Table I. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses[a]

Zr–Cp(1)	2.219 (4)	Cp(1)–Zr–Cp(2)	129.8 (2)
Zr–H_b	1.99 (4)	Cp(1)–Zr–H_b	109 (1)
Zr–H_t	1.82 (7)	Cp(1)–Zr–$H_{b'}$	104 (1)
Zr–H_b–Zr′	121 (3)	Cp(1)–Zr–H_t	104 (1)
Zr–Cp(2)	2.220 (4)	Cp(2)–Zr–H_b	121 (1)
Zr–$H_{b'}$	2.00 (4)	Cp(2)–Zr–$H_{b'}$	100 (1)
Zr···Zr′	3.4708 (7)	Cp(2)–Zr–H_t	99 (1)
H_b–Zr–$H_{b'}$	59 (3)		
H_b–Zr–H_t	64 (2)		
$H_{b'}$–Zr–H_t	121 (2)		

[a] Cp(1) and Cp(2) are the centroids of the [C(1), C(2), C(3), C(4), C(5)] and [C(10), C(11), C(12), C(13), C(14)] rings, respectively.

in the EPR cavity with the deuterated compound $[\{\eta^5\text{-}C_5H_4C(CH_3)_3\}_2ZrD(\mu\text{-}D)]_2$ (prepared from $AlLiD(OCMe_3)_3$ via $AlLiD_4$, purity checked by NMR spectroscopy). The signal obtained (Figure 3B) is composed of a central quintet with partially overlapping components, and the features are in agreement with what is expected for an unpaired electron interacting with two deuterium nuclei (quintet of relative intensities 1:2:3:2:1). The magnitude of the deuterium hyperfine interaction constant $a(D) = 1.38$ G is one-sixth of the value of the starting compound, as expected. The reduction of the signal bandwidth in the deuterated compound also has a consequence on the frozen-solution spectrum, which now exhibits a well-resolved **g** tensor anisotropy with pseudoaxial symmetry ($g_{\parallel} = 2.003$ and $g_{\perp} = 1.989$). Also detectable, though poorly resolved, are the perpendicular components of the Zr hyperfine tensor on both sides of the central signal, roughly measured to give 80 G. From the $g_{\parallel}$ value it can be deduced that the unpaired electron lies in the d_{z^2} metal orbital.

Reduction of **1** to the Zr(III) hydride species can also be performed by treatment with sodium or potassium naphthalenide in THF. The solution obtained exhibits an intense spectrum consisting of a quartet of triplets due to interaction of the unpaired electron with two hydrogens and with the nuclear spin ($I = {}^3/_2$) of the alkali metal ($g_{iso} = 1.992$; $a(H) = 8.3$ G; $a(^{23}Na) = 10.1$ G; $a(^{39}K) = 2.0$ G; $A(^{91}Zr) = 10.4$ G). This solution can be kept in a sealed tube for at least 2 weeks without change in the signal intensity.

The following steps can be proposed to account for the overall phenomenon observed by cyclic voltammetry combined with electrochemical reduction in the EPR cavity ($Cp' = \eta^5\text{-}C_5H_4C(CH_3)_3$):

$$\underset{\mathbf{1}}{[Cp'_2ZrH(\mu\text{-}H)]_2} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{A}{[Cp'_2ZrH(\mu\text{-}H)]_2} \qquad (1)$$

$$A \rightleftharpoons \underset{B}{[Cp'_2ZrH_2]^-} + \underset{C}{[Cp'_2ZrH_2]} \qquad (2)$$

$$C \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} B \qquad (3)$$

$$2C \rightleftharpoons \mathbf{1} \qquad (4)$$

Reaction 1 is the primary step that dominates the pseudoreversible process observed by cyclic voltammetry. The capture of one electron is expected to give a mixed-valence Zr(IV)/Zr(III) compound, but this species, which should exhibit a characteristic EPR spectrum, was not detected in the course of electrolysis in the EPR cell even down to −60 °C. The EPR results show therefore that the signal generated under a steady reductive current is due to a chemical process subsequent to the primary electron transfer, such as cleavage of dimer A in reaction 2, to give the neutral monomer C and the radical anion B responsible for the observed spectrum. C may also capture an electron as in (3) to give B or give back the dimer according to (4). However, other mechanisms are also possible and should not be excluded.

In conclusion, the above results show that the zirconium dihydride monomer is the only species detectable by EPR spectroscopy as the radical anion generated by electrochemical reductive cleavage of the corresponding dimer. This behavior appears to be common to the substituted (cyclopentadienyl)zirconium dihydride dimers, since we observed similar electrochemical results with $[Cp^*_2ZrH(\mu\text{-}H)]_2$ ($Cp^* = \eta^5\text{-}C_5H_4Si(CH_3)_3$). It can be reasonably expected therefore that cleavage of the dimer by chemical reductive methods should also lead to the monomer with more interesting reactivity properties. Moreover, these results support previous findings that bis(cyclopentadienyl)zirconium(IV) compounds tend to give stable radical anions by one-electron addition without secondary chemical complications.[16,17]

Supplementary Material Available: Tables of fractional atomic coordinates, hydrogen positional and thermal parameters, final anisotropic thermal parameters, bond lengths and angles, and least-squares planes (6 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

---

(16) Samuel, E.; Vedel, J. *Organometallics* **1989**, *8*, 237.

(17) Chaloyard, A.; Dormond, A.; Tirouflet, J.; El Murr, N. *J. Chem. Soc., Chem. Commun.* **1980**, 214.

Reversible, Stepwise Addition of 1,2-Diester-Substituted Alkenes to $Ru_2[(CH_3)_2PCH_2P(CH_3)_2]_2(CO)_5$. Crystal and Molecular Structure of the Diruthenacyclobutane Complex $Ru_2[(CH_3)_2PCH_2P(CH_3)_2]_2(CO)_4[\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(H)_2(CO_2CH_3)_2]\cdot C_7H_8$

Kimberly A. Johnson and Wayne L. Gladfelter*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received October 1, 1990

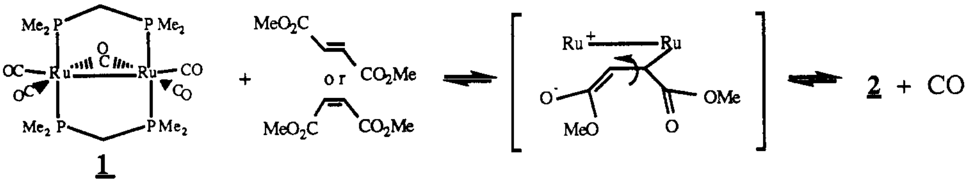
Summary: cis- and *trans-*Diester-substituted alkenes react with $Ru_2(dmpm)_2(CO)_5$ (dmpm = bis(dimethylphosphino)methane) to form the trans-substituted diruthenacyclobutane. This process was shown to be stepwise and reversible, and a zwitterionic intermediate is proposed.

In 1980, a report by Brady and Pettit stirred widespread interest in dimetallacycloalkanes by providing evidence for the importance of coupling between surface-bound methylene groups in the Fischer–Tropsch reaction.[1] Despite

---

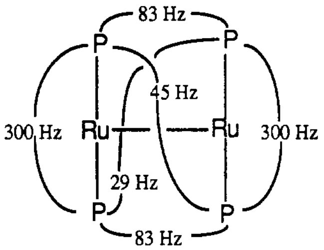
(1) Brady, R. C. I.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

Scheme I



this interest, examples of dimetallacyclobutanes remain scarce and very little is known about the mechanism of their formation.[2-11] In this communication we describe the synthesis and characterization of a new diruthenacyclobutane along with stereochemical evidence that it is formed in a stepwise reaction.

The reaction of $Ru_2(dmpm)_2(CO)_5$ (1)[12] with 1,2-diester-substituted alkenes such as dimethyl maleate (cis) or dimethyl fumarate (trans) in aromatic solvents resulted in formation of a yellow, crystalline product in 65% yield following solvent removal. The mass spectrum and elemental analysis were consistent with the formula $Ru_2(dmpm)_2(CO)_4[C_2(H)_2(CO_2CH_3)_2]$ (2), and the four-band pattern in the ν_{CO} region[13] was very similar to that observed for the diruthenacyclobutene previously reported for this system.[12] The ^1H NMR spectrum of 2 showed only one signal for the two methoxy groups, indicating the molecule was symmetric. The signal at 7.3 ppm in the ^{13}C NMR spectrum was assigned to the ruthenium-bound carbons of the alkene and indicated complete loss of the C–C double-bond character. The coupling information extracted from the AA′BB′ pattern in the ^{31}P NMR spectrum by simulation suggested the ester groups in 2 were in a trans arrangement. NMR studies of the reaction solutions have failed to yield any evidence for a second isomer.



The trans-diester-substituted diruthenacyclobutane structure deduced from the solution spectroscopic data was confirmed by single-crystal x-ray crystallography (Figure 1).[14] The Ru–C distances of 2.258 (9) and 2.25 (1) Å are within the expected range for a Ru–C single bond, and the C1A–C2A distance of 1.51 (1) Å is indicative of a C–C single bond. The slight twisting of the four-membered ring (6.4°) is less than the range of 18.5–27° observed for related $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-alkene})$ complexes.[4,5,11]

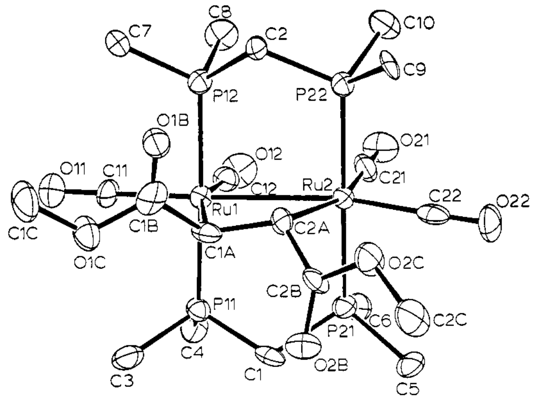
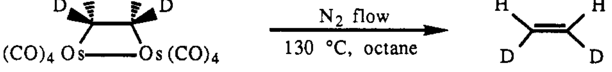


Figure 1. View of $Ru_2(dmpm)_2(CO)_4[\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(H)_2(CO_2CH_3)_2]$ showing the atom labels. Thermal ellipsoids were drawn at the 50% probability level. Selected distances (Å): Ru1–Ru2, 2.920 (2); Ru1–C1A, 2.25 (1); Ru2–C2A, 2.258 (9); C1A–C2A, 1.51 (1). Selected angles (deg): Ru1–C1A–C2A, 107.7 (7); Ru2–C2A–C1A, 107.9 (8); C1A–Ru1–Ru2, 71.3 (3); C2A–Ru2–Ru1, 71.6 (3). Twist angle (the angle between planes defined by C1A–Ru1–Ru2 and C2A–Ru2–Ru1): 6.4°.

In 1987, Norton and co-workers reported that the extrusion of ethylene from $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_4)$ occurred by a concerted mechanism:[10]



In contrast to their results, the observation that both the cis and trans alkenes react with 1 to give the same trans-substituted product proves that, in this system, addition of the olefin must be a stepwise process. Somewhere along the reaction pathway free rotation must be allowed about the C–C double bond, enabling steric interactions to direct the chemistry toward the trans product. Takats has reported that photolysis of benzene solutions containing $Os_3(CO)_{12}$ and dimethyl maleate resulted in mono- and binuclear complexes of both the cis and trans alkenes.[11]

Further investigations of this system have shown the entire reaction to be a reversible process. Simply bubbling CO (1 atm) through a solution of 2 at 25 °C resulted in loss of dimethyl fumarate and regeneration of 1. Scheme I shows the simplest view of the mechanism based on our current data.

The presence of the ester functional groups on the olefin will stabilize the negative charge in the zwitterionic in-

---

(2) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.
(3) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339.
(4) Norton, J. R.; Motyl, K. M.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325.
(5) Takats, J.; Burke, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 4092.
(6) Bergman, R. G.; Theopold, K. H. *Organometallics* **1982**, *1*, 1571.
(7) Vioget, P.; Bonivento, M.; Roulet, R.; Vogel, P. *Helv. Chim. Acta* **1984**, *67*, 1630.
(8) Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25.
(9) Poë, A. J.; Sekhar, C. V. *J. Am. Chem. Soc.* **1986**, *108*, 3673.
(10) Norton, J. R.; Hembre, R. T.; Scott, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 3468.
(11) Takats, J. *Polyhedron* **1988**, *7*, 931.
(12) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1989**, *8*, 2866.
(13) IR (cm^{-1}, toluene): 1979 (m), 1949 (s), 1919 (m), 1894 (w), 1661 (w). ^1H NMR (ppm, C_6D_6): 1.10 (d, J_{HP} = 7 Hz, Me), 1.17 (d, J_{HP} = 7 Hz, Me), 1.35 (d, J_{HP} = 7 Hz, Me), 1.55 (d, J_{HP} = 7 Hz, Me), 1.50 (m, RuC*H*), 2.45 (m, CH_2), 3.63 (s, OCH_3), 3.9 (m, CH_2). ^{13}C NMR (ppm, CD_2Cl_2): 7.3 (s, br, Ru*C*H), 17.7 (m, Me), 20.7 (m, Me), 23 (m, Me), 39.4 (quintet, J_{CP} = 11.5 Hz, CH_2), 49.8 (s, CO_2CH_3), 185.9 (s, CO_2CH_3), 197 (t, J_{CP} = 8.6 Hz, *C*O), 212 (q, J_{CP} = 6.4 Hz, *C*O).

(14) X-ray diffraction data for $Ru_2C_{27}H_{44}P_4O_8$: fw 822.67; ρ_{calc} = 1.580 g cm^{-3}; crystal system monoclinic; space group $P2_1/n$ (No. 14); T = −88 °C; a = 11.432 (6) Å, b = 20.830 (9) Å, c = 14.675 (6) Å, β = 98.19 (3)°; V = 3459 (5) Å^3; Z = 4; μ = 10.80 cm^{-1} (empirical correction applied); radiation Mo Kα; scan range 0–48°; reflections collected 5897, unique reflections 5590 with $I > 3.00\sigma(I)$; R = 0.057; R_w = 0.074.

378 *Organometallics* 1991, *10*, 378-380

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 $Os_2(CO)_8(\mu$-η^1:η^1-$C_2H_2D_2)$,[10] and we believe it is less likely to occur in this electron-rich (phosphine)ruthenium case.

^{1}H 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.

Acknowledgment. This research was supported by a grant from the National Science Foundation (Grant No. CHE-8714326).

Registry No. 1, 123810-59-3; 2, 131322-71-9; 2·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.

---

[15] Gjaldbaek, J. C. *Acta Chem. Scand.* 1952, *6*, 623.

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

Ming-Chou Chen, Yi-Jong Tsai, Chun-Ting Chen, Ying-Chih Lin,* Tian-Wen Tseng,
Gene-Hsiang Lee, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Received September 27, 1990

Summary: The ketene complex $[Cp(CO)_2W]_2(\mu$-$CH_2CO)(\mu$-$CO)$ (Cp = η^5-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 = η^5-C_5H_5) leads to the dinuclear methylene complex $[Cp(CO)_2Ru]_2(\mu$-$CH_2)$, 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 $\{Cp(CO)_2[P(OMe)_3]W\}_2(\mu$-$CH_2)$ (**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 ^{1}H 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 ^{1}H NMR spectrum, the CH_2 protons of **2b** appear as a triplet signal, coupled with $P(OMe)_3$ (J_{P-H} = 5.1 Hz), at δ 2.34.[5] A triplet ^{13}C signal with J_{P-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 $[Cp(CO)LW]_2(\mu$-$CH_2CO)(\mu$-$CO)$ (**3b**)[4] in 100% NMR

---

[1] (a) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* 1983, *105*, 1679. (b) Lin, Y. C. *J. Chin. Chem. Soc.* 1985, *32*, 295. (c) Doherty, N. M.; Fildes, M. J.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1986, 1355. (d) Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* 1981, *215*, C30. (e) Akita, M.; Kondoh, A.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* 1986, 1296.

[2] (a) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* 1989, *111*, 1319. (b) Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* 1989, *8*, 8.

[3] (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 117. (b) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, *20*, 159. (c) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* 1988, *28*, 1. (d) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* 1983, *105*, 4104; 1984, *106*, 4783. (e) Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* 1989, *111*, 7279. (f) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* 1985, *107*, 254, 3541. (g) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* 1989, *111*, 3079. (h) Ewing, P.; Farrugia, L. J. *Organometallics* 1988, *7*, 871. (i) Casey, C. P.; O'Connor, J. M. *J. Am. Chem. Soc.* 1983, *105*, 2919. (j) Puddephatt, R. J. *Comments Inorg. Chem.* 1982, *2*, 69. (k) Bassner, S. L.; Geoffroy, G. L.; Rheingold, A. L. *Polyhedron* 1988, *7*, 791. (l) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* 1987, *6*, 2207.

[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]

0276-7333/91/2310-0378$02.50/0