ppm vanishes, probably as the result of spin saturation transfer. The signal at 3.11 ppm then appears as a singlet while the signal at 4.43 ppm remains a doublet.[14] These data[14a] indicate that the signal at 8.59 ppm is coupled to that at 3.11 ppm. Moreover, they show that the rate of the intramolecular exchange reaction is less that 150 Hz, being the chemical shift difference in Hz between the two imine signals. Unfortunately, temperature-dependent measurements are severely hindered by decomposition above 30 °C and precipitation below −10 °C. Evidently, more experiments are needed to get a clear picture of the dynamic behavior of **2** in solution.

Generally for a reaction of a metalate (M^-) with a metal halide, several reaction routes have to be considered.[15] Until now, reactions of M^- with $MnBr(CO)_3(R\text{-DAB})$ have yielded heterodinuclear MnM–R-DAB complexes only, which results can be interpreted on basis of simple substitution reactions.[4,16] In the present reaction, however, only homodinuclear compounds are obtained. A likely reaction route[17] involves an electron transfer mechanism and is outlined in eq 2 and 3. The $[Mn(CO)_3(t\text{-Bu-DAB})]\cdot$

$$MnBr(CO)_3(R\text{-DAB}) + e^- \xrightarrow[R\,=\,t\text{-Bu}]{-Br^-} [Mn(CO)_3(R\text{-DAB})]\cdot \rightarrow 1 + 2 \quad (2)$$

$$[CpFe(CO)_2]^- - e^- \rightarrow [CpFe(CO)_2]\cdot \rightarrow [CpFe(CO)_2]_2 \quad (3)$$

radical, which possibility of existence has been proven in 2-Me-THF at 230 K, has spin density on Mn (a_{Mn} = 9.53 G) and on the imine N and C atoms (a_N = 7.40 and a_H = 4.75 G).[18] Mn–Mn coupling, followed by elimination of one *t*-Bu-DAB ligand and coordination of the two imine bonds of the other, then may yield **1**, while C–C coupling may yield the IAE complex **2**.[19] It seems not possible to convert **2** into **1** (or vice versa) which excludes the possibility that **2** is formed first via a coupling reaction after which **1** is formed as the result of an elimination reaction.

The following conclusions can be drawn from these results: i, *t*-Bu-DAB can act as an eight-electron donor ligand; ii, *t*-Bu-IAE formation is possible on Mn, probably via an electron-transfer mechanism;[19] iii, *t*-Bu-IAE can act as an asymmetrically bridging, eight-electron donor.[20]

Acknowledgment. We thank the Netherland Foundation for Chemical Research (S.O.N.) and the Netherland Organization for Pure Research (Z.W.O.) for their financial support.

Registry No. 1, 96481-47-9; 2, 96455-74-2; $[CpFe(CO)_2]_2$, 12154-95-9; $[CpFe(CO)_2]^-$, 12107-09-4; $[Mn(CO)_3(t\text{-Bu-DAB})]\cdot$, 96455-75-3; $MnBr(CO)_3(t\text{-Bu-DAB})$, 70749-13-2.

Supplementary Material Available: Tables of atomic coordinates, all geometric data, anisotropic thermal parameters, and structure factors (21 pages). Ordering information is given on any current masthead.

---

[14] (a) Alternatively, irradiation of the doublet at 4.43 ppm causes disappearance of the signal at 3.11 ppm, while the signal at 8.04 ppm appears as a singlet and that at 8.59 ppm still as a doublet. This indicates that the signal at 4.43 ppm is coupled to that at 8.04 ppm. (b) For an analogous spin saturation transfer in a coupled system see, e.g., Fung, B. M. *J. Chem. Phys.* **1967**, *47*, 1409.

[15] (a) Dessy, R. E.; Weissman *J. Am. Chem. Soc.* **1966**, *88*, 5124. (b) Dessy, R. E.; Weissman, *Ibid.* **1966**, *88*, 5129.

[16] Interestingly, however, is that when the R-DAB containing metalate $[Mo(CO)_4(R\text{-DAB})]^-$ is oxidized by $MnBr(CO)_3(R'\text{-DAB})$, the C–C coupled product $Mo_2(CO)_6(R\text{-IAE})$ is obtained after an oxidative CO elimination, together with a dinuclear Mn_2 species.[3a] This oxidation reaction closely resembles the present reaction with $[Mo(CO)_4(R\text{-DAB})]^-$ probably playing the electron-donating role of $[CpFe(CO)_2]^-$, and it seems therefore worthwhile to characterize carefully the Mn_2 product obtained in this reaction.[3a]

[17] Another possible reaction route involves a substitution reaction, yielding a $(t\text{-Bu-DAB})(CO)_3MnFeCp(CO)_2$ complex, followed by a redistribution reaction[15] that affords the $[CpFe(CO)_2]_2$ dimer and a $[Mn(CO)_3(t\text{-Bu-DAB})]^-$ anion. The latter anion may react with the starting complex to yield finally **1** and **2**.

[18] Kokkes, M. W.; Stufkens, D. J.; Oskam, A., to be submitted for publication.

[19] It is interesting to note that R-IAE formation in the reaction of R-DAB with Et_2Zn proceeds via a $[EtZn(R\text{-DAB})]\cdot$ radical.[12]

[20] Until now, R-IAE formation has only been observed on Mo, Ru,[3a] and Zn,[12] and in all complexes so far, R-IAE has acted as a symmetrically bridging, 10-electron-donating ligand.

A Novel Rearrangement of α-Zirconocenyl Thioethers

Eric A. Mintz,* A. Steven Ward, and Douglas S. Tice

Department of Chemistry, West Virginia University
Morgantown, West Virginia 26506-6045

Received November 26, 1984

Summary: The thermolysis of $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3]$ (**2**) in toluene solution follows first-order kinetics to give $(\eta^5\text{-}C_5H_5)_2Zr(SCH_3)[CH(Si(CH_3)_3)C_6H_5]$ (**4**), whereas under similar conditions $(\eta^5\text{-}C_5H_5)_2ZrX[CH(Si(CH_3)_3)SCH_3]$, X = Cl, CH_3, and $CH_2C_6H_5$, were found to be unreactive. A mechanism is put forward to account for the rearrangement of complex **2** to **4**, which also accounts for the observed lack of this reactivity pattern for $(\eta^5\text{-}C_5H_5)_2ZrX[CH(Si(CH_3)_3)SCH_3]$ under these conditions. Further thermolysis of complex **4** produces benzyltrimethylsilane and an as yet unidentified yellow precipitate.

Early-transition-metal alkyl complexes have been shown in recent years to exhibit a rich and varied chemistry. As a part of our investigation of the effect of α-heteroatom substituents on the reactivity of alkyl complexes of the early transition metals we have investigated the thermolysis of α-zirconocenyl thioethers.[1] Preliminary results of this study are reported here. The high oxygen affinity of Zr(IV) in Cp_2ZrR_2 and $Cp^*{}_2ZrR_2$ derivatives has been found in recent years to figure prominently in zirconocene chemistry. The reactivity of α-zirconocenyl ethers[2] and zirconocene-η^2-acyl,[3] -η^2-ketone,[2b,3c,4] and -η^2-ketene complexes[5] are dominated by the electrophilic nature of zirconium. We have found that the reactivity of α-zirconocenyl thioethers is sufficiently attenuated that these complexes are indefinitely stable in the dark at room temperature in contrast to the analogous α-zirconocenyl ether $Cp_2ZrCl[C(C_6H_5)_2OCH_3]$ which Erker et al.[2] have reported to be unstable with a half-life of 48 h at room temperature.

Many of these new α-zirconocenyl thioethers require prolonged heating in solution to undergo significant de-

---

[1] (a) Mintz, E. A.; Ward, A. S. 15th Central Regional Meeting of the American Chemical Society, Oxford, OH, May 1983; American Chemical Society: Washington, DC, 1983; Abstract No. 137. (b) Mintz, E. A.; Ward, A. S.; Lindeman, J. A. 186th National Meeting of the American Chemical Society: Washington, DC, August 1983; American Chemical Society: Washington, DC, 1983; Abstract No. INOR 339.

[2] (a) Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* **1981**, *22*, 1379–1382. (b) Erker, G.; Rosenfeldt, F. *Tetrahedron* **1982**, *38*, 1285–1291.

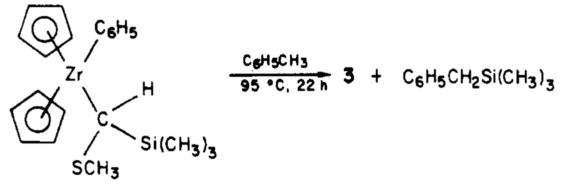
[3] (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605–606. (c) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29–42. (d) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747–1748. (e) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109.

[4] Rosenfeldt, F.; Erker, G. *Tetrahedron Lett.* **1980**, *21*, 1637–1640.

[5] (a) Straus, J. E.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499–5500. (b) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiera, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070.

0276-7333/85/2304-1308$01.50/0

composition. For example we have found that $Cp_2ZrCl[CH(Si(CH_3)_3)SCH_3]$[6] (1) is stable indefinitely at room temperature in the solid state and has a half-life in toluene at 100 °C of greater than 1 month. In contrast to the thermolysis of complex 1, thermolysis of $Cp_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3]$ (2)[8] at 95 °C for 22 h produces an as yet unidentified insoluble yellow organometallic complex (3) and benzyltrimethylsilane.[9] The origin of the benzyltrimethylsilane formed was of particular interest to us. In an attempt to determine the mechanism of benzyltrimethylsilane formation, the thermolysis of 2 was carried out in $C_6D_5CD_3$ in an NMR tube at 95 °C and ^1H NMR spectra were recorded periodically during the course of the reaction. At this temperature we observed two new cyclopentadienyl resonances which we attribute to a new zirconocene derivative $Cp_2Zr(SCH_3)[CH(Si(CH_3)_3)C_6H_5]$ (4) (vide infra) initially appearing at approximately the same rate as the rate of disappearance of cyclopentadienyl resonances of 2, and then the resonances due to 4 disappeared at a slower rate while resonances due to benzyltrimethylsilane increased with the simultaneous formation of a yellow precipitate.

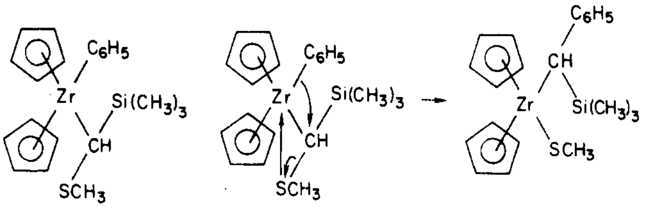


2

In order to follow the thermolysis of 2 and minimize the interference of the thermolysis of 4, the rearrangement of an 0.2 M solution of 2 was followed by ^1H NMR at a lower temperature (82 °C) in $C_6D_5CD_3$ in an NMR tube. Under these conditions we have found that 2 undergoes rearrangement to form complex 4 with a first-order rate constant of 8.14×10^{-6} s^{-1} (which corresponds to a free energy of activation for this rearrangement of 29.2 kcal/mol), while complex 4 undergoes decomposition only slowly under these conditions.

Preparative thermolysis of 2 at 82 °C in toluene for 5 days alllowed the formation and isolation of complex 4 (58% isolated yield) as the major organometallic product from this reaction which can be readily isolated upon proper workup.[11] We have found that complex 4 once isolated upon thermolysis in toluene at 100 °C produces 3 and benzyltrimethylsilane.[9]

Scheme I



2a 2b

In contrast to the η^1-(diphenylphosphino)methyl and (dimethylphosphino)methyl groups in $Cp_2Zr(X)CH_2PR_2$[12,13] the (thiomethyl)(trimethylsilyl)methyl group in complex 2 with its sterically less demanding thiomethyl group would be expected to bond as an η^2 four-electron ligand.[14] This η^2-bonding mode would be analogous to that reported in $CpMo(CO)_2(\eta^2\text{-}CH_2SCH_3)$[15] and the well-known (η^2-acyl)- and (η^2-iminoacyl)zirconocene complexes, $Cp_2Zr(X)COR$[3,16,17] and $Cp_2Zr(X)[C(NR)R']$,[17,18] respectively.

The methylene carbon in complex 2 would be expected to be susceptible to intramolecular nucleophilic substitution with anchimeric activation of the thiomethyl group by the neighboring Cp_2Zr.[20] This zirconium-activated electrophilic behavior of the α-carbon is analogous to that found for the acyl carbon in (η^2-acyl)zirconocene complexes.[3e,13,16,21] Complex 2 is thus "set up" to undergo thermally induced intramolecular nucleophilic attack (migration) of the phenyl group to the methylene with commensurate breaking of the C–S bond to produce com-

---

[6] Complex 1 was prepared by the dropwise addition of $Li[CH(Si(CH_3)_3SCH_3]$, prepared by treating $CH_3SCH_2Si(CH_3)_3$[7] (54.0 mol) in 30 mL of THF with 25.7 mL of 2.1 M *n*-butyllithium in hexane at room temperature for 4 h to Cp_2ZrCl_2 (51.4 mmol) in 100 mL of THF at −74 °C. The reaction mixture was allowed to warm to room temperature and allowed to stir overnight. After removal of the solvent under vacuum, the reaction mixture was extracted with toluene, the toluene was removed under vacuum and the residue was washed with pentane to give 16.1 g (80.3% yield) of 1, as a white microcrystalline solid: mp 113–114 °C dec; ^1H NMR (60 MHz, C_6D_6) δ 0.15 (9 H, s, $Si(CH_3)_3$), 1.20 (1 H, s, CH), 1.75 (3 H, s, SCH_3), 5.75 (5 H, s, Cp), 5.80 (5 H, s, Cp); $^{13}C\{^1H\}$ NMR (20 MHz, C_6D_6) δ 1.18 $(SiCH_3)_3$, 24.98 (SCH_3), 46.56 (CH), 109.30 (Cp), 111.25 (Cp). Anal. Calcd for $C_{15}H_{23}ClSSiZr$: C, 46.18; H, 5.94. Found: C, 46.07; H, 5.84.

[7] Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717–1720.

[8] Complex 2 was prepared by the dropwise addition of phenylmagnesium bromide (13.5 mmol) in 25 mL of ether to $Cp_2Zr(Cl)[CH(Si(CH_3)_3)SCH_3]$ (12.8 mmol) in 150 mL of ether at room temperature in the absence of light. After removal of the ether, the residue was extracted with pentane to yield 82.2% of 2 as a white, microcrystalline solid: mp 84–85 °C; ^1H NMR (60 MHz, C_6D_6) δ 0.15 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, s, CH), 1.60 (3 H, s, SCH_3), 5.45 (5 H, s, Cp), 5.60 (5 H, s, Cp), 7.1–7.4 (3 H, m Ar), 7.6–7.9 (2 H, m, Ar); $^{13}C\{^1H\}$ NMR (20 MHz, C_6D_6) δ 2.06 ($Si(CH_3)_3$), 25.72 (SCH_3), 36.29 (CH), 107.35 (Cp), 108.73 (Cp), 123.73 (*p*-Ar), 127.16 (*o*-Ar), 143.20 (*m*-Ar), 175.81 (*i*-Ar). Anal. Calcd for $C_{21}H_{28}SSiZr$: C, 58.41; H, 6.54. Found: C, 58.18; H, 6.53.

[9] Benzyltrimethylsilane identified by spectroscopic and GC/MS comparison with authentic sample[10] was formed in over 80% yield and was the only observed organic product in these thermolyses.

[10] Gilman, H.; Marshall, F. J. *J. Am. Chem. Soc.* **1949**, *71*, 2066–2069.

[11] Complex 2 (2.32 mmol) in 10 mL of toluene was heated at 82 °C for 5 days in the dark. The resulting reaction mixture was allowed to cool to room temperature and the solvent removed under vacuum. The resulting residue was extracted with pentane, and the solvent removed under vacuum to give a viscous oil. Low-temperature recrystallization from pentane gave 4 (1.34 mmoles, 58% yield) as a viscous oil: ^1H NMR (60 MHz, C_6D_6) δ 0.10 (9 H, s, $Si(CH_3)_3$), 2.18 (3 H, s, SCH_3), 2.24 (1 H, s, CH), 5.65 (5 H, s, Cp), 5.88 (5 H, s, Cp), 6.8–7.2 (5 H, m, C_6H_5); $^{13}C\{^1H\}$ NMR (20 MHz, C_6D_6) δ 3.19 ($Si(CH_3)_3$), 20.93 (SCH_3), 62.09 (CH), 111.06 (Cp), 101.15 (Cp), 120.67 (*p*-Ar), 128.15 (*o*,*m*-Ar), 152.32 (*i*-Ar). Anal. Calcd for $C_{21}H_{28}SSiZr$: C, 58.51; H, 6.54. Found: C, 58.06; H, 6.51.

[12] (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251–4253. (b) Schore, N. E.; Young, S. J.; Olmstead, M. M. *Organometallics* **1983**, *2*, 1769–1780.

[13] Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195–212.

[14] It has been suggested that the η^1 structure of the [(diphenylphosphino)methyl]zirconocene derivatives is due to unfavorable steric interactions, whereas it has been reported that for the model compound $Cp_2Zr(Cl)CH_2PH_2$, an extended Hückel MO calculation favors an η^2 structure; Hofmann, P.; Stauffert, P.; Schore, E. N. *Chem. Ber.* **1982**, *115*, 2153–2174.

[15] de Gil, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3751–3756.

[16] Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596–5598.

[17] The ground-state structure for (η^2-acyl)zirconocene complexes have been shown to have the oxygen in the inside position;[3] however the oxygen atom outside conformation has been shown to be close enough in energy to be chemically significant,[13,19] and in (η^2-iminoacyl)zirconocene complexes the nitrogen inside and outside conformations are close enough in energy to coexist at 25 °C.[18]

[18] Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35–C37.

[19] Hofmann, P.; Stauffert, P.; Tatsumi, K.; Nakamura, A.; Hoffmann, R. *Organometallics* **1985**, *4*, 404–406.

[20] This intramolecular nucleophilic substitution requires an η^2-S-outside conformation; however the structure of these complexes is yet to be determined. If the ground-state structure of complexes 2 are analogous to that of $Cp_2Zr(COR)R'$ and $Cp_2Zr[C(NR)R']$, the η^2-S-outside structure would be expected to be chemically accessible under our reaction conditions.[17]

[21] Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45–60.

plex 4 (Scheme I). An analogous rearrangement is implied along the reaction path to a zirconium-substituted indan formed by the addition of CO to 1,1-bis(η-cyclopentadienyl)-1-zirconaindan.[3e,21]

Upon heating 0.2 M solutions of the methyl and benzyl analogues of complex 2, $Cp_2ZrCH_3[CH(Si(CH_3)_3)SCH_3]$ (5) and $Cp_2ZrCH_2C_6H_5[CH(Si(CH_3)_3)SCH_3]$ (6), at 82 °C for ca. 1 week in $C_6D_5CD_3$, complexes 5 and 6 were found by NMR measurement to be less than 5% decomposed. In a control experiment under similar conditions complexes 5 and 6 were recovered in over 90% yield after 1 week in solution at 82 °C.[22] The greater propensity of complex 2 relative to complexes 5 and 6 to undergo rearrangement to form complex 4 is consistent with the mechanism in Scheme I and can be understood in terms of the greater migratory aptitude of a phenyl group, relative to the methyl and benzyl groups in nucleophilic migrations.[23] The rearrangement of 2 to 4 appears in this respect to reflect the well-known migratory aptitudes of the pinacole rearrangement.[23] To test this idea of a nucleophilic attack of the phenyl group on the α-carbon, the anisole derivative $Cp_2Zr(p\text{-}C_6H_4OCH_3)[CH(Si(CH_3)_3)SCH_3]$ (8)[22] was prepared and subjected to thermolysis as the anisole group is well-known to undergo nucleophilic migration faster than a phenyl group.[23] Complex 8 was found to undergo thermolysis to form $Cp_2ZrSCH_3[CH(Si(CH_3)_3)C_6H_4OCH_3]$ with first-order kinetics five times faster than the analogous rearrangement of complex 2.[22]

The α-thiomethyl group in these complexes not only imparts greater stability to these complexes than has been reported for α-zirconocenyl ethers but also opens up reaction pathways which are not available to other alkylzirconocene and -titanocene complexes bearing simple hydrocarbon ligands.[24]

The novel rearrangement reported here may shed light on another possible reaction pathway in the conversion of CO and H_2 to hydrocarbons. Further work is in progress to investigate this possibility as well as the importance of varying steric and electronic effects on this rearrangement.

Acknowledgment. We thank the National Science Foundation (Grant RII-8011453) and the West Virginia University Energy Research Center for generous support of this research.

---

[22] Mintz, E. A.; Tice, D. S., unpublished results.

[23] March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw-Hill: New York, 1968; p 788.

[24] (a) Waters, J. A.; Vickroy, V. V.; Mortimer, G. A. *J. Organomet. Chem.* **1971**, *33*, 41-52. (b) Bokel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 161-165. (c) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629-1634.

Reaction of Zirconocene Complexes with Phosphorus Ylides: Evidence for the Formation of $Cp_2Zr(C_6H_5)CHPPh_3$ from Diphenylzirconocene and CH_2PPh_3 by an Aryne Mechanism

Gerhard Erker,* Peter Czisch, Richard Mynott, Yi-Hung Tsay, and Carl Krüger

Max-Planck-Institut für Kohlenforschung
D-4330 Mülheim a.d. Ruhr, West Germany

Received March 22, 1985

Summary: The reactions of methylenetriphenylphosphorane with $[Cp_2Zr(H)Cl]_x$, $Cp_2Zr(CH_3)_2$, and $Cp_2Zr(C_6H_5)_2$ have been studied. At 60 °C methylene transfer from $CH_2{=}PPh_3$ to the hydridozirconocene chloride occurs producing methylzirconocene chloride and triphenylphosphine. In contrast to dimethylzirconocene, which turns out to be unreactive up to 170 °C, diphenylzirconocene at 80 °C reacts with the ylide to form $Cp_2Zr(C_6H_5)CHPPh_3$ (**1c**). This reaction proceeds through an (η^2-aryne)zirconocene intermediate as revealed by a labeling experiment. The $Cp_2Zr(C_6H_5)$-substituted ylide has been characterized by NMR spectra at various temperatures and an X-ray structure analysis. **1c** crystallizes in space group *Pbca* with a = 10.927 (1) Å, b = 17.998 (3) Å, c = 28.992 (2) Å, and Z = 8. The preferred conformation and a rather short Zr–C7 bond distance (2.157 (4) Å) indicate substantial π-interaction of the Zr–C(ylide) linkage.

Although π-conjugation accounts for the wealth of structures and chemical reactivities of organic compounds, it has been considered less important in inorganic chemistry.[1] However, conjugative effects in organometallic systems are attracting increasing attention.[2] Many of the unique stereoelectronic features observed for organometallic systems of electron-deficient early-transition-metal centers are caused by π-interaction across a rigid σ-framework. For example, partial multiple-bond character has been demonstrated both structurally and chemically for molecules involving Cp_2Zr–C, –O, –N, or –P linkages.[3]

Zirconocene-substituted ylides $Cp_2Zr(X)CHPPh_3$ (1) are most interesting substrates in this regard. $Cp_2Zr(Cl)CHPPh_3$ (1a) has been shown to exhibit a substantial Zr–C(ylide) double-bond character (bond distance = 2.15 Å; rotational barrier $\Delta G^{\ddagger}_{-95\,^\circ C}$ = 8.6 kcal/mol).[4]

1a has been prepared by the slow reaction of Cp_2ZrCl_2 with a large excess of methylenetriphenylphosphorane (2), the ylide serving as both a nucleophile and a base in subsequent second-order reaction steps.[4] In an attempt to improve this interesting synthetic sequence, we tried to change the intermolecular second reaction step into an intramolecular hydrogen abstraction from the ylide carbon atom. We had hoped to obtain the $Cp_2Zr(X)$-substituted ylides 1a–c (X = Cl, CH_3, C_6H_5) by the reaction of $CH_2{=}PPh_3$ with $[Cp_2Zr(H)Cl]_x$ (3), $Cp_2Zr(CH_3)_2$ (4), or $Cp_2Zr(C_6H_5)_2$ (5) and subsequent elimination of H_2, methane, or benzene, respectively. This led to the unexpected discovery of a new reaction type leading to 1c.

Hydridozirconocene chloride (3) does not react with 2 via an ylide addition/hydrogen abstraction reaction sequence. Instead a clean methylene-transfer reaction is observed at 60 °C, producing methylzirconocene chloride (7)[5] and triphenylphosphine in high yield. Apparently, by

---

[1] See, however: Chisholm, M. H. *Transition Met. Chem.* (Weinheim, Ger.) 1978, *3*, 321.

[2] See, e.g.: Herrmann, W. A.; Weichmann, J.; Küsthardt, U.; Schäfer, A.; Hörlein, R.; Hecht, C.; Voss, E.; Serrano, R. *Angew. Chem.* **1983**, *95*, 1019. Herrmann, W. A.; Hecht, C.; Ziegler, M. L.; Balbach, B. *J. Chem. Soc., Chem. Commun.* **1984**, 686. Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie: Weinheim, 1983.

[3] Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1. Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E.; *Organometallics* **1983**, *2*, 1555. Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 5510. Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1984**, *96*, 72. Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049.

[4] (a) Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289. (b) See also: Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207. Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980.

0276-7333/85/2304-1310$01.50/0