

## The Three-membered Metallacyclic Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}$ -substituted Dimethyl Ether

Gerhard Erker,<sup>\*a</sup> Ruger Schlund,<sup>b</sup> and Carl Kruger<sup>b</sup>

<sup>a</sup> *Institut fur Organische Chemie der Universitat Wurzburg, Am Hubland, D-8700 Wurzburg, Federal Republic of Germany*

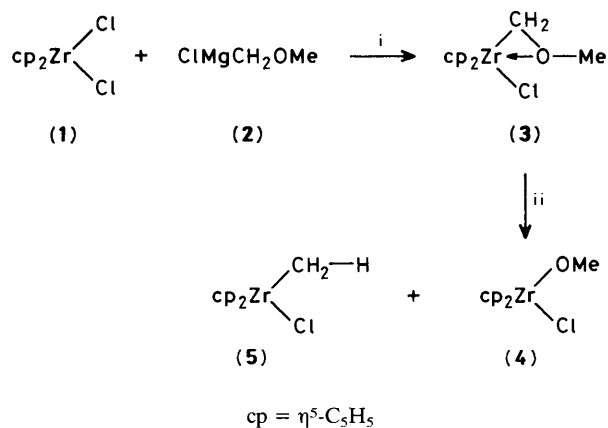
<sup>b</sup> *Max-Planck-Institut fur Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mulheim a.d. Ruhr, Federal Republic of Germany*

The title compound  $\text{cp}_2\text{Zr}(\text{Cl})\text{CH}_2\text{OMe}$  (**3**) ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) was prepared by treating  $\text{cp}_2\text{ZrCl}_2$  with  $\text{MeOCH}_2\text{MgCl}$  in  $\text{CH}_2(\text{OMe})_2$ ; a three-membered metallacyclic onium-type structure was observed by X-ray diffraction.

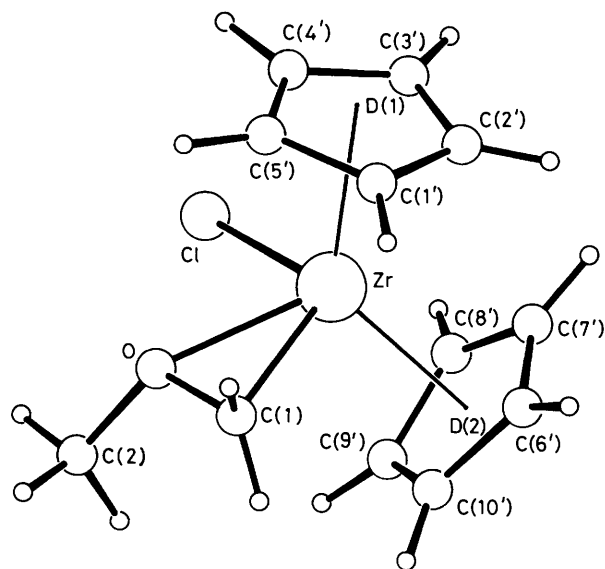
Some features of  $\alpha$ -metallated functionalized methanes  $\text{M-CH}_2\text{-X}$  can be explained by assuming a strong intramolecular  $\text{M} \cdots \text{X}$  interaction.<sup>1</sup> The ability to undergo alkylidene transfer reactions makes similarly structured early transition metal complexes valuable molecular model compounds for Fischer-Tropsch type chemistry.<sup>2</sup> Therefore, the disclosure of three-membered metallacyclic structures which are favoured for transition metal substituted methane derivatives is important.

We have treated  $\text{cp}_2\text{ZrCl}_2$  (**1**) ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) with a twofold excess of  $\text{MeOCH}_2\text{MgCl}$  (**2**) in  $\text{CH}_2(\text{OMe})_2$  solvent at  $-5^\circ\text{C}$ .<sup>3</sup> After recrystallization of the crude product from diethyl ether at  $-25^\circ\text{C}$ ,  $\text{cp}_2\text{ZrCl}(\text{CH}_2\text{OMe})$  (**3**) (m.p. =  $159^\circ\text{C}$ )<sup>†</sup> was obtained in 34% yield (Scheme 1). (**3**) exhibits three singlets in the  $^1\text{H}$  n.m.r. spectrum ( $[\text{C}_6\text{H}_6]$ benzene) at  $\delta$  2.59, 3.29, and

<sup>†</sup> Satisfactory elemental (C, H) analyses were obtained.



**Scheme 1.** i,  $\text{CH}_2(\text{OMe})_2$  solvent,  $-5^\circ\text{C}$ ; ii  $[\text{cp}_2\text{Zr}(\text{H})\text{Cl}]_x$ ,  $40^\circ\text{C}$ , 2.5 h.



**Figure 1.** A view of the molecular structure of (3) as determined by X-ray diffraction. [D(1) and D(2) are centroids.]

5.68 in a 2:3:10 ratio. Similarly, three resonances are observed in the  $^{13}\text{C}$  n.m.r. spectrum ( $\{[{}^2\text{H}_8]\text{toluene}\}$ ):  $\delta$  64.8 (q,  $^1J_{\text{CH}}$  146 Hz,  $-\text{OMe}$ ), 71.5 (t,  $^1J_{\text{CH}}$  150 Hz,  $\text{CH}_2$ ),<sup>4</sup> 109.8 (d,  $^1J_{\text{CH}}$  173 Hz, cp-C). Upon hydrolysis ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , equimolar in benzene) a 1:2 mixture of  $\text{cp}_2\text{Zr}(\text{Cl})\text{O}-\text{Zr}(\text{cp})_2(\text{Cl})$  and dimethyl ether was formed.

The molecular structure of (3) in the crystal was determined by X-ray diffraction (Figure 1).<sup>‡</sup> Two  $\eta$ -cyclopentadienyl groups and a chlorine ligand are bound to the metal centre.

<sup>‡</sup> *Crystal data:*  $\text{C}_{12}\text{H}_{15}\text{ClOZr}$ ,  $M = 301.9$ , orthorhombic, space group  $Pbca$ ,  $a = 11.296(1)$ ,  $b = 15.906(1)$ ,  $c = 13.808(2)$  Å,  $U = 2481$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.62$  g cm<sup>-3</sup>,  $\mu = 10.61$  cm<sup>-1</sup>, 4495 reflections measured, 2156 observed reflections [ $I \geq 2\sigma(I)$ ] were used in the solution and refinement of the structure. They were corrected for Lorentz and polarization effects. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. Hydrogen atoms were placed at calculated positions and not refined;  $R = 0.031$ ,  $R_w = 0.046$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

The remarkable structural feature of (3) is that both C(1) and the ether oxygen of the  $-\text{CH}_2\text{OMe}$  ligand are strongly co-ordinated to zirconium. The Zr–C(1) distance [2.271(5) Å] is clearly in the range expected for a  $\text{cp}_2\text{Zr}-\text{C}(\text{sp}^3)$   $\sigma$ -bond. Together with a strong Zr–O bond [2.204(3) Å] and a C(1)–O linkage of 1.414(6) Å it forms a three-membered metallacyclic (a metallaoxirane type) subunit.<sup>5</sup> C(1), O, and Cl are located in the major plane of the bent metallocene unit bisecting the  $\text{cpMcp}$  angle. Of the two possible bonding situations for  $\text{cp}_2\text{ZrCl}(\eta^2\text{-CH}_2\text{OMe})$  (3) apparently represents the thermodynamically favoured geometrical isomer exhibiting the ether oxygen in the central position.<sup>6</sup> The chlorine ligand [ $d(\text{Zr}-\text{Cl}) = 2.555(1)$  Å] occupies an adjacent lateral bonding site. The C(2)–O vector [1.449(6) Å] clearly points away from the  $\sigma$ -ligand plane. To put it in another way, the tri-coordinate oxygen in (3) lies 0.51 Å above the plane determined by its neighbouring atoms Zr, C(1), and C(2). This compares rather favourably with an observed value of 0.41 Å for the deviation of the oxygen atom in the oxonium cation  $(\text{MeCH}_2)_3\text{O}^+$  from the plane through its three adjacent carbon atoms.<sup>7</sup> An observed angle C(1)–O–C(2) of  $115.6(4)^\circ$  is in accord with an onium character of (3).

In a way, (3) can be regarded structurally as being an intramolecularly stabilized oxonium ylide.<sup>8</sup> Indeed, there appears to be chemical evidence supporting this view. (3) rapidly loses its 'bridging'  $\text{CH}_2$ -group when exposed to  $[\text{cp}_2\text{Zr}(\text{H})\text{Cl}]_x$  at  $40^\circ\text{C}$ , leaving the template  $\text{cp}_2\text{Zr}(\text{OMe})\text{Cl}$  (4). The methylene group has been transferred to the zirconocene hydride and inserted into the Zr–H bond to yield  $\text{cp}_2\text{Zr}(\text{Me})\text{Cl}$  (5). Exactly the same type of reaction had been observed upon treatment of  $[\text{cp}_2\text{Zr}(\text{H})\text{Cl}]_x$  with a real ylide, the Wittig reagent  $\text{CH}_2=\text{PPh}_3$ .<sup>9</sup>

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

Received, 30th May 1986; Com. 723

## References

- P. v. R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk, and N. G. Rodan, *J. Am. Chem. Soc.*, 1984, **106**, 6467, and references therein.
- (a) F. Fischer and H. Tropsch, *Brennst.-Chem.*, 1926, **7**, 97; R. C. Brady, III, and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 6181; (b) K. Kropp, V. Skibbe, G. Erker, and C. Krüger, *ibid.*, 1983, **105**, 3353; G. Erker, *Acc. Chem. Res.*, 1984, **17**, 103; (c) G. Erker, U. Dorf, J. L. Atwood, and W. E. Hunter, *J. Am. Chem. Soc.*, 1986, **108**, 2251.
- F. Runge, E. Taeger, C. Fiedler, and E. Kahlert, *J. Prakt. Chem.*, 1963, **19**, 37.
- See for a comparison: G. Erker, K. Kropp, C. Krüger, and A.-P. Chiang, *Chem. Ber.*, 1982, **115**, 2437, and ref. 2(b).
- See for a comparison: S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1983, **105**, 1690; G. Erker, U. Dorf, P. Czisch, and J. L. Petersen, *Organometallics*, 1986, **5**, 668, and refs. 2(b),(c).
- The same situation is found for  $\eta^2$ -acyl zirconocene complexes; for leading refs. see: G. Erker and F. Rosenfeldt, *J. Organomet. Chem.*, 1980, **188**, C1; K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert, and R. Hoffmann, *J. Am. Chem. Soc.*, 1985, **107**, 4440.
- M. I. Watkins, W. M. Ip, G. A. Olah, and R. Bau, *J. Am. Chem. Soc.*, 1982, **104**, 2365.
- G. A. Olah, H. Doggweiler, J. D. Felberg, S. Frohlich, M. J. Grdina, R. Karpeles, T. Keumi, S.-I. Inaba, W. M. Ip, K. Lammertsma, G. Salem, and D. C. Tabor, *J. Am. Chem. Soc.*, 1984, **106**, 2143; G. A. Olah, H. Doggweiler, and J. D. Felberg, *J. Org. Chem.*, 1984, **49**, 2112, 2116, and references therein.
- G. Erker, P. Czisch, R. Mynott, Y.-H. Tsay, and C. Krüger, *Organometallics*, 1985, **4**, 1310.