Transfer and coupling of zirconocene-bound alkenyl ligands. An alternative route to (s-trans-.eta.4-conjugated diene)ZrCp2 complexes

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We speculate that the two-electron character of eq 1 derives from creation of a single metal–metal bond and structural rearrangement within the binuclear unit upon forming the oxidized product. Complex 2 (R = *t*-Bu) is reported[6] to have an Mo–Mo distance of 2.98 Å and an acute Mo–S–Mo bridge angle of ca. 74°. These facts are consistent with the presence of a single metal–metal bond in $Mo_2(CO)_8(SR)_2$ to produce an 18-electron configuration about each Mo. $[Mo_2(CO)_8(SR)_2]^{2-}$ satisfies the 18-electron rule without a metal–metal bond and is expected to have a substantially different $Mo_2(SR)_2$ core structure.[22] The related 18-electron phosphido-bridged complexes $Fe_2(CO)_6(PPh_2)_2$ and $[Fe_2(CO)_6(PPh_2)_2]^{2-}$ exhibit remarkably distinct core structures,[23,24] yet undergo reversible two-electron transfer ($E_{1/2}$ = –1.26 V in MeCN).[25] We believe the $Mo_2(SR)_2$ and $Fe_2(PPh_2)_2$ complexes share a similar phenomenological explanation[23,25] of their electrochemical behavior in which formation or cleavage of a metal–metal single bond coupled with structural rearrangement in a bridged bimetallic center leads to simultaneous transfer of two electrons. This behavior is a marked contrast to the stepwise transfer of single electrons that is commonly observed in strongly coupled bi- and polynuclear complexes.[26]

Additional interesting chemistry associated with the $Mo_2(SR)_2$ centers is illustrated by the remaining voltammetric traces in Figure 1. In Figure 1b, a small oxidation wave (E_{pa} = –0.54 V) is observed prior to the major oxidation of 1 in MeCN. This wave is quenched when a voltammogram is run under CO, but the corresponding cathodic peak (E_{pc} = –0.59 V) is still apparent (Figure 1c). This cathodic peak and a more negative one (E_{pc} = –0.82 V) are observed when a voltammogram of 2 is run under CO (Figure 1d). The –0.82-V peak is assigned to reduction of $Mo_2(CO)_6(MeCN)_2(SR)_2$ based on a voltammogram of 3 in the absence of CO (Figure 1e). In keeping with the chemistry of Scheme I, we attribute these observations to successive replacement of CO by MeCN in the Mo(I) oxidation state and assign the cathodic peaks at ca. –0.4, –0.6, and –0.8 V to reduction of $Mo_2(CO)_8(SR)_2$, $Mo_2(CO)_7(MeCN)(SR)_2$, and $Mo_2(CO)_6(MeCN)_2(SR)_2$, respectively. Purging with CO in MeCN does not completely reverse these reactions (Figure 1c,d). In contrast to Mo(I), the Mo(0) species display a greater affinity for CO and are less susceptible to solvolytic reactions. The small anodic wave at –0.54 V (Figure 1b), which we attribute to oxidation of $[Mo_2(CO)_7(MeCN)(SR)_2]^{2-}$, is the only evidence of Mo(0) solvolysis; this artifact is removed by purging briefly with CO (Figure 1c). Furthermore, CV of 2 or 3 in the presence of CO (Figure 1d) exhibits no anodic waves in conjunction with the cathodic peaks at –0.6 and –0.8 V, only the reoxidation of 1 at –0.35 V. Thus, the MeCN-substituted species appear to be rapidly carbonylated upon electrochemical reduction to Mo(0).

Finally, we note that continued purging of 1 with CO results in complete loss of the reversible couple at –0.40 V and generation of an irreversible oxidation wave at +0.17 V (Figure 1c,f). When the solution in Figure 1f is bubbled with N_2, the original CV (Figure 1b) is restored. This behavior is attributed to the reversible formation of two equivalents of $[Mo(CO)_5(SR)]^-$ (4) (Scheme I), whose irreversible oxidation occurs at +0.17 V. We have not isolated salts of these pentacarbonyl anions, but their existence is reasonable because $[Mo(CO)_5(SH)]^-$ is a well-characterized species.[7] It is interesting that the SH species apparently[7] does not decarbonylate to $[Mo_2(CO)_8(SH)_2]^{2-}$, whereas the SR derivatives readily convert to 1 upon purging with inert gas.

Acknowledgment. This research was supported by grants from the USDA/SEA Competitive Research Grants Office (59-2394-1-1-675-0) to J.W.M. and W.E.N. and the National Science Foundation (CHE-8211694) to F.A.S.

Registry No. 1 (R = *t*-Bu), 90029-14-4; 1 (R = Ph), 90029-16-6; **2** (R = *t*-Bu), 77593-56-7; **2** (R = Ph), 90029-17-7; **3** (R = *t*-Bu), 90029-18-8; **3** (R = Ph), 90029-19-9; **4** (R = *t*-Bu), 90029-20-2; **4** (R = Ph), 90029-21-3; $Mo(CO)_6$, 13939-06-5; $Mo_2(CO)_7(MeCn)(SBu\text{-}t)_2$, 90029-22-4; $Mo_2(CO)_7(MeCn)(SPh)_2$, 90029-23-5; $[Mo_2(CO)_7(MeCN)(SBu\text{-}t)_2]^{2-}$, 90029-24-6; $[Mo_2(CO)_7(MeCn)(SPh)_2]^{2-}$, 90029-25-7; I_2, 7553-56-2; $[Et_4N]BH_4$, 17083-85-1.

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[22] Structural characterization of 1 is planned to determine the Mo–Mo distance and other appropriate dimensions in the $Mo_2(SR)_2$ core.

[23] Ginsberg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

[24] The neutral complex contains a single metal–metal bond with Fe–Fe = 2.623 Å and an Fe–P–Fe bridge angle of 72°, whereas the dianion exhibits a nonbonding Fe–Fe distance of 3.630 Å and an Fe–P–Fe angle of 106°.

[25] Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

[26] (a) Ott, V. R.; Swieter, D. S.; Schultz, F. A. *Inorg. Chem.* **1977**, *16*, 2538. (b) Schultz, F. A.; Ott, V. R.; Rolison, D. S.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *Ibid.* **1978**, *17*, 1758. (c) Wenk, S. E.; Schultz, F. A. *J. Electroanal. Chem.* **1979**, *101*, 89. (d) Gagne', R. R.; Koval, C. A.; Smith, T. J.; Cimolino *J. Am. Chem. Soc.* **1979**, *101*, 4571. (e) Morrison, M. M.; Sawyer, D. T. *Ibid.* **1977**, *99*, 257. (f) Salmon, D. J.; Walton, R. A. *Ibid.* **1978**, *100*, 991. (g) Duncan, J.; Malinski, T.; Zhu, T. P.; Hu, Z. S.; Kadish, K. M.; Bear, J. L. *Ibid.* **1982**, *104*, 5507. (h) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *Ibid.* **1983**, *105*, 4950.

Transfer and Coupling of Zirconocene-Bound Alkenyl Ligands. An Alternative Route to (*s-trans*-η^4-Conjugated diene)$ZrCp_2$ Complexes

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Summary: Dibenzylzirconocene (**3a**) and (*s-trans*-η^4-*trans,trans*-1,4-diphenylbutadiene)zirconocene (**5**) are formed rapidly upon irradiation of benzyl(β-styryl)zirconocene (**2a**) in benzene at ambient temperature. Trapping and crossover experiments using benzyl chloride and (β-styryl)zirconocene chloride and the kinetic influence of added "moderators" trimethyl phosphite and triphenylphosphine in addition to ESR experiments point to a radical reaction mechanism for alkenyl group transfer. Transfer and coupling of alkenyl ligands can also be initiated in a dark reaction when starting from methyl(β-styryl)zirconocene (**2b**).

The synthetic procedures presently applied for the preparation of the unique (*s-trans*-η^4-conjugated diene) group 4 metallocene complexes **5** have in common that they use an intact 1,3-diene as a starting component.[2,3b] We have now found an example where the preparation of **5** is achieved in a rather different fashion. The compound

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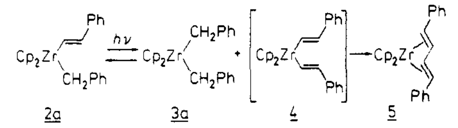
[1] (a) Ruhr-Universität Bochum. (b) Universität Essen, ESR experiments.

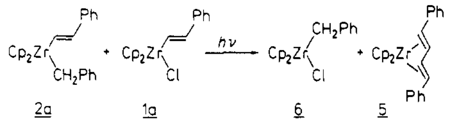
(*s-trans*-η^4-*trans,trans*-1,4-diphenylbutadiene)zirconocene has been obtained by forming the conjugated diene ligand at the transition-metal center by CC coupling of alkenyl ligands starting from benzyl(β-styryl)zirconocene (**2a**).

2a was obtained by hydrozirconation of phenylacetylene (to yield **1a**) and subsequent treatment with benzylmagnesium chloride. Upon photolysis of **2a** (0.5 M in benzene, HPK 125, Pyrex filter, $\tau_{1/2} \approx 2$ h) two new organometallic products, dibenzylzirconocene (**3a**)[3a] and (*s-trans*-η^4-*trans,trans*-1,4-diphenylbutadiene)zirconocene (**5**),[3b] are found in an equimolar ratio. We assume that photolysis of benzyl(β-styryl)zirconocene leads to a mixture of equilibrating σ complexes **2a** $\rightleftarrows$ **3a** + **4**, which is shifted in favor of the disproportionation products **3a** and **4** by the irreversible coupling reaction of the bis(β-styryl)zirconocene to form the (diene)zirconocene π complex **5**.



Several observations have been made that might help us to understand this reaction. Formation of the disproportionation products **3a** and **5** is no longer observed if **2a** is irradiated in the presence of benzyl chloride (~2-fold molar excess). A 1:1 mixture of (β-styryl)zirconocene chloride (**1a**) and bibenzyl (**8**) is formed almost quantitatively.

Upon irradiation of an equimolar mixture of **2a** and **1a** both starting materials are consumed at identical rates. Again, the (diene)zirconocene complex **5** is obtained. However, the expected individual disproportionation products, zirconocene dichloride **7** and **3a**, are not found. The exclusive formation of the crossover product benzylzirconocene chloride (**6**)[3c] is observed, instead.



The overall rate of the photochemically induced disproportionation of **2a** is influenced by certain reagents that appear not to take part in the net reaction. Thus, in the presence of trimethyl phosphite (~2 equiv/Zr) or triphenylphosphine the rate of formation of **3a** and **5** is substantially reduced.[4] The ESR spectrum of a transient zirconium(III) species, $Cp_2Zr(CH_2Ph)(P(OCH_3)_3)$ (**11a**) ($a(^{31}P) = 28.3$ G (1 P), $a(^1H) = 4.3$ G (2 H), $g_{iso} = 1.987$; see Figure 1), can be observed if the irradiation (Hanovia 977B-1, 360-nm filter) of a sample of **2a** with trimethyl phosphite is carried out in the cavity of an ESR spectrometer.[5] This assignment is supported by an independent photochemical generation of **11a** from **3a**. Analogously, Cp_2ZrCH_3 (**10b**), photochemically generated from dimethylzirconocene (**3b**)[6b] is trapped by trimethyl phosphite and its $P(OCH_3)_3$ adduct observed by ESR spectroscopy[5,6] ($a(^{31}P) = 28.3$ G (1 P), $a(^1H) = 7.6$ G (3 H), $g_{iso} = 1.989$, see Figure 1).

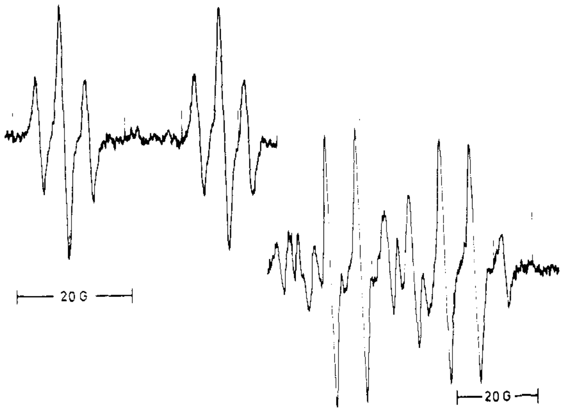
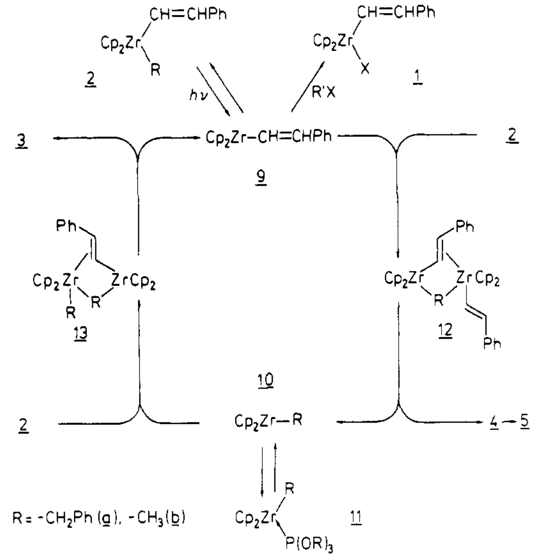


Figure 1. ESR spectra of $Cp_2ZrCH_2Ph[P(OCH_3)_3]$ (**11a**) (upper left, $g = 1.987$, from irradiation of **2a** in benzene at ambient temperature) and $Cp_2ZrCH_3[P(OCH_3)_3]$ (**11b**) ($g = 1.989$).

Scheme I



Our observations clearly indicate a radical reaction mechanism for the alkenyl ligand transfer. However, a reaction course avoiding the intermediacy of organic free radicals is implied from the experimental material. We propose that a reaction sequence leading to **5** can be initiated by the formation of an "organometallic radical", the zirconium(III) complex **9**. Immediate termination of the reaction cycle occurs if **9** is trapped, e.g., by benzyl chloride to form **1a** and **8**. The participation of **10a** as a second actively involved "zirconium radical" is inferred from the kinetic influence of added phosphine and phosphite in connection with the ESR experiment. **10a** appears not to be a primary product but is formed later in the reaction cycle (Scheme I). A direct participation of alkenylzirconium(IV) complexes in the course of the alkenyl

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(2) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.*, in press and references cited therein. Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462. Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Ibid.* **1982**, *1*, 388.

(3) (a) **3a**: Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, 654. (b) **5**: Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344; Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300. (c) Treatment of **3a** with $PhICl_2$ yielded **6**: Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419. (d) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

(4) Remaining fraction (C/C_0) of the starting material **2a** after (20/60/130/250) min of irradiation: reference (0.86/0.68/0.46/0.30); $P(OCH_3)_3$ (0.97/0.91/0.83/0.76); PPh_3 (0.92/0.86/0.81/0.74). Added amines do not appear to slow down the disproportionation rate of **2a**: $N(C_2H_5)_3$ (0.83/0.62/0.42/0.27); $PhN(CH_3)_2$ (0.85/0.63/0.47/0.30).

(5) (a) Williams, G. M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1122. (b) Schore, N. E.; Hope, H. *Ibid.* **1980**, *102*, 4251. (c) Hudson, A.; Lappert, M. F.; Pichon, R. *J. Chem. Soc., Chem. Commun.* **1983**, 374. (d) Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

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transfer linking **9** with **10a** is likely in view of our crossover experiment. As attractive intermediates we propose the binuclear (μ-alkyl)(μ-alkenyl)dizirconium(III, IV) complexes **12** and **13**, whose formation could be equally favorable as that of the previously described,[7] analogously structured mixed-valence Zr(II), Zr(IV) compounds $Cp_2Zr(\mu\text{-}CH{=}CHR)(\mu\text{-}X)ZrCp_2$.

The photolysis of methyl (β-styryl)zirconocene (**2b**) takes a similar reaction course. Surprisingly, the disproportionation of **2b** can apparently also be initiated in a dark reaction. We conclude this from the observation that we have isolated **2b** only in ~10% yield from reactions of **1a** with methylmagnesium bromide but have recovered dimethylzirconocene (**3b**)[3d] and **5** in 75% and 60% isolated yields, respectively, after ambient temperature workup.

The fact that transfer as well as coupling of alkenyl ligands at the Cp_2Zr unit can be initiated under such mild reaction conditions is rather surprising and unexpected. It may be of importance in view of the many useful applications the readily available alkenyl zirconocene complexes[8] have found in organic synthesis.[9-11]

Acknowledgment. Financial support by the Fonds der Chemischen Industrie, Frankfurt/Main, West Germany (grant to G. E), is gratefully acknowledged.

Registry No. **1a**, 81939-33-5; **2a**, 87737-52-8; **2b**, 87737-51-7; **3a**, 37206-41-0; **3b**, 12636-72-5; **5**, 84142-89-2; **6**, 78163-00-5; **10b**, 59954-62-0; **11a**, 89959-00-2; **11b**, 89959-01-3; $P(OCH_3)_3$, 121-45-9; PPh_3, 603-35-0; phenylacetylene, 536-74-3; benzyl chloride, 100-44-7; methyl bromide, 74-83-9.

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[8] (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373. (b) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (c) Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. *Ibid.* **1975**, *97*, 3851.

[9] (a) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (b) Matsushita, H.; Negishi, E. *Ibid.* **1981**, *103*, 2883. (c) Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027. (d) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521 and references cited therein.

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[11] (a) Negishi, E.; Van Horn, D. E.; Yoshida, T.; Rand, C. L. *Organometallics* **1983**, *2*, 563. (b) Yoshida, T.; Negishi, E. *J. Am Chem. Soc.* **1981**, *103*, 4985. (c) Van Horn, D. E.; Negishi, E. *Ibid.* **1978**, *100*, 2252.

Additions and Corrections

Richard D. Adams, Donald F. Foust, and Pradeep Mathur: Cluster Synthesis. 3. The Role of Sulfido Ligands in the Synthesis of High Nuclearity Metal Carbonyl Cluster Compounds. The Crystal and Molecular Structures of $Os_4(CO)_{12}(\mu_3\text{-}S)$ and $Os_7(CO)_{19}(\mu_4\text{-}S)$. **1983**, *2*, 990.

The correct IR spectrum of $Os_7(CO)_{19}(\mu_4\text{-}S)$ is as follows: ν(CO) (in CH_2Cl_2) 2074 (s), 2066 (s), 2059 (s), 2033 (sh), 2031 (m), 2013 (w), and 2006 (w) cm^{-1}.

Manny Hillman and Åke Kvick: Structural Consequences of Oxidation of Ferrocene Derivatives. 1. [0.0]-Ferrocenophanium Picrate Hemihydroquinone. **1983**, *2*, 1780.

The name of one of the authors is Åke Kvick and not Åbe Kvick. Table I has about half of the lines misaligned. The corrected part is given below. In the Experimental Section, the sentence beginning "Intensities were collected" should read: "Intensities were collected by using θ–2θ scans and were corrected for Lorentz and polarization effects."

reflctns collected	8025
reflctns used ($F > 3\sigma$)	5245
parameters refined	463
scan width	$0.75 + 0.35 \tan\theta$
$R(F) = \Sigma\lvert F_o - F_c\rvert/\Sigma\lvert F_o\rvert$	0.039
$R_w(F) = \Sigma\lvert F_o - F_c\rvert w^{1/2}/\Sigma\lvert F_o\rvert w^{1/2}$ ($w = 1/(\sigma^2(F) + 0.0005F^2)$)	0.038
max shift/error (non-H)	0.07
mas shift/error (H)	0.12
residual electron density, e nm^{-3}	510

Robert T. Paine, Eileen N. Duesler, and David C. Moody: Synthesis and Structure of a Supersandwich Pentanuclear Uranium(IV) Complex, $U\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_4$. **1982**, *1*, 1097.

Typographical errors appear in Table S-3 of the supplementary material. Two lines should read as follows:

	x/a	y/b	z/c
O(19)	−0.1177 (6)	0.2962 (7)	0.0883 (5)
CA(1)	−0.1460 (9)	−0.0409 (11)	−0.0443 (8)

Satoru Masamune, Shu Murakami, James T. Snow, Hiromi Tobita, and David J. Williams: Molecular Structure of Tetrakis(2,6-diethylphenyl)disilene. **1984**, *3*, 333.

On page 333, the following words are missing between the fourth and fifth lines of the first paragraph of text: "...recent years crystalline tetramesityl- and tetrakis(2,6-dimethylphenyl)disilene (1 and 2), respectively.[3] Unfortu-".

Anthony Tsarbopoulos and John Allison: Chemistry of Co^+ and Co(ligand)$^+$ with Mono- and Bisubstituted *n*-Butanes in the Gas Phase: Using a Simple "Ligand Competition" Model and Collision-Induced Dissociation Analysis To Provide Insights into Product Structures. **1984**, *3*, 86.

In Table II, the reaction enthalpies (kcal/mol) for the process $HO(CH_2)_4X \rightarrow C_4H_6 + H_2O + HX$ (line 6) *should* read 10.4 (X = F), 18.1 (X = Cl), and 19.5 (X = Br). Thus, the results reported in Table I suggest that $D(Co^+\text{–}C_4H_6) > 43.3$ kcal/mol, *not* >85.9 kcal/mol as stated in the abstract and on p 94.