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[1,2-Bis(dimethylphosphino)ethane](cyclopentadienyl)methylzirconium(II) [CpZrMe(DMPE)$_2$]: A Catalyst Precursor for the Selective Dimerization of Ethylene to 1-Butene

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Summary: Room-temperature reaction of CpZrCl(dmpe)$_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] with MeLi led to the formation of the Zr(II) alkyl derivative CpZrMe(dmpe)$_2$ (**1**), as deep red crystals. Compound **1** is monoclinic, space group $C2/c$, with a = 11.675 (5) Å, b = 14.871 (5) Å, c = 28.154 (14) Å, β = 97.08 (4)°, V = 4851 Å^3, and Z = 8. Room-temperature reaction of **1** with 3 equiv of ethylene gave 1 equiv of methane and CpZr(dmpe)(η^4-butadiene)(CH$_2$CH$_3$) (**2**), which catalyzes the selective dimerization of ethylene to 1-butene.

The chemistry of the M–C bond is well-established for zirconium.[1] Insertion reactions,[2] metallacycle formation,[3] and homogeneous Ziegler–Natta[4] catalysis are the most attractive features subject to continuous study. With the exception of very few half-sandwich compounds,[5] this chemistry is almost exclusively limited to the bis(cyclopentadienyl) derivatives. A common feature of these systems, with no exceptions, is the presence of the metal in its highest formal oxidation state.[6] By reacting CpZrCl(dmpe)$_2$[7] [Cp = cyclopentadienyl, dmpe = 1,2-bis(dimethylphosphino)ethane] in THF with MeLi, we have obtained the novel Zr(II) alkyl complex CpZrMe(dmpe)$_2$[8] (**1**) in 40% yield (after recrystallization from pentane) as deep red crystals. We report herein its synthesis, X-ray structure determination, and a preliminary study on its reactivity with light olefins.

$$\mathrm{CpZrCl(dmpe)_2 + MeLi \xrightarrow[-LiCl]{THF} \underset{\mathbf{1}}{CpZrMe(dmpe)_2}} \quad (1)$$

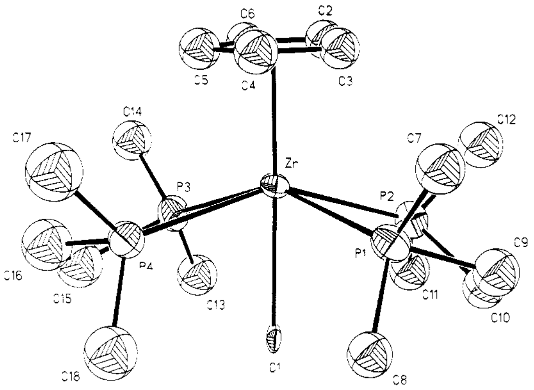
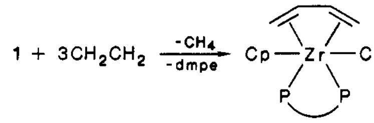


Figure 1. ORTEP drawing of **1**. Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): Zr–C(1) = 2.47 (2), Zr–P(1) = 2.676 (7), Zr–P(2) = 2.687 (7), Zr–P(3) = 2.714 (7), Zr–P(4) = 2.679 (7), Zr–cp (centroid) = 2.20 (12); P(1)–Zr–P(2) = 74.4 (2), P(1)–Zr–P(3) = 151.5 (2), P(2)–Zr–P(4) = 150.1 (2); P(3)–Zr–P(4) = 75.0 (2), P(1)–Zr–C(1) = 77.3 (4).

The X-ray analysis[9] revealed a structure similar to the chloro analogue[7] with comparable bond distances and angles (Figure 1). A unique feature of complex **1** is the unusual Zr–Me distance [Zr–C(1) = 2.47 (2) Å] which is considerably longer than in the corresponding methylzirconocene complexes [e.g. 2.255 (6) Å in (η^5-C$_9$H$_7$)$_2$Zr(CH$_3$)$_2$,[10] 2.273 (5) Å in Cp$_2$ZrMe$_2$[11]], probably as a result of increased steric hindrance.

A large value of $J_{\text{P-H}}$ has been observed for the methyl group signal in the ^{1}H NMR spectrum (δ −1.86 [quintet, $J_{\text{P-H}}$ = 9.0 Hz)]. Curiously, no resonance attributable to the Me group has been observed in the ^{13}C NMR spectrum in the range +250 to −50 ppm.

The reactivity of **1** with light olefins has been the subject of a preliminary investigation (Scheme I). A deep red solution of **1** in ether (as well as in pentane and benzene) reacts with 3 equiv of ethylene at room temperature and atmospheric pressure with the evolution of 1 equiv of methane.[12a] From the resulting light brown solutions, bright yellow crystals of CpZr(dmpe)(η^4-butadiene)(CH$_2$CH$_3$)[12b,13] (**2**) were obtained in 25% yield after recrystallization (eq 2).


(2)

2

The evolution of stoichiometric amount of CH$_4$ during the formation of **2** (Scheme I) together with the absence

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(1) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Ltd: 1986.

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(8) Anal. Calcd. (Found) for C$_{18}$H$_{40}$P$_2$Zr: C, 52.81 (52.77); H, 9.78 (9.74); Zr, 22.25 (22.23). ^{1}H NMR (90 MHz, C$_6$D$_6$, 27 °C): δ 4.44 (qt, $J_{\text{P-H}}$ = 2.0 Hz, 5 H, Cp), 1.52–1.38 (m, 8 H, CH$_2$ of dmpe), 1.26 (s, 12 H, CH$_3$ of dmpe), 1.03 (s, 12 H, CH$_3$ of dmpe), −1.86 (qt, $J_{\text{P-H}}$ = 9.0 Hz, 3 H, CH$_3$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ 82.7 (d, $J_{\text{C-H}}$ = 165.9 Hz, Cp), 31.3 (t, $J_{\text{C-H}}$ = 150.8 Hz, CH$_2$ of dmpe), 20.1 (q, $J_{\text{C-H}}$ = 128.2 Hz, CH$_3$ of dmpe), 18.1 (q, $J_{\text{C-H}}$ = 127.4 Hz, CH$_3$ of dmpe).

(9) X-ray diffraction data: monoclinic, space group $C2/c$, a = 11.675 (5) Å, b = 14.871 (5) Å, c = 28.154 (14) Å; β = 97.0 (4)°; V = 4851 (4) Å^3; Z = 8, d_{calcd} = 1.29 g cm^{-3}; μ(Mo Kα) = 7.1 cm^{-1} (absorption coefficient); F(000) = 1984; R = 0.074, R_ω = 0.071, and GOF = 1.514 for a fit of 123 variables to 1041 reflections used in analysis. Supplementary material contains complete details of the structural study.

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(12) (a) Toepler pump–GC combined experiments. (b) The structure of **2** is inferred from its analytical and spectroscopic data,[13] chemical degradation with HCl (GC–Toepler pump combined experiments), and direct synthesis (eq 3).

$$\mathrm{CpZr(dmpe)(\eta^4\text{-}butadiene)Cl + EtMgBr \xrightarrow{ether} \underset{\mathbf{2}}{CpZr(dmpe)(butadiene)(CH_2CH_3)}} \quad (3)$$

(13) Full spectroscopic and analytical details are available as supplementary material.

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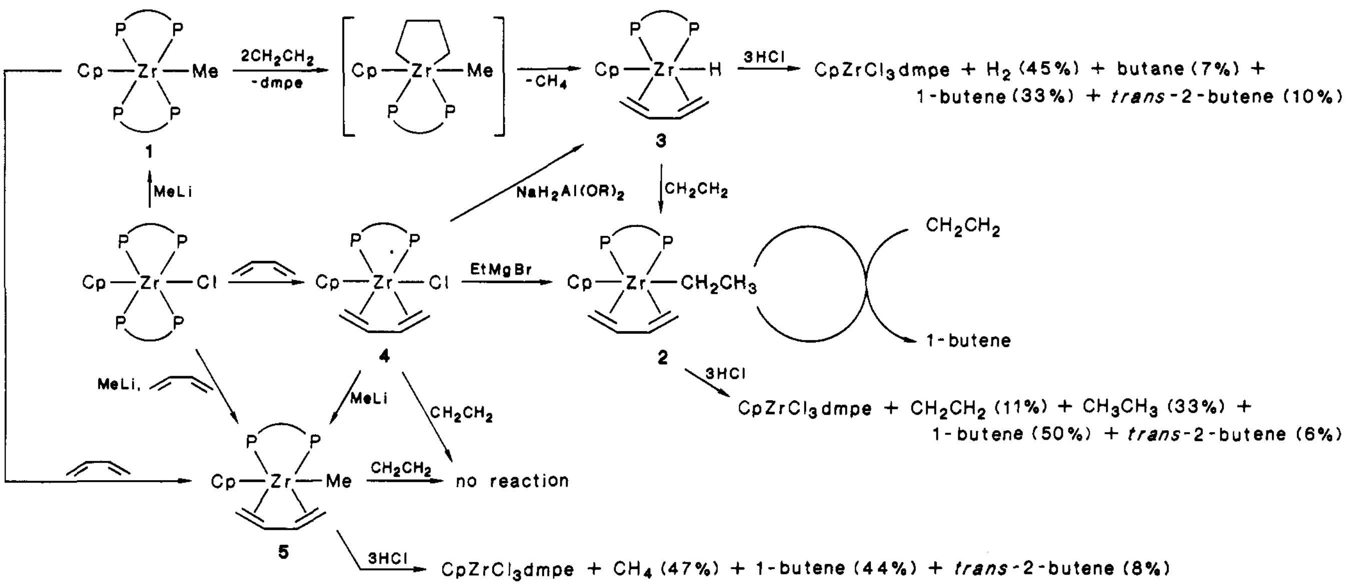
Scheme I



of any C_3 and C_5 products points out the inability of the Zr(II)–Me bond in the present case to undergo olefin insertion reactions. Furthermore this indicates that reductive coupling of ethylene is a possible pathway for the formation of the C_4 framework (Scheme I). In a following step, methane elimination together with hydrogen transfer to the metal center possibly leads to an intermediate butadiene–hydrido Zr species,[14] which forms **2** via ethylene insertion reaction into the Zr–H bond (Scheme I). To verify this hypothesis, we have prepared in crystalline form the unprecedented CpZr(dmpe)(η^4-butadiene)H[13,15] (**3**) by reacting CpZr(dmpe)(η^4-butadiene)Cl (**4**) with $NaH_2Al(OCH_2CH_2OCH_3)_2$ (Red-Al) (Scheme I). As expected, **3** undergoes fast ethylene insertion into the Zr–H bond giving **2** in quantitative yield (Scheme I). The CH_4-elimination reaction seems a rather specific step in the reaction of **1** with light olefins and apparently not possible for conjugated olefins like butadiene.[16] Reaction of **1** with butadiene led in fact to the formation of CpZr(dmpe)(η^4-butadiene)Me (**5**) as bright orange crystals.[13]

In contrast to **5**, complex **2** is rather unstable and slowly decomposes in solution at room temperature. However, as shown in Scheme I, **2** acts as homogeneous catalyst for slow and selective mild condition dimerization of ethylene to 1-butene (ca. 3 turnovers/day at room temperature, atmospheric pressure). It is noteworthy that the isostructural[17] Me (**5**) and Cl (**4**) derivatives do not display any reactivity with ethylene under the same reaction conditions. Furthermore the absence of C_6 and C_8 products, previously observed in the Zr- and Ti-promoted oligomerization of ethylene,[18] suggests that the mechanism in the present system is highly selective, a dominant role being probably played by the bulky dmpe.

More work to clarify the mechanism of the catalytic cycle and attempts to characterize possible intermediates are included in our continuous studies on these systems.

Acknowledgment. This work has been supported by the University of Groningen and by a NATO travel grant (0402/87); we are also indebted to the generosity of Chemistry Department at Columbia University.

Registry No. **1**, 115227-32-2; **2**, 115227-33-3; **3**, 115227-34-4; **4**, 115227-38-8; **5**, 115227-35-5; $CpZrCl(dmpe)_2$, 114238-07-2; $NaH_2Al(OCH_2CH_2OCH_3)_2$, 22722-98-1; CpZr(dmpe)(η^4-butadiene)($CH_2CH_2CH_3$), 115227-36-6; $CpZrCl_3dmpe$, 115227-37-7; CH_4, 74-82-8; H_2, 1333-74-0; CH_3CH_3, 74-84-0; ethylene, 74-85-1; butadiene, 106-99-0; 1-butene, 106-98-9; propylene, 115-07-1; isobutene, 115-11-7; 2-butene, 107-01-7; 2,3-dimethyl-2-butene, 563-79-1; butane, 106-97-8; *trans*-2-butene, 624-64-6.

Supplementary Material Available: Spectroscopic and analytical data of complexes **2**–**5** and tables of crystal data, anisotropic thermal parameters, atomic coordinates, and bond lengths and angles (10 pages); a listing of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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[14] An analogous mechanism has been suggested for the catalytic dimerization of ethylene promoted by Ta and Ti complexes (a) Fellmann, D. J.; Rupprecht, G. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5099. (b) Cohen, S. A.; Auburn, P. R., Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

[15] X-ray structure: Wielstra, Y.; Meetsma, A.; Gambarotta, S., manuscript in preparation.

[16] An analogous reaction has been found with propylene, while no reaction has been observed with isobutene, 2-butene, and 2,3-dimethyl-2-butene.

[17] The close similarity in the structures of CpZr(dmpe)(η^4-butadiene)X (X = Et, Me, Cl) derivatives is deduced from the almost complete overlapping of the IR spectra.

[18] (a) Datta, S.; Fisher, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353. (b) Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1977**, 560. (c) Erker, G.; Krüger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1 and references cited therein.

The New Binary Carbonyl $Os_4(CO)_{14}$: An Example of Carbonyl Exchange on the Infrared Time Scale?

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Summary: The new binary carbonyl $Os_4(CO)_{14}$ has been synthesized by the pyrolysis of $Os_4(CO)_{15}$. The structure of the compound shows an irregular tetrahedral Os_4 skeleton with 14, essentially terminal, carbonyl ligands. The spectroscopic properties of the cluster suggests it may be fluxional on the infrared time scale.

We have recently reported the synthesis and structure of $Os_4(CO)_{15}$[1] and $Os_4(CO)_{16}$,[2] the first tetranuclear binary

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