termediate. Subsequent closure of the ring may occur to yield the more stable trans geometry. The formation of the intermediate could occur by a single-electron-transfer route or by direct conjugate addition of 1 to the Michael acceptor. Whether CO is lost before or after the formation of the intermediate is not yet known. The other possible mechanism that would allow rotation about the C–C bond involves a diradical intermediate. The diradical path was ruled out in the experiments involving $Os_2(CO)_8(\mu\text{-}\eta^1:\eta^1\text{-}C_2H_2D_2)$,[10] and we believe it is less likely to occur in this electron-rich (phosphine)ruthenium case.

^1H NMR spectroscopy of reactions conducted in sealed tubes at 22 °C established $K_{eq} = 0.023$ for the equation in Scheme I. The solubility of CO in benzene was taken from the literature.[15] This preliminary study has shown the equilibrium for the system lies toward the starting materials and that the reaction is driven toward the products by purging CO from the system in a stream of N_2. A full kinetic study of this reaction is underway.

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Registry No. 1, 123810-59-3; 2, 131322-71-9; $2\cdot C_7H_8$, 131432-36-5; (*Z*)-dimethyl maleate, 624-48-6; (*E*)-dimethyl maleate, 624-49-7.

Supplementary Material Available: Tables of the crystallographic data, atom positions, anisotropic thermal factors, and bond distances and angles (20 pages); a listing of structure factors (24 pages). Ordering information is given on any current masthead page.

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Transformation of a Bridging Ketene to a Metal-Substituted Acetylene in Dinuclear Tungsten Complexes: Crystal and Molecular Structure of a Dinuclear Tungsten Complex Containing a Bridging σ-Acetylene Ligand

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Summary: The ketene complex $[Cp(CO)_2W]_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)$ (Cp = $\eta^5\text{-}C_5H_5$), prepared directly from the reaction of $Cp(CO)_3W^-$ with CH_2I_2, is transformed at −5 °C to a dinuclear σ-acetylene complex, $Cp(CO)_3WC{\equiv}CW(CO)_3Cp$, the structure of which has been confirmed by a single-crystal X-ray diffraction analysis.

In 1983, an initial disclosure was made that addition of CH_2Cl_2 to 2 equiv of the ruthenium anion $CpRu(CO)_2^-$ (Cp = $\eta^5\text{-}C_5H_5$) leads to the dinuclear methylene complex $[Cp(CO)_2Ru]_2(\mu\text{-}CH_2)$, where the CH_2 unit is the only bridging ligand.[1a] The chemical reactivity of the complex is dominated by C–C bond formation through a facile CO insertion into one of the Ru–C bonds to form a bridging ketene complex. In the absence of an external ligand, CO insertion also produces a dinuclear ketene complex with a metal–metal bond and a bridging CO ligand.[1b] Similar reactivity has been reported in the case of a heteronuclear methylene complex lacking the metal–metal bond.[2] The lack of additional bonding between the two metal centers in these methylene complexes may be responsible for their much greater reactivity toward CO insertion, as compared to that of the corresponding methylene complexes with metal–metal bonds.[3] As part of a study of this chemistry of methylene/ketene complexes, we intended to prepare tungsten methylene complexes so as to extend our earlier work on ruthenium analogues. Herein, we describe the spectroscopic observation of some tungsten ketene complexes as well as an unprecedented transformation of a bridging ketene to a metal-substituted σ-acetylene.

The phosphite-substituted tungsten methylene complex $\{Cp(CO)_2[P(OMe)_3]W\}_2(\mu\text{-}CH_2)$ (**2b**)[4] is obtained from the reaction of 2 equiv of the tungsten anion $Cp(CO)_2[P(OMe)_3]W^-$ (**1b**) with CH_2Br_2 in THF at −20 °C for 24 h (see Scheme I). Complex **2b** must be stored below 0 °C. The ^1H and ^{13}C NMR spectra[4] of **2b** are consistent with a CH_2 group bridged between two W metals with no other supporting ligand. In the ^1H NMR spectrum, the CH_2 protons of **2b** appear as a triplet signal, coupled with $P(OMe)_3$ ($J_{P\text{-}H}$ = 5.1 Hz), at δ 2.34.[5] A triplet ^{13}C signal with $J_{P\text{-}C}$ = 11.2 Hz at δ −50.4 is assigned to the CH_2 carbon. In the presence of CH_3CN, **2b** is readily converted to $[Cp(CO)LW]_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)$ (**3b**)[4] in 100% NMR

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(4) Spectroscopic data are given in the supplementary material.

(5) The chemical shift of the methylene protons of the Ru system is at δ 2.30.[1]

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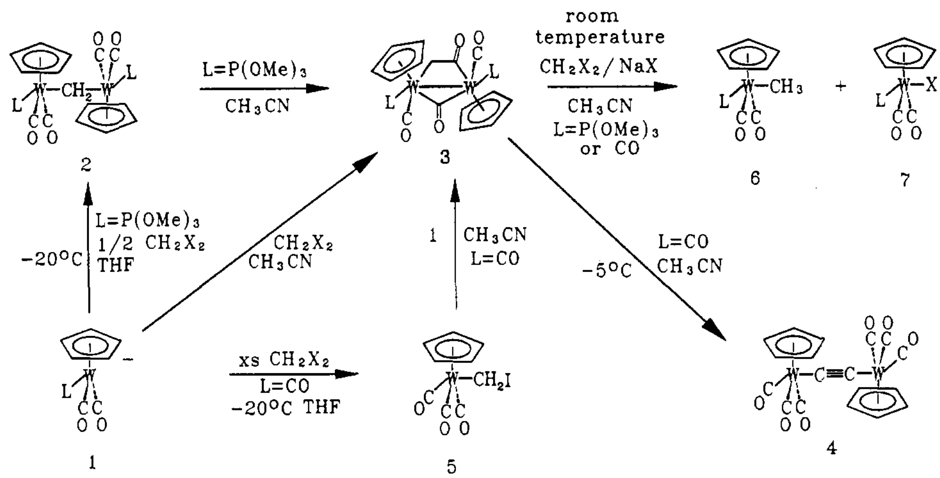
Scheme I



yield, indicating a facile C–C bond formation on the bridging methylene ligand. Unlike that in the triosmium system,[3f] such a transformation does not seem to be promoted by the presence of X^- anion. With use of CD_3CN, instead of THF, complex **3b** can be prepared directly from the reaction of CH_2Br_2 or CH_2Cl_2 with **1b** at -20 °C. The ^1H NMR spectrum of **3b** shows two sets of doublets of doublets ($J_{H\text{-}H}$ = 6.12, $J_{P\text{-}H}$ = 3.12, 3.70 Hz) at δ 2.99 and 3.49, which are assigned to inequivalent CH_2 protons coupled with each other and with $P(OMe)_3$. In the ^{31}P NMR spectrum, resonances with equal intensity are found at δ 183.8 and 153.1 assignable to two $P(OMe)_3$ ligands bound to metals with CH_2 and with ketene CO, respectively. In the presence of CH_2X_2/NaX (X = Br, Cl), both **2b** and **3b** are slowly converted to $Cp(CO)_2[P(OMe)_3]WCH_3$ (**6b**) and $Cp(CO)_2[P(OMe)_3]WX$ (**7**), in each of which both cis and trans isomers[6] are detected. The proton source is not from solvent, since no MCH_2D is observed in deuterated solvent. The methylene-deuterated complex **3b** prepared from CD_2Cl_2 gives all MCH_3, $MCDH_2$, and MCD_2H products, indicating scrambling of the methylene protons. Details of such a transformation are currently under investigation.

Reaction of $Cp(CO)_3W^-$ (**1a**) with CH_2I_2 in CD_3CN directly produces $[Cp(CO)_2W]_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)$ (**3a**)[4] in 76% yield. If the reaction is carried out in THF with excess CH_2I_2, the metal iodomethyl complex $Cp(CO)_3WCH_2I$ (**5**)[4] is first obtained in 85% yield. Further reaction of **5** with **1a** in CH_3CN also produces **3a**. In the ^1H NMR spectra of **3a** at 251 K, there are the three observable isomers A–C, each of which contains the following respective resonances with an AB or AX coupling pattern and two Cp resonances: δ 3.11, 3.52 ($J_{H\text{-}H}$ = 3.7 Hz), 5.63, 5.66; δ 2.08, 2.23, ($J_{H\text{-}H}$ = 7.5 Hz) 4.87, 5.56; δ 2.24, 2.62, ($J_{H\text{-}H}$ = 6.6 Hz) 4.56, 5.28. These can be assigned to the geometrical isomers of **3a** originating from the arrangement of the cyclopentadienyl and two terminal CO ligands about W metal centers. The kinetic product is isomer A, which forms in the initial stage of the reaction and slowly transforms to the mixture of isomers B and C. All three complexes are too unstable to obtain their IR spectra. In the ruthenium complex $[Cp(CO)Ru]_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)$ with a cyclopentadienyl and a terminal CO ligand on each Ru metal, one would anticipate two isomers. These are indeed observed in their NMR spectra.[1b] The analogous ruthenium complex $[(C_5Me_5)(CO)Ru]_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)$, as well as **3b**, shows only one isomer.[1c] These structural phenomena may be due to the steric effect of the ligands such that a single isomeric complex is more stable than others.

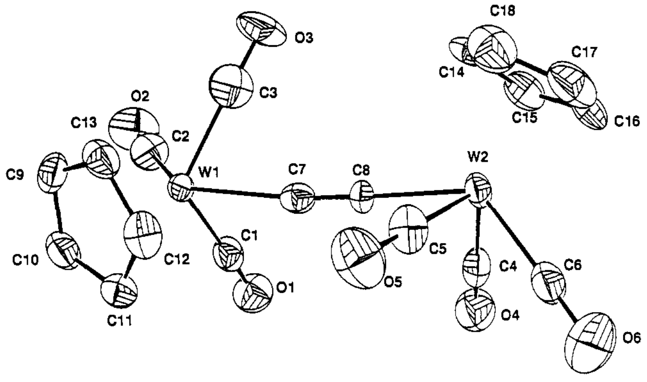


Figure 1. ORTEP diagram of $Cp(CO)_3WC{\equiv}CW(CO)_3Cp$, showing the atom-labeling scheme. Selected bond distances (Å) and bond angles (deg) are as follows: W–C(7), 2.172 (22); W–C(8), 2.148 (20); C(7)–C(8), 1.18 (3); C(2)–W(1)–C(7), 131.9 (9); C(8)–W(2)–C(6), 129.7 (10); W(1)–C(7)–C(8), 172.3 (18); W(2)–C(8)–C(7), 173.1 (17).

While complex **3a**, similar to **3b**, could be converted to the methyl and iodo complexes at room temperature, it is converted to the dimer $[Cp(CO)_3WC{\equiv}CW(CO)_3Cp]$ (**4**)[4] in CH_3CN at -5 °C. Complex **4** can be envisaged as involving the loss of H_2O from **3a** with the concomitant gain of a CO ligand from another molecule. This explains the low yield (25%) of the reaction. Ketene is known to react with H_2O to produce acetic acid. However, in the NMR monitoring experiment, no acetic acid is observed nor do we observe any significant organic product. The product analysis is currently under investigation. Complex **4** has been reported recently as a trace product from the reaction of $Cp(CO)_3W^-$ anion with $ClC{\equiv}CCl$.[7] The CO-induced conversion of η^1-ketenyl ligands into alkynyl ligands by a deoxygenation reaction has been reported,[8] but its mechanism is unknown.

Complex **4** is also identified on the basis of its single-crystal X-ray analysis,[4] as illustrated in Figure 1. The W atoms are connected by an essentially linear C_2 bridge with W(1)–C(7)–C(8) and W(2)–C(8)–C(7) angles of 172.3 (18) and 173.1 (17)°, respectively. One end of the molecule is

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rotated with respect to the other, resulting in a dihedral angle of 55.6 (6)° between the planes of the Cp ligands. The C(7)-C(8) distance is 1.18 (3) Å, short compared to the C≡C distance in unbound acetylene and the C≡C distances in the Chatt type acetylene complexes.[9] The structure of the similar dirhenium complex $(CO)_5ReC \equiv CRe(CO)_5$ has recently been reported.[9c] The C≡C distance is again slightly longer than that in 4.

Since **1a** is a relatively weak nuclophile compared with the substituted anion **1b**, it is therefore not surprising that CH_2Br_2 or CH_2Cl_2 would not react with **1a**. The reaction of **1b** with CH_2I_2 directly produces $Cp(CO)_2[P(OMe)_3]WI$ and **6b**. No ketene intermediate was observed. The reaction of **1b** with CH_2Br_2 or with CH_2Cl_2 gives a ketene intermediate, which is then converted to $Cp(CO)_2[P(OMe)_3]WX$ (X = Br, Cl) and **6b** at room temperature, but at a slower rate. The halide anion may play an important role in such a transformation. Preliminary results indicate that the reaction of **5** with **1b** in CD_3CN directly produces $Cp(CO)[P(OMe)_3]W(\mu\text{-}COCH_2)(\mu\text{-}CO)W(CO)_2Cp$. The CO insertion takes place at the substituted metal center. The decomposition products, which contain mostly $Cp(CO)_3WCH_3$ and $Cp(CO)_2[P(OMe)_3]WI$, provide further evidence that CO insertion takes place at the substituted site.

With the tungsten metal, we have demonstrated facile C-C bond formation of the dinuclear methylene complex with no other supporting ligand. The unprecedented transformation of ketene to acetylene may provide another mechanism to account for the deoxygenation of CO in the Fischer-Tropsch synthesis. Further work is in progress, and detailed studies on the formation of methyl complexes and chemical reactivity of the ketene complexes will be the subject of future reports.

Acknowledgment. This research has been supported by the National Science Council (NSC) of the Republic of China.

Supplementary Material Available: Details of the structural determination for complex 4, including tables of data collection parameters, temperature factor expressions, positional parameters, and intramolecular distances and angles, and a table of spectroscopic data for complexes **2b**, **3a**,**b**, **4**, and **5** (7 pages); a table of observed and calculated structure factors for 4 (11 pages). Ordering information is given on any current masthead page.

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$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-}Ph_2PCH_2PPh_2)_3][BF_4]$, a Triangulo Copper(I) Complex with an Unprecedented Bicapping System of Two Asymmetric $\mu_3\text{-}\eta^1$-Acetylide Ligands

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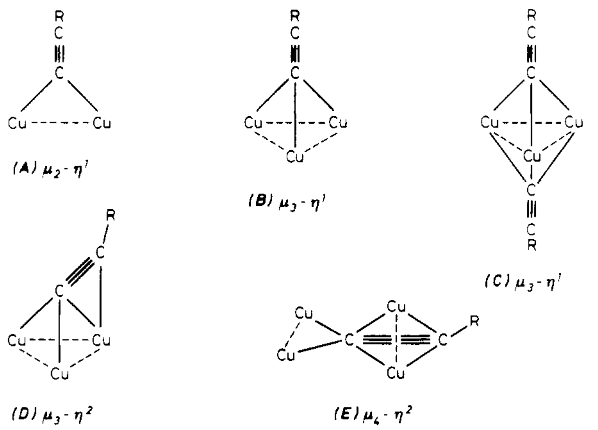
Summary: The synthesis and characterization of $[Cu_3(C{\equiv}CPh)_2(Ph_2PCH_2PPh_2)_3][BF_4]$ (**1**), the first cationic trinuclear copper(I) complex bicapped by two bridging σ-bonded phenylacetylide groups, is described. An X-ray single-crystal structure determination shows that the two linear phenylacetylide groups are bonded in a $\mu_3\text{-}\eta^1$ fashion, representing an unprecedented structure in organocopper(I) chemistry. The electronically deficient bonding can be formally described as a five-center-four-electron system.

The chemistry of organocopper derivatives is of increasing interest due to their wide and selective applications in organic chemistry.[1] Much of the work done has been devoted specifically to synthetic studies through low or higher order mixed cuprates,[2] i.e. $[R_TRCuLi]$, $[R_TRCu(CN)Li_2]$. However, the formulas only reflect the ratio of the copper salt to the organolithium reagent and the active species or their molecular structures are scarcely known.[3] At present, there are only a small number of structurally characterized organocopper derivatives, most

Chart I



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