RHF triplet calculation. Our results demonstrate that the assumption by Davidson and Borden[12b] of a frozen σ core obtained from a calculation on the triplet state is extremely good for the low-lying electronic states of TMM. Since these workers[12b] employed a π CI, they could not treat the ${}^1B_1$ state except at the RHF level; we can, however, treat the ${}^1B_1$ state at the same level as the other electronic states.[35] We predict a ${}^3A'_2$–${}^1B_1$ energy splitting that is in good agreement with the SCF–CI calculations of Hood, Schaefer, and Pitzer who employed a double zeta basis. We note that the rotation barrier, i.e., the ${}^1B_1$–${}^1B_2$ energy difference, is predicted to be 7 kcal/mol, significantly higher than previous estimates.

SOGVB calculations on the states of TMM were done to provide a better physical understanding of the energetics. For the ${}^1B_1$ state, the SOGVB and MCSCF calculations are formally identical, since they incorporate the same configurations. For the ${}^3A'_2$ state the SOGVB–MCSCF energy difference is $<10^{-2}$ mhartree, while for the ${}^1B_2$ state, the difference is $<10^{-1}$ mhartree. In contrast, the SOGVB–MCSCF energy difference for the ${}^1A_1$ state is 12.70 mhartree, and the energy of the ${}^1A_1$ state must be determined at the MCSCF level. Since the SOGVB and MCSCF calculations are in such good agreement and because the SOGVB calculations are more computationally efficient, the final calculations for the ${}^3B_2$, ${}^1B_1$, and ${}^1B_2$ states of **6** were done at the SOGVB level, and only the energies of the ${}^1A_1$ and ${}^1A'$ states were obtained by using the MCSCF method.

The SOGVB calculations provide further information about the physical nature of these states. The calculations show that only two configurations besides the Hartree–Fock configuration are required to determine the energies for the ${}^3A'_2$ (${}^3B_2$), ${}^1B_1$, and ${}^1B_2$ states. The ${}^1A_1$ state requires more configurations. The Hartree–Fock configuration for the ${}^1B_2$ of TMM can be written as *2011* where the first two orbitals are the bonding and antibonding orbitals of the allylic fragment and the final two orbitals are the singly occupied nonbonding allylic orbital and the singly occupied lone pair on the unique methylene group. This configuration enters with a coefficient of -0.9450. The GVB (pp)-like configuration corresponds to promoting two electrons from the allylic bonding orbital to the antibonding orbital, *0211*, and enters with a coefficient of 0.1736. Besides the Hartree–Fock configuration, the most important configuration, however, is the configuration *1111* where the first two electrons are coupled into a triplet as are the final two electrons; these two triplet pairs are then coupled overall into a singlet. This configuration has a coefficient of -0.2770. Similar results are observed for the other states of TMM and the appropriate states of **6**. In order to determine why this last configuration is so important, we carried out calculations on the cations generated by removing an open-shell electron from the ${}^1B_2$ state of TMM. This leads to a ${}^2A_2$ state (removal of an electron from the lone pair orbital on the unique methylene) or a ${}^2B_1$ state (removal of an electron from the nonbonding orbital of the allyl radical). The GVB (pp)–SOGVB energy difference for the ${}^2A_2$ cation (allyl-like fragment) is 0.04232 au, while for the ${}^1B_2$ state of the neutral this difference is 0.04129 au. In contrast, the energy difference for the ${}^2B_1$ cation (allyl-cation-like fragment) is only 0.00239 au. This result suggests that the dominant error in treating most of the states at the GVB (pp) (or RHF) level is an improper treatment of the allylic moiety due to neglect of the spin recoupling term.

Comparison of the energy results given in Table I shows that the energies of the states of **6** are similar to those of TMM. The major changes are that the ${}^1A_1$ state of **6** is significantly lower in energy than the ${}^1B_2$ state, in contrast to the TMM results where the two states are of comparable energy. Furthermore, for **6** another form of the ${}^1A_1$ state is present which has the diradical electrons paired in a bond to form a bicyclic system with C_s symmetry. (This state is equivalent to methylenecyclopropane (MCP) in the case of TMM). The energy of this bonded ${}^1A'$ state is 10 kcal/mol above the ${}^3B_2$ state. In comparison, MCP is 25–30 kcal/mol more stable than the ${}^3A'_2$ state of TMM. The energy of this closed-shell form of the ${}^1A'$ state of **6** should show the largest basis set error since it has the most strain. Consequently, its energy relative to the ${}^3B_2$ ground state could be somewhat lower. It is possible that this closed-shell ${}^1A'$ state can be invoked to explain the low value for the singlet–triplet splitting observed in the trapping experiments of Berson and Platz.[26] Experimental estimates of the rotation barrier about the C–CH_2 (unique methylene) bond in substituted trimethylenemethanes range from $\sim$2–4 kcal/mol. Our value for this barrier on the basis of the ${}^1B_1$–${}^1B_2$ splitting is 7 kcal/mol for TMM and 8 kcal/mol for **6**. If the ${}^1B_1$–${}^1A_1$ splitting is employed, the rotation barriers are 6 kcal/mol for TMM and 3 kcal/mol for **6**. These latter values agree somewhat better with the experimental results. We note, however, that an exact comparison between theory and experiment is difficult, since substituent effects could easily affect the experimentally determined rotation barriers by 1–3 kcal/mol and there is a likely error of 1–2 kcal/mol in the calculations. Thus an exact comparison must await more detailed calculations and experimental studies.

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[35] We employed only the p–π orbitals in determining the configurations for the MCSCF calculations on the ${}^1B_1$ state. These orbitals correspond to the three allyl π orbitals and the lone p orbital on the rotated methylene group. The GVB (pp) calculations employed as the starting guess for the MCSCF calculations were already highly localized and did not include a significant contaminant from the "π-type" CH_2 orbital on the unique methylene group. The wave functions for the ${}^1B_1$ and ${}^1B_2$ states were very similar which demonstrated that the two states, ${}^1B_1$ and ${}^1B_2$, were being treated in the same manner. The SOGVB calculations on the ${}^1B_1$ and ${}^1B_2$ states rigorously gave only the three configurations described below. Since the SOGVB and MCSCF results are in excellent agreement, this provides further evidence that we are treating the two states in a comparable fashion.

Metal–Metal Bonded Complexes of the Early Transition Metals. 2. Synthesis of Quadruply Bonded Tungsten(II) Trifluoroacetate Complexes

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Twenty years ago Wilkinson and co-workers reported the synthesis of molybdenum(II) carboxylate complexes[1] which were subsequently shown to be dimeric,[2] quadruply bonded[3] molecules. Numerous efforts, published and unpublished,[4] have been made since that time to prepare tungsten analogues but without any conclusive success. Attempts to mimic the original Wilkinson synthesis (eq 1) by substituting $W(CO)_6$ for $Mo(CO)_6$ have

$$2Mo(CO)_6 + 4HO_2CR \xrightarrow{\Delta} Mo_2(O_2CR)_4 + 12CO + 2H_2 \quad (1)$$

produced an interesting series of trinuclear tungsten(IV) cluster compounds, but no binuclear tungsten(II) species were isolated from the reactions of tungsten hexacarbonyl with acetic, propionic, or pivalic acids.[5] Metathetical reactions between preformed

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(1) (a) Abel, E. W.; Singh, A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3097–3099. (b) Bannister, E.; Wilkinson, G. *Chem. Ind.* (*London*) **1960**, 319. (c) Stephenson, T. A.; Bannister, E.; Wilkinson, G *J. Chem. Soc.* **1964**, 2538–2541.

(2) Lawton, D.; Mason, R. *J. Am. Chem. Soc.* **1965**, *87*, 921–922.

(3) Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334–336.

(4) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725–4732 and references cited therein.

(5) Bino, A.; Cotton, F. A.; Dori, Z., Koch, S.; Kuppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245–3253.

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quadruply bonded tungsten complexes and acetic acid (eq 2) have also been unsuccessful,[6,7] whereas the analogous molybdenum

$$[Li(Et_2O)]_4W_2(CH_3)_8 \text{ or } W_2Cl_4(PBu_3)_4 + HO_2CCH_3 \not\rightarrow W_2(O_2CCH_3)_4 \quad (2)$$

reactions proceed smoothly to molybdenum(II) acetate.[8,9] As a part of an overall program to explore the chemistry of M–M bonded complexes of the early transition metals,[10] we have been investigating synthetic routes to tungsten(II) carboxylate complexes and report here the synthesis and characterization of two such complexes and some preliminary observations concerning their chemistry.

The reaction of $W_2(mhp)_4$ (mhp = anion of 2-hydroxy-6-methylpyridine)[4] (**1**) with 4 equiv of trifluoroacetic acid (TFAH) in toluene at room temperature led to rapid decomposition of the starting material. No discrete products could be isolated from the resultant brown solution. When the reactants were mixed at −78 °C, the course of the reaction was quite different. As the mixture warmed to 0 °C an air-sensitive orange powder precipitated from solution in ~80% yield. Recrystallization from ether/hexane at −40 °C produced feathery orange needles. Elemental analyses[11] and a mass spectrum revealed that this product was *not* the anticipated tetracarboxylate complex but was instead the mixed ligand dimer (stereochemistry unknown), $W_2(mhp)_2(TFA)_2$ (**2**). Further reaction of **2** with TFAH, under a variety of conditions, gave no indication (by mass spectroscopy) for the formation of $W_2(TFA)_4$. However, **1** is easily regenerated from **2** via reaction of Namhp in THF (eq 3). Although successful

$$\underset{\mathbf{1}}{W_2(mhp)_4} \underset{2\text{Namhp}}{\overset{2\text{TFAH}}{\rightleftharpoons}} \underset{\mathbf{2}}{W_2(mhp)_2(TFA)_2} \quad (3)$$

at introducing two carboxylate groups into a quadruply bonded tungsten dimer, we had failed in our primary objective. This led us to examine alternatives to an "acid" synthesis, one of which was ultimately successful and straightforward.

Reduction of $W_2Cl_6(THF)_4$ with 2 equiv of sodium amalgam in THF at −20 °C produced the intense blue solution reported previously.[7] Addition of sodium trifluoroacetate and subsequent warmup produced a brown solution. Careful workup[12] provided the crude product as a yellow brown powder. Sublimation (10^{-3} mm) at 130 °C gave a bright *yellow* solid and a brown residue which was discarded. Resublimation of the yellow solid provided an analytically pure[13] microcrystalline sample [in ~20% yield based on $W_2Cl_6(THF)_4$] of $W_2(TFA)_4$ (**3**) (eq 4).[14] The tetra-

$$W_2Cl_6(TFA)_4 \xrightarrow{2\text{Na/Hg}} [W_2Cl_4(THF)_4] \xrightarrow{4\text{NaTFA}} \underset{\mathbf{3}}{W_2(TFA)_4} \quad (4)$$

carboxylate is air sensitive in the solid state and more so in solution, but it does have reasonable thermal stability, decomposing at ~200 °C in a sealed evacuated capillary. A cryoscopic molecular weight measurement in benzene (calcd 820; found 805) *and* a parent peak in the mass spectrum of **3** support the dimer formulation. The ^{19}F NMR spectrum of **3** shows a single resonance at δ −70.1 (vs. $CFCl_3$, δ 0.0) consistent with the presence of bidentate TFA ligands.[15] There is an obvious peak for peak correspondence in the IR spectrum of **3** when compared with that of $Mo_2(TFA)_4$[16] (ν_{asym} (O_2CCF_3) appears at 1592, 1572 cm^{-1} in the molybdenum dimer and at 1559, 1542 cm^{-1} in **3**). The solid-state Raman spectra of $Mo_2(TFA)_4$ and $W_2(TFA)_4$ are also very similar (see supplementary material). We have assigned the 313 (3)-cm^{-1} band in the tungsten spectrum as the "W–W stretching mode". It is the highest value yet observed for a quadruply bonded tungsten complex.[17] Using the harmonic oscillator approximation,[4] we calculate a W–W force constant of 5.30 mdyn Å^{-1}.

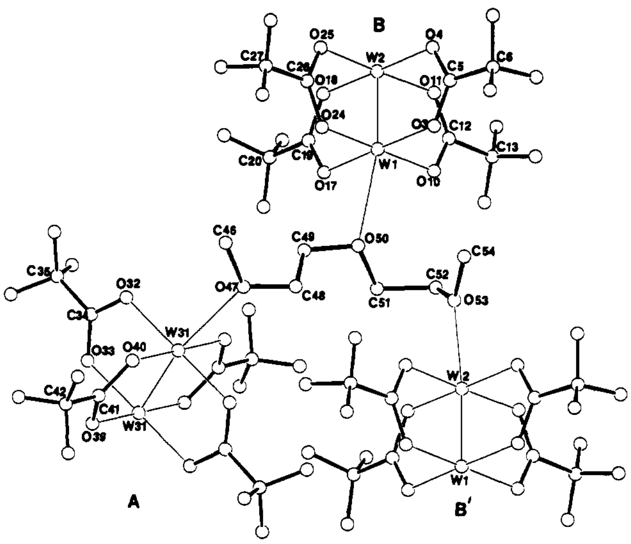

Figure 1. ORTEP drawing of $W_2(TFA)_4\cdot{}^2/_3$diglyme showing the partial contents of two unit cells (see text). Selected data not presented in the text: W(1)–O(50) 2.70 (1), W(1)–O(3) 2.11 (1), W(2)–O(53) 2.48 (1), W(31)–O(47) 2.52 (1) Å; W(2)–W(1)–O(3) 90.4 (2), W(2)–W(1)–O(50) 166.6 (2), W(1)–W(2)–O(53) 174.9 (3), W(31)–W(31)–O(47) 164.3 (2)°.

Reaction of **3** with 4 equiv of Namhp in THF provides **1**. Addition of 2 mol of triphenylphosphine for 1 mol of **3** in toluene yields a yellow-orange crystalline complex, $W_2(TFA)_4\cdot 2PPh_3$ (**4**) in ~80% yield.[19] The ^{19}F NMR spectrum of **4** shows a single resonance at δ −70.0, indicating that the bidentate TFA ligands remain intact.[15] The solid-state Raman spectra of **4** is similar to that of **3** in the 0–1000-cm^{-1} region. The W–W stretching mode shifts to 285 cm^{-1}, suggesting a modest W···P interaction. Finally, we note that **3** reacts with concentrated aqueous hydrochloric acid at 25 °C to give, as expected,[20] hydrogen (by mass spectroscopy) and the tungsten(III) dimer, $W_2Cl_9^{3-}$, which can be precipitated from solution as the cesium salt in ~80% yield[21] by the addition of cesium chloride. If the reaction is run at low temperature (~−10 °C), a mixture of two compounds is obtained, one of which is $Cs_3W_2Cl_9$. We believe that the other compound is $Cs_3W_2Cl_8H$, since the IR spectrum (Nujol mull) of the mixture is featureless

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(6) Cotton, F. A., Koch, S.; Mertis, K.; Millar, M.; Wilkinson, G. *J. Am. Chem. Soc.* **1977**, *99*, 4989–4992.

(7) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430–1431.

(8) Cotton, F. A.; Troup, J. M.; Webb, T. R.; Williamson, D. H.; Wilkinson, G. *J. Am. Chem. Soc.* **1974**, *96*, 3824–3828.

(9) San Filippo, J., Jr.; Snaidock, H. *Inorg. Chem.* **1976**, *15*, 2209–2215.

(10) Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111–7113.

(11) Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Anal. Calcd. for $W_2(mhp)_2(TFA)_2(W_2C_{16}H_{12}F_6N_2O_6)$: C, 23.73; H, 1.49; N, 3.46; F, 14.07. Found: C, 23.46; H, 1.48; N, 3.46; F, 13.90.

(12) The brown solution was filtered through Celite (to remove NaCl and Hg) and stripped. The residue was extracted with toluene, filtered through Celite, and stripped to provide the crude product. All operations were conducted under inert (He or Ar) atmosphere, and all solvents were dried and deoxygenated by standard methods.

(13) Anal. Calcd. for $W_2(TFA)_4(W_2C_8F_{12}O_8)$: C, 11.72; F, 27.81. Found, C, 11.56; F, 27.53. ^{19}F NMR (ppm, C_6D_6, 84.26 MHz) −70.1 (s).

(14) We assume in eq 4 that the thermally unstable blue intermediate is $W_2Cl_4(THF)_4$, but this has not been proven. The formation of $W_2(TFA)_4$ appears to be competitive with its decomposition.

(15) Girolami, G. S.; Mainz, V. V.; Anderson, R. A. *Inorg. Chem.* **1980**, *19*, 805–810.

(16) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161–172.

(17) The W–W stretching mode is found at 260 (10) cm^{-1} in $W_2Cl_4(PBu_3)_4$[7] where the W–W bond length is ~2.26 Å[18] and at 295 (3) cm^{-1} in $W_2(mhp)_4$ where the W–W bond length is 2.161 (1) Å.[4]

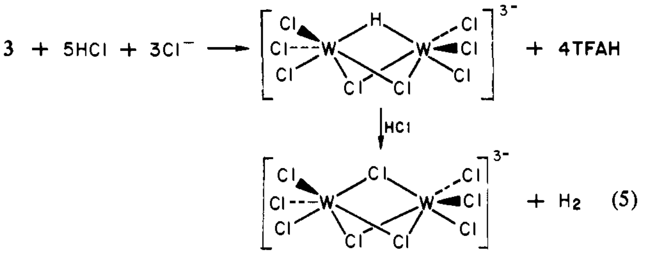
(18) Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1431–1433. A W–W bond length of 2.262 (1) Å was found for $W_2Cl_4(PMe_3)_4$. We assume that the analogous bond length in $W_2Cl_4(PBu_3)_4$ is very close to this value.

(19) Anal. Calcd. for $W_2(TFA)_4\cdot 2PPh_3$ ($W_2C_{44}H_{30}F_{12}O_8P_2$): C, 39.31; H, 2.25; F, 16.96. Found: C, 39.49; H, 2.34; F, 16.71. ^{31}P NMR (ppm, C_6D_6, ^1H decoupled; 36.20 MHz) 2.42 (br s). ^{19}F NMR (ppm, C_6D_6, 84.26 MHz) −70.0 (s).

(20) DeMarco, D.; Nimry, T.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 575–577.

(21) Anal. Calcd. for $Cs_3W_2Cl_9$: Cl, 29.40; W, 33.87. Found: Cl, 29.22; W, 33.90.

except for bands at 1538 and 1240 cm^{-1}. We tentatively assign these bands to the symmetric and antisymmetric W–H–W vibrations[22] of confacial bioctahedral $W_2Cl_8H^{3-}$. These bands are absent when the reaction is run in concentrated aqueous DCl and are replaced by new bands at 1120 and 896 cm^{-1}. Dissolution of the mixture in aqueous HCl produced hydrogen and clean conversion (by UV spectroscopy) to $W_2Cl_9^{3-}$ (eq 5).[25]



X-ray quality crystals of unsolvated 3 have not yet been isolated, but we have prepared and crystallized (by vacuum sublimation) a diglyme adduct of 3. The structure of $W_2(O_2CCF_3)_4\cdot{}^2/_3(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$ was determined from diffraction data collected at −160 °C.[27] A view of the structure, which emphasizes the "tridentate" nature[29] of the diglyme, is shown in Figure 1. Tungsten dimers A and B are crystallographically independent and are in the same unit cell as the polyether.[30] Tungsten dimer B′ is related to B by a unit translation. As anticipated, each $W_2(TFA)_4$ molecule has idealized D_{4h} symmetry with the tungsten atoms bridged by trifluoroacetate ligands. The W–W bond lengths are 2.211 (2) and 2.207 (2) Å for dimers A and B, respectively. The axial solvent oxygen contacts with the dimers vary from 2.48 (1) to 2.70 (1) Å (see Figure 1). Full details of the structure will be reported elsewhere.

The results presented here clearly demonstrate that quadruply bonded tungsten(II) carboxylate complexes are isolable and stable in the absence of potential oxidizing agents. We believe that they will serve as valuable synthetic intermediates in dimeric tungsten(II) chemistry. Further elaboration of the chemistry and physical properties of tungsten(II) carboxylates will be reported in the near future.

Acknowledgment. The Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for support of this work. We also thank the Marshall H. Wrubel Computing Center, Indiana University, for a generous gift of computing time. The Finnegan mass spectrometer used in this research was purchased, in part, by funds provided by the National Science Foundation.

Supplementary Material Available: The solid-state Raman spectra of $Mo_2(O_2CCF_3)_4$ and $W_2(O_2CCF_3)_4$ and tables of fractional coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[22] These vibrational assignments fit nicely with the data of Katovic and McCarley[23] on $Mo_2Cl_8H^{3-}$ and $MoWCl_8H^{3-}$. Essentially identical results are obtained with $W_2(mhp)_4$[4] dissolved in concentrated aqueous HCl and DCl.[24]

[23] Katovic, V.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1268–1270.

[24] Sattelberger, A. P.; McLaughlin, K. W., unpublished results.

[25] Metathetical primary products such as $W_2Cl_8^{4-}$ or $W_2Cl_7(H_2O)^{3-}$ are conceivable intermediates in this reaction, but we have no proof for their existence. For a discussion of binuclear oxidative addition to molybdenum–molybdenum quadruple bonds, see ref 26.

[26] Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1976**, *15* 522–524.

[27] $W_2(TFA)_4\cdot{}^2/_3(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 23.046$ (9), $b = 9.108$ (2), $c = 9.222$ (2) Å; $\alpha = 99.64$ (1), $\beta = 59.45$ (1), $\gamma = 103.55$ (1)°; $V = 1617.9$ Å^3; ρ (calcd) = 2.800 g cm^{-3} for M_r 909.2 and $Z = 3$. Diffraction data were collected at −160 °C by a θ–2θ scan technique with equipment described in detail elsewhere.[28] Data were corrected for absorption (μ 110.35 cm^{-1}) and the structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All atoms, excluding diglyme hydrogen atoms, have been located and their positional and thermal parameters (anisotropic for W, C, O, and F) refined. The current discrepancy indices are $R_f = 0.047$ and $R_{wf} = 0.046$ for those 3486 reflections with $F_o \geq 3.0\,\sigma(F_o)$. The limits of data collection were $6 \leq 2\theta \leq 45°$ (Mo Kα radiation).

[28] Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755–2762.

[29] (a) The crystal structure[29b] of $Mo_2(O_2CPh)_4\cdot 2(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$ reveals two dilgyme molecules bound axially to the molybdenum(II) carboxylate in a monodentate fashion, i.e., one methoxy oxygen from each solvent molecule binds to the dimer. The Mo···O distance in this example is 2.633 (6) Å. (b) Collins, D. M.; Cotton, F. A.; Murillo, C. A. *Inorg. Chem.* **1976**, *15*, 2950–2951.

[30] The symmetry related partner of tungsten dimer B has not been included in the drawing.

Palladium-Catalyzed Stereo- and Regiospecific Coupling of Allylic Derivatives with Alkenyl- and Arylmetals.[1] A Highly Selective Synthesis of 1,4-Dienes

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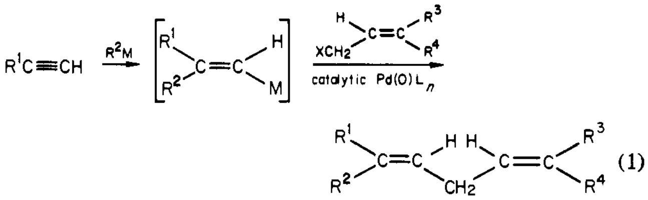
We wish to describe a remarkably facile and highly selective Pd-catalyzed cross-coupling reaction[2] of alkenylmetals containing Al or Zr with allylic halides or acetates, which not only proceeds with essentially complete retention of the stereo- and regiochemistry of both alkenyl and allyl groups but is free from the formation of the homocoupled products. When used in conjunction with hydroalumination,[3] hydrozirconation,[4] or carboalumination[5] of acetylenes, the reaction provides a uniquely expeditious route to 1,4-dienes[6,7] (eq 1). We further report that the corresponding



R^1 = carbon group; R^2 = H or alkyl; R^3 and R^4 = two hydrogens or two alkyl groups; M = Al or Zr

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† On leave from the Japan Tobacco & Salt Public Corp.

[1] Selective Carbon–Carbon Bond Formation via Transition-Metal Catalysis. 18. Part 17: Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276.

[2] (a) For a review, see: Negishi, E. In "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J. H., Ed.; Plenum: New York, 1978; p 285. (b) Negishi, E.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976**, 596. (c) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729. (d) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821. (e) King, A. O.; Okukado, N.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1977**, 683. (f) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (g) Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027. (h) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, *100*, 2254. (i) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358. (j) Negishi, E.; Valente, L. F.; Kobayashi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298. (k) Kobayashi, M.; Negishi, E. *J. Org. Chem.* **1980**, *45*, 5223.

[3] Wilke, G.; Müller, H. *Liebigs Ann. Chem.* **1960**, *629*, 222.

[4] Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373. See also: Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

[5] Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252.

[6] The reactions of allylmetal derivatives with alkenyl halides are generally nonstereoselective. For a review on the reaction of π-allylnickel complexes with organic halide, see: Semmelhack, M. F. *Org. React.* **1972**, *19*, 117.

[7] Stereo- and regiodefined alkenylmetals containing Al, B, and Cu have been shown to cross couple with allylic halides. The scope of the selective alkenyl–allyl coupling involving Al and B is practically limited to γ-unsubstituted allylic halides. Although the reactions of alkenylcoppers with allylic electrophiles are highly promising, examples of the reactions of stereodefined alkenylcoppers with stereodefined allylic electrophiles appear to be essentially unknown. Al: (a) Lynd, R. A.; Zweifel, G. *Synthesis* **1974**, 658. (b) Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927. (c) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. (d) Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2215. B: Yamamoto, Y.; Yatagai, H.; Sonoda, A.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1976**, 452. Cu: (a) Normant, J. F.; Bourgain, M. *Tetrahedron Lett.* **1971**, 2583. (b) Corey, E. J.; Cane, D.; Libit, L. *J. Am. Chem. Soc.* **1971**, *93*, 7016. (c) Raynolds, P. W.; Manning, M. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1977**, 499. (d) Alexakis, A.; Cahiez, G.; Normant, J. F. *Synthesis* **1979**, 826.

0002-7863/81/1503-2882$01.25/0