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# Facile Reduction of Organometallic Halides with Bis(pentamethylcyclopentadienyl)ytterbium and the X-Ray Structure of $(C_5Me_5)_2YbCl(THF)$

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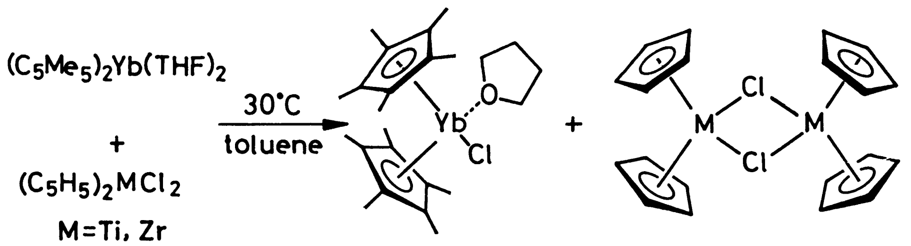
Reduction of $(C_5H_5)_2MCl_2$ (M=Ti, Zr) and $TiCl_4$ with one equiv. of $(C_5Me_5)_2Yb(THF)_2$ gave rise to the formation of $[(C_5H_5)_2MCl]_2$ and $TiCl_3(THF)_3$, respectively, together with $(C_5Me_5)_2YbCl(THF)$. The molecular structure of $(C_5Me_5)_2YbCl(THF)$ has been determined by the X-ray analysis. The reaction of $(C_5Me_5)_2Yb(THF)_2$ with $Me_3SiCl$ yielded a mixture composed of $[(C_5Me_5)YbCl]_n$ and $C_5Me_5$-$(CH_2)_4OSiMe_3$.

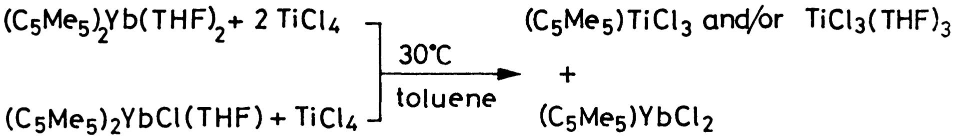
Oxidative addition reaction constitutes one of the most important subject in the organolanthanide chemistry. $(C_5Me_5)_2Yb(OEt_2)$(1) is known to be readily oxidized by alkyl halides,$^{1)}$ organic peroxides, and alkyl disulfides.$^{2)}$ The 1:1 complexations of 1 with metal carbonyl compounds$^{3,4)}$ and trialkylaluminum$^{5)}$ are also reported. This paper describes the utility of permethylytterbocene as an effective agent for reduction of high valent organometallic halides.

The 1:1 reaction of $Cp_2TiCl_2(Cp=C_5H_5)$ with $Cp*_2Yb(THF)_2$(2)$(Cp*=C_5Me_5)$ in toluene at 30 °C for 2 h was found to give a 1:1 mixture of $[Cp_2TiCl]_2$$^{6)}$ and $Cp*_2YbCl(THF)$(3) in 85-96% yield(see Eq. 1). Resulting products could be



(1)

separated into individual paramagnetic compound by recrystallization from THF-hexane as identified by the $^1$H NMR, EIMS, and elemental analyses. Similarly, $Cp_2ZrCl_2$ could also be reduced to $[Cp_2ZrCl]_2$ quantitatively as confirmed by the NMR spectrum.[7a)] The isolated $[Cp_2ZrCl]_2$ gradually decomposes into $Cp_2ZrCl_2$ and $[Cp_2Zr]_2$ as reported by Fochi et al., because of its thermal instability.[7b)] Reduction of $TiCl_4$ also underwent smoothly by the addition of one equiv. of **2** in hexane at 30 °C. The resulting less soluble $TiCl_3(THF)_3$ could be easily separated from **3** by recrystallization from THF-hexane in 85% yield. However, the 2:1 reaction of $TiCl_4$ with **2** predominates the ligand exchange reaction as shown in Eq. 2. This type of reaction may arise from the ligand exchange reaction between the initially formed compound **3** and $TiCl_4$. Actually, the 1:1 reaction of **3** with $TiCl_4$ in toluene produced the expected $Cp^*TiCl_3$ in 65% isolated yield, together with blue $Cp^*YbCl_2$.[8)] Reduction of Group 5 organometallics, $Cp_2NbCl_2$, $CpNbCl_4$, $Cp_2TaCl_2$ and $CpTaCl_4$, is also possible as confirmed by the formation of the expected $Cp^*_2YbCl(THF)$ in good yield (>65%). Details of these reactions will be reported separately.



$$\left.\begin{array}{l}(C_5Me_5)_2Yb(THF)_2 + 2\,TiCl_4 \\ (C_5Me_5)_2YbCl(THF) + TiCl_4\end{array}\right] \xrightarrow[\text{toluene}]{30\,^\circ C} \begin{array}{c}(C_5Me_5)TiCl_3 \text{ and/or } TiCl_3(THF)_3 \\ + \\ (C_5Me_5)YbCl_2\end{array} \qquad (2)$$

Molecular structure of the paramagnetic $Cp^*_2YbCl(THF)$(**3**) was established by the single crystal X-ray analysis. Crystal data: $C_{24}H_{38}OClYb$, M=551.06, triclinic, space group, $P\bar{1}$, $a$=17.138(4) Å, $b$=8.527(1) Å, $c$=18.570(6) Å, $\alpha$=90.42°, $\beta$=118.65°, $\gamma$=88.01°, $V$=2380(1) $Å^3$, and $Z$=4. $D_c$=0.926 g/cm$^3$, $\mu$(MoK$\alpha$)=40.4 cm$^{-1}$. A total of 10891 independent reflections was collected up to $2\theta$=50° by the $\theta$-$2\theta$ scan method, of which 9411 were observed reflections $[|F_o|>3\sigma(F_o)]$. The crystal structure was solved by the conventional heavy atom method and was refined by the full matrix least-squares (XRAY-76).[9)] The $R(R_w)$ index is 0.052(0.074). Weighting scheme applied was $w=[\sigma^2(F_o)+0.003(F_o)^2]^{-1}$.

Figure 1 shows the ORTEP diagram of **3** with numbering scheme of the selected atoms. The compound is monomeric although the base-free $(C_5H_4Me)_2YbCl$ is known to be dimeric.[10)] The ytterbium atom is tetra-coordinated if the Cp* ligand is considered to occupy one coordination site. The whole geometry of the compound resembles well that of Cp*$_2$YbCl[1,1-bis(dimethylphosphino)methane](4).[11] The bond distances of Yb-C(Cp*)(av. 2.64(1) Å) and Yb-Cl(2.539(4) Å) are nearly equal to 2.65(3) Å and 2.532(3) Å, respectively, reported for 4, while the bent angle of Cp*(centr.)-Yb-Cp*(centr.), 136.1(1)°, is a little larger than 134.9° observed for 4. The Yb-C(Cp*) distance of 3 also compares very closely with that(2.66(2) Å) of a Yb(II) species, Cp*$_2$Yb(THF)(2').[12] The Yb-O distance of 3 is however shorter by 0.05 Å and the Cp*(centr.)-Yb-Cp*(centr.) angle is smaller by 7.4° than those (2.412 Å and 143.5°) reported for 2'. This may arise from the difference in oxidation state together with coordination number between 2' and 3. Comparison of 3 with a dimeric ytterbocene chloride, [(C$_5$H$_4$Me)$_2$YbCl]$_2$(5), reveals marked differences, i.e. the complex 5 exhibits longer Yb-Cl bond (av. 2.64(1) Å), shorter Yb-C(Cp) bond (av. 2.587(7) Å) and smaller Cp(centr.)-Yb-Cp(centr.) angle (126.7°).

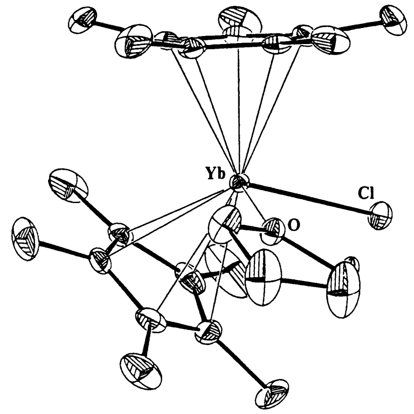
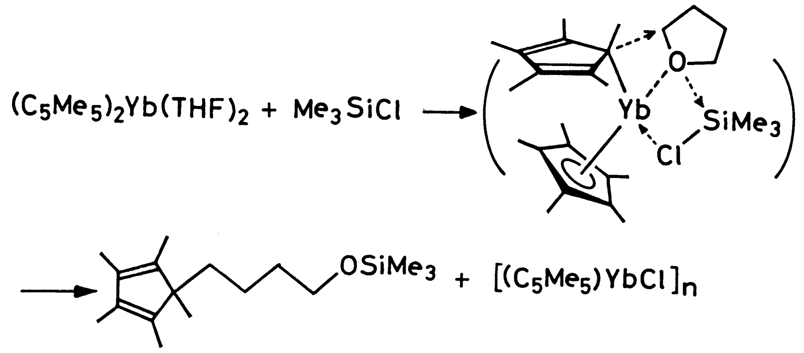


Fig. 1. Molecular structure of (C$_5$Me$_5$)$_2$YbCl(THF)(3).

As an extension of this study, we have also examined the reaction of Me$_3$SiX (X=Cl, Br) with 2. If Me$_3$SiX takes place the oxidative addition to 2, it should give rise to the formation of 3 together with Me$_3$SiSiMe$_3$ or trimethylsilylated ytterbocene chloride. However, the reaction proceeded as the following Eq. 3 opposed to our expectation. Thus, the 1:1 reaction of 2 with Me$_3$SiCl in benzene



(3)

at 30 °C for 10 h afforded $C_5Me_5(CH_2)_4OSiMe_3$ in 90% yield together with insoluble yellow precipitate, $[Cp^*YbCl]_n$,13) in ca. 65% yield. The reaction should occur presumably through an intermediate shown in Eq. 3. The reaction of $Cp^*_2Yb(OEt_2)_2$ with $Me_3SiCl$ also provided corresponding products composed of (ethyl)pentamethylcyclopentadiene and ethyl trimethylsilyl ether, together with (trimethylsilyl)-pentamethylcyclopentadiene and $[Cp^*YbCl]_n$ in a 12:11:6:8 ratio (total yield, 88%). Similarly, a tetrahydropiranate, $Cp^*_2Yb(C_5H_{10}O)_2$, reacts with $Me_3SiCl$ to lead to $C_5Me_5(CH_2)_5OSiMe_3$ and (trimethylsilyl)pentamethylcyclopentadiene in ca. 2:1 ratio. The reaction of $Me_3SiBr$ with **2** or $Cp^*_2Yb(OEt_2)_2$ also proceeds in a similar fashion. $Cp^*_2YbBr(OEt_2)$ was not formed. Thus the reaction of ytterbocene etherates with $Me_3SiX$ generally proceeds accompanying the cleavage of the ligated ether and the Cp*-Yb linkage to give alkylated pentamethylcyclopentadiene and $[Cp^*YbX]_n$ in good yields.

## References

1) P. Finke, S. R. Keenan, and P. L. Watson, Organometallics, 8,263 (1989) and references cited therein.
2) D. J. Berg, R. A. Andersen, and A. Zalkin, Organometallics, 7, 1898 (1988).
3) T. D. Tilley and R. A. Andersen, J. Chem. Soc., Chem. Commun., 1981, 985.
4) J. M. Boncella and R. A. Andersen, Inorg. Chem., 23, 432 (1983).
5) H. Yamamoto, H. Yasuda, K. Yokota, A. Nakamura, Y. Kai, and N. Kasai, Chem. Lett., 1988, 1963.
6) M. L. H. Green and R. R. Lucas, J. Chem. Soc., Dalton Trans, 1972, 1000.
7) a) T. Cuenca and P. Royo, J. Organomet. Chem., 293, 61 (1985); b) G. Fochi, G. Guidi, and C. Floriani, J. Chem. Soc., Dalton Trans, 1984, 1523.
8) Determined based on the $^1H$ NMR (see Ref. 1); $^1H$ NMR (benzene-$d_6$) $\delta$ 19.17ppm (bs, $\nu_{1/2}$=45 Hz). The color of the solid is light blue.
9) J. M. Stewart, XRAY-76, Report TR-446, University of Maryland, MD (1976).
10) E. C. Baker, L. D. Brown, and K. N. Paymon, Inorg. Chem., 14, 1376 (1975).
11) T. D. Tilley, R. A. Andersen, and A. Zalkin, Inorg. Chem., 22, 856 (1983).
12) T. D. Tilley, R. A. Andersen, B. Spencer, H. Ruben, A. Zalkin, and D. H. Templeton, Inorg. Chem., 19, 2999 (1980).
13) Anal. Found: Cp*, 39.2(GC analysis); Yb 50.2(oxidation method); Cl, 10.6(AgCl method). Calcd for Cp*YbCl: Cp*, 39.34; Yb, 50.34; Cl, 10.31.

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