $1,1\text{-}W_2(CCR)_2Cl_2(PMe_3)_4$ type may span the same broad range as those of their organic counterparts. Such compounds are currently under investigation.

**Acknowledgment.** We thank the National Science Foundation for the financial support of this research. We gratefully acknowledge the experimental assistance of Dr. Virgil Simplaceanu with the $^1H\{^{31}P\}$-NMR experiments.

**Registry No. 1**, 140149-36-6; $W_2Cl_4(PMe_3)_4$, 73495-54-2; W, 7440-33-7; propyne, 74-99-7.

**Supplementary Material Available:** Tables of anisotropic displacement coordinates, hydrogen atom coordinates, isotropic displacement coefficients, and supplementary bond distances and bond angles (4 pages); listing of observed and calculated structure factors for **1** (19 pages). Ordering information is given on any current masthead page.

---

(18) Coles, B. F.; Hitchcock, P. B.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1975**, 442–445.

(19) Hopkins, M. D.; Schaefer, W. P.; Bronikowski, M. J.; Woodruff, W. H.; Miskowski, V. M.; Dallinger, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 408–416.

(20) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 1153–1154.

(21) Concomitantly, the $^1$H-NMR resonance arising from the $^{31}$P-decoupled trimethylphosphine ligands collapses from a virtual triplet to a singlet, while the corresponding resonance for the $^{31}$P-coupled trimethylphosphine ligands remains a virtual triplet.

(22) The observation in the $^1H\{^{31}P\}$ spectrum of a virtual triplet resonance, in lieu of a doublet of doublets, is presumably the result of strong coupling between the trans phosphorus nuclei; $^2J_{PP'}$ has been determined to be ca. 100 Hz from NMR measurements of $Mo_2Me_4(PR_3)_n(PR'_3)_{4-n}$,[10a] and we have found that the propynyl $^1$H-NMR resonance of **1** (Figure 2a) is adequately simulated for $^2J_{PP} = 100 \pm 20$ Hz.

(23) (a) McConnell, H. M. *J. Mol. Spectrosc.* **1957**, *1*, 11–17. (b) Karplus, M. *J. Chem. Phys.* **1960**, *33*, 1842–1849.

(24) (a) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: New York, 1966; pp 365–367. (b) Hudson, B. S.; Kohler, B. E.; Schulten, K. *Excited States* **1982**, *6*, 1–95.