New metallocenes of early transition metals with functional groups in organic ligands. Red-ox transformations*

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Abstract: The reduction behavior of the novel zirconocene dichlorides, $(\eta^5\text{-}C_5Me_5)$ $(\eta^5\text{-}C_5Me_4CH_2CH_2ER_2)ZrCl_2$ (ER_2 = NMe_2, PMe_2, PPh_2), $(\eta^5\text{-}C_5Me_4CH_2CH_2PMe_2)_2ZrCl_2$, and $(\eta^5\text{-}C_5Me_4CH_2CH_2PPh_2)(\eta^5\text{-}C_5Me_4CH_2CH_2PMe_2)ZrCl_2$, together with the new types of intramolecular activation of inert C–H and C-heteroatom bonds are presented and discussed. A remarkably thermally stable zirconocene alkylhydryde type framework complex $(\eta^5\text{-}C_5Me_5)[\eta^5,\sigma\text{-}C_5Me_4CH_2CH_2N(Me)CH_2\text{-}]ZrH$, zirconocene arylhydryde complex $(\eta^5\text{-}C_5Me_5)[\eta^5,\sigma\text{-}C_5Me_4CH_2CH_2P(Ph)\text{-}o\text{-}C_6H_4\text{-}]ZrH$, tetramethylfulvene hydride-type complexes $(\eta^5\text{-}C_5Me_5)[\eta^6\text{:}\eta^1\text{-}(CH_2C_5Me_3)CH_2CH_2PR_2]ZrH$ (R = Me, Ph) and $(\eta^5\text{-}C_5Me_4CH_2CH_2PPh_2)[\eta^6\text{:}\eta^1\text{-}(CH_2C_5Me_3)CH_2CH_2PMe_2]ZrH$ are reported. The first unusually thermally stable zirconocene $(\eta^5,\eta^1\text{-}C_5Me_4CH_2CH_2PMe_2)_2Zr$ with the Zr(II) center stabilized by intramolecular coordination of two Me_2P-groups is described.

INTRODUCTION

Nowadays, the number of transition-metal complexes with side-chain functionality substituted cyclopentadienyl ligands grows exponentially [1–4]. This special interest in the complexes of question is caused, primarily, by the needs of the modern chemical industry, namely, the industry of polymers.

During the last years the efforts of our research group were focused on the elaboration of the preparative routes to the novel sandwich and half-sandwich zirconium complexes derived from $C_5Me_4CH_2CH_2OMe$, $C_5Me_4CH_2CH_2SMe$, $C_5Me_4CH_2CH_2NMe_2$, $C_5Me_4CH_2CH_2PMe_2$, and $C_5Me_4CH_2CH_2PPh_2$ ligands (Cp^O, Cp^S, Cp^N, Cp^{PMe}, and Cp^{PPh}, respectively) [5–9]. However, since the very beginning of our investigations, we have been also particularly interested in the elucidation of the abilities of various side-chain heteroatom functionalities to provide intramolecular stabilization of highly reactive biscyclopentadienyl derivatives of divalent zirconium. From our point of view, such an intramolecular mode of a Zr(II) center stabilization can open a path to the new class of catalytic systems for inert C–H and C–element bond activation.

Earlier, we reported [8], that a direct reduction of a series of zirconocene dichlorides derived from Cp^O and Cp^S ligands with amalgamated magnesium in tetrahydrofuran (THF) leads to the formation of the methyl–oxygen and/or methyl–sulfur bond cleavage products (Scheme 1).
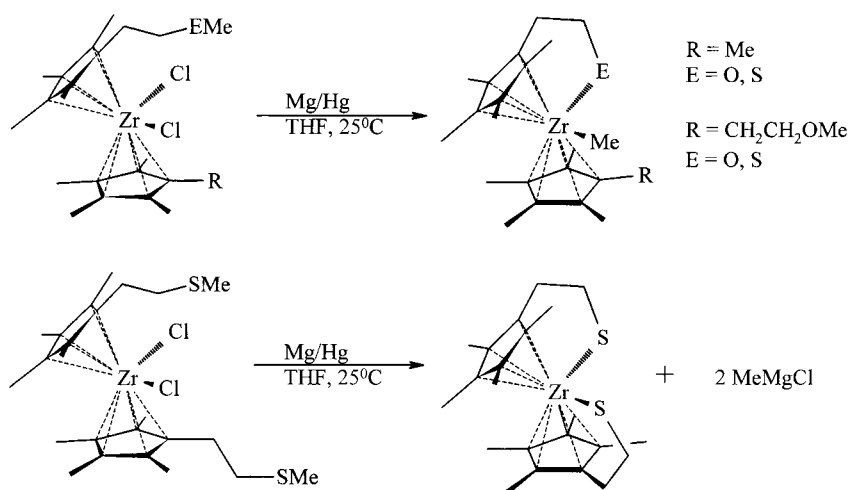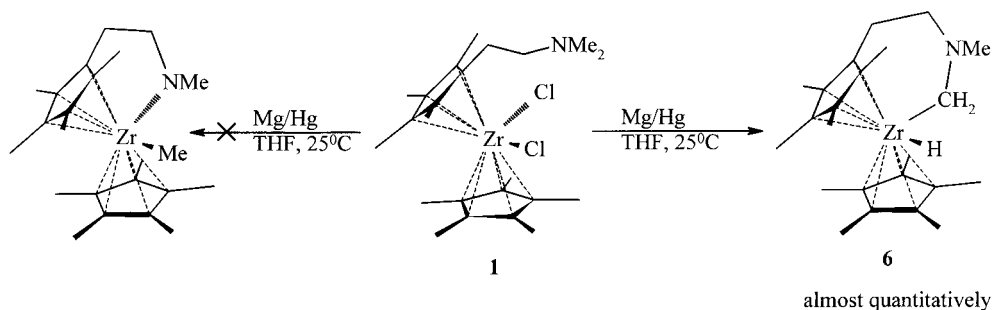

Scheme 1

This paper presents our latest results concerning the reduction behavior of zirconocene dichlorides containing Cp^N, Cp^{PPh}, and Cp^{PMe} ligands.

STUDIES OF THE REDUCTION BEHAVIOR OF SANDWICH Zr(IV) COMPLEXES WITH Cp^N, Cp^{PPh}, AND Cp^{PMe} LIGANDS

The novel zirconocene dichlorides $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4CH_2CH_2ER_2)ZrCl_2$ (ER_2 = NMe_2 (**1**), PMe_2 (**2**), PPh_2 (**3**)), $(\eta^5\text{-}C_5Me_4CH_2CH_2PMe_2)_2ZrCl_2$ (**4**), and $(\eta^5\text{-}C_5Me_4CH_2CH_2PPh_2)(\eta^5\text{-}C_5Me_4CH_2CH_2PMe_2)ZrCl_2$ (**5**) were prepared in good yields accordingly to the procedures developed previously via corresponding Li cyclopentadienides, their trimethylsilyl derivatives, and half-sandwich complexes of Zr(IV). Lithium salt $LiC_5Me_4CH_2CH_2PMe_2$ was prepared analogously to that described for $LiC_5Me_4CH_2CH_2PPh_2$ [7,9] by a reaction of 4,5,6,7-tetramethylspiro[2,4]heptadiene-4,6 and lithium dimethylphosphide in THF.

All the reduction reactions were carried out under mild conditions (room temperature) and reducing agent (Mg activated with $HgCl_2$ in THF or THF-d_8). Almost in all cases, the observed selectivities of reactions were not lower than 95% (NMR spectroscopy data for the reaction mixtures). The structures of the reduction products in solutions were unambiguously determined by means of appropriate NMR techniques including 2D and ^1H NOE difference NMR spectroscopy.

Surprisingly, reduction of $Cp^N(C_5Me_5)ZrCl_2$ **1** resulted in an almost quantitative formation of an intramolecular NCH_2–H bond activation zirconocene alkylhydryde-type product $(\eta^5\text{-}C_5Me_5)$ $(\eta^5,\sigma\text{-}C_5Me_4CH_2CH_2N(Me)CH_2\text{-})ZrH$ (**6**), with no N–Me bond cleavage product formed (Scheme 2).

Scheme 2

For the mono Me$_2$P-functionalized ring-permethylated zirconocene dichloride **2**, the reduction resulted in an almost quantitative formation of the only remarkably thermally stable product **7** (see Scheme 3), which remains unchanged after prolonged heating (100 °C, more than 10 h, solution in THF-d$_8$ or C$_6$D$_6$) and can be even sublimed (**!**) in high vacuum (>200 °C) with only partial decomposition. Compound **7** possesses a tetramethylfulvene hydryde-type framework structure that can be described as (η^5-C$_5$Me$_5$)[η^6:η^1-(CH$_2$C$_5$Me$_3$)CH$_2$CH$_2$PMe$_2$]ZrH. In complex **7** the methylene group at the Cp-ring (former Cp–CH$_3$ group that underwent CH-activation) is adjacent to the -CH$_2$CH$_2$PMe$_2$ substituent. The PMe$_2$ functionality is coordinated to the Zr(IV) center and, what is mostly remarkable, located *between* the CH$_2$ and H groups. It is noteworthy that the products of P–C and/or PCH$_2$–H bond cleavage are not present in the reaction mixture in noticeable amounts.

The reduction of the PPh$_2$ analog of compound **2**, zirconocene dichloride **3**, results in formation of two products **8** and **9** (55 and 45% in the reaction mixture; the ^{1}H NMR data). Complex **8** possesses a structure similar to that observed for compound **7**, with the phosphanyl group located between the methylene and hydride ligands. The structure of the second product **9** is markedly different. Analysis
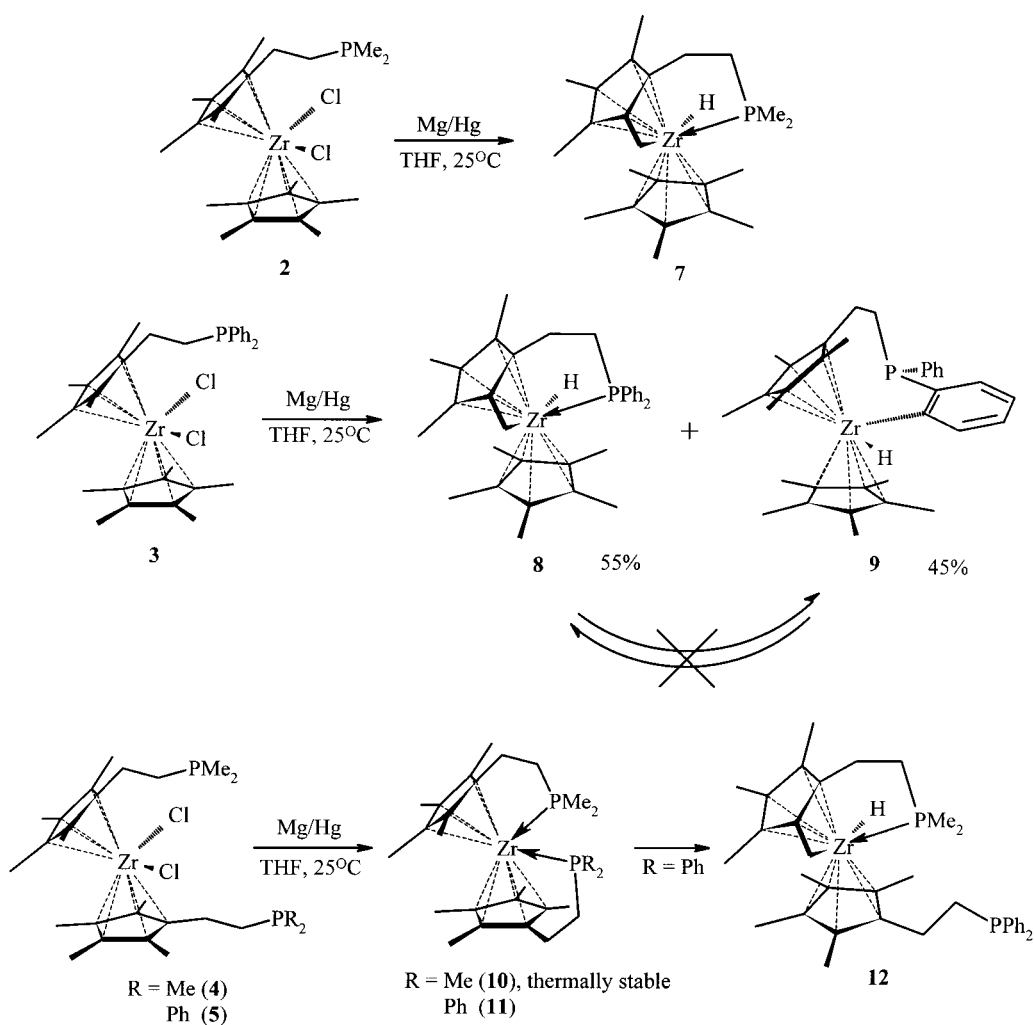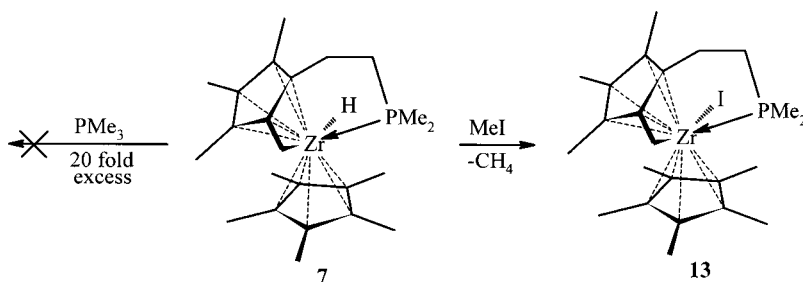

Scheme 3

of the NMR spectral data indicates that complex **9** is a product of an activation of one of the phenyl group CH–bonds in the *ortho*-position to the P-atom. In *o*-CH bond activation product **9**, the phosphorous atom is not coordinated to the metal center.

Similar to that observed for zirconocene tetramethylfulvene hydride **7**, complexes **8** and **9** are also markedly thermally stable. Interestingly, despite the fact that **8** and **9** are coproducts of the reaction, no interconversion of them one into another was observed even at elevated temperatures (80 °C, THF-d_8 or C_6D_6). It is worth mentioning here that performing the reduction of complex **3** in the presence of a great (20 fold) excess of PMe_3 does not affect the course of the reaction, and the same mixture of C-H bond activation products **8** and **9** is formed even in this case.

Under the identical reduction conditions, zirconocene dichloride **4**, possessing two $CH_2CH_2PMe_2$ substituents, gives the true Zr(II) complex $(\eta^5:\eta^1-C_5Me_4CH_2CH_2PMe_2)_2Zr$ **10**. The ^1H, ^{13}C, and ^{31}P NMR spectral data unambiguously indicate that both of two PMe_2 groups in **10** are coordinated to the Zr(II) center. It is a remarkable fact that, according to our preliminary data, complex **10** in a C_6D_6 solution reversibly activates C-D bonds of the solvent at ambient temperature. However, no incorporation of deuterium atoms into **10** was observed.

Similar to zirconocene dichloride **4**, the reduction of the closely related complex **5** (PMe_2 and PPh_2 groups in side chains) initially leads to an analogous Zr(II) complex **11**. However, compound **11** is not stable thermally and, at elevated temperature (~80 °C), gradually converts into a product of an oxidative addition of one of the C-H bonds of CH_3 groups adjacent to the $CH_2CH_2PMe_2$ substituent **12**. Zirconocene alkylhydride-type complex **12** is a thermally stable compound and can be considered as the final product of the reduction of **5**.

Complex **7** is rather stable under the conditions of the ligand exchange reactions. Thus, treatment of it with a 20-fold excess of PMe_3 causes no changes in its NMR spectra even at elevated temperatures. However, when treated with excess of CH_3I, zirconocene hydride complex **7** converts into the tetramethylfulvene iodide complex **13**, with an equivalent of methane evolved (Scheme 4). No attack of CH_3I at the -CH_2–Zr moiety was observed.

Scheme 4

CONCLUDING REMARKS

The nature of the pendant functionality in Zr(IV) sandwich complexes derived from Cp^O, Cp^S, Cp^N, Cp^{PMe}, and Cp^{PPh} ligands and the number of such functionalities in a molecule of a complex, evidently, present the main factors that determine the reduction behavior of the complexes of question. Thus, only in the case of two phosphanyl functionalities was it possible to obtain the intramolecularly stabilized Zr(II) complexes **10** and **11**. However, even compound **11** exhibits lower thermal stability comparatively to **10**, probably, due to the weaker coordination of the bulky PPh_2 group to the Zr(II) center.

In all of the other studied reduction reactions, activation of inert C–H or C–heteroatom bonds takes place with at least four dramatically different pathways of these activations observed. We believe, however, that even in these cases, Zr(II) biscyclopentadienyl complexes participate as non-observable

intermediates. The course of the further conversion of these Zr(II) intermediates (i.e., which bond undergoes the oxidative addition to the low-valent metal center), from our viewpoint, is determined by their spatial organization, namely, by the closeness of one or another bond to the divalent Zr center.

The unusually high thermal stability of the tetramethylfulvene hydride-type complexes **7**, **8** and **12** can be explained by the spatially compelled positioning of the phosphanyl ligand *between* the methylene and hydride ligands and, by this way, blocking the reverse reductive elimination reaction.

ACKNOWLEDGMENT

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