4132 *Organometallics* **2001,** *20,* 4132−4134

Metalations with Group 4 Alkylmetal(IV) Halides: Expeditious Route to Metallocene and Nonmetallocene Procatalysts[1]

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Received June 4, 2001

Summary: Group 4 alkylmetal(IV) halides of the type $Bu_2M_tCl_2$, generated in hydrocarbon media at −78 °C by treating M_tCl_4 with 2 equiv of n-butyllithium, function as strong bases toward a variety of Brønsted acids, E−H, where E = cyclopentadienyl or substituted cyclopentadienyl, 1-alkynyl, indenyl, alkoxy, aryloxy, and disubstituted amino, to form metallocene and nonmetallocene procatalysts, E_2MCl_2, expeditiously and generally in high yield.

Because of the central importance of the σ carbon−transition-metal bond, $C-M_t$, as the active site in both Ziegler−Natta heterogeneous[2] and metallocene homogeneous olefin polymerization catalysts,[3] our group has been exploring the synthesis and chemical reactivity of early transition metal alkyls over the past decade.[4−7] Such studies have led to the discovery of an extraordinary and most useful kinetic solvent effect. As exemplified by the di-*n*-butylmetal dichlorides of the group 4 metals, $Bu_2M_tCl_2$ (**1**), such alkyls synthesized in ether solvents at −78 °C from M_tCl_4 and 2 equiv of *n*-butyllithium undergo a ready reductive elimination of its alkyl groups[8] upon warming to 0 °C and provide M_tCl_2 (**2**) quantitatively.[5,9] M_tCl_2 can be utilized to achieve a useful variety of reductions in organic synthesis[5,7] or can effect the metalative dimerization of fulvenes, such as the 6,6-dimethyl derivative **3**, to form the corresponding *ansa*-metallocene (**4**) in high yield[9] (Scheme 1). In contrast to this mode of decomposition, when **1** is generated in hydrocarbon media such as hexane or toluene it shows a remarkable stability toward reductive elimination (**1** → **2**) and instead behaves as a hydrometalating agent, with loss of 1-butene,[10] toward a wide variety of unsaturated organic substrates (**6**; E = O, NR, cyclopentadienylidene), such as ketones, imines, and fulvenes.[11] The resulting metallocene or nonmetallocene group 4 metal derivatives (**7**) constitute a variegated structural array of olefin polymerization procatalysts[12] (Scheme 1).

Our most recent studies have now uncovered yet a third type of most useful and versatile reactions for the kinetically stable alkyls $Bu_2M_tCl_2$ (**1**), and this is their facile metalation of a broad range of Brønsted acids, E−H (**8**), even at −78 °C in hydrocarbon media. With E equal to cyclopentadienyl or substituted cyclopentadienyl, to 1-alkynyl, alkoxy (RO), or aryloxy (ArO), and to disubstituted amino (R_2N) groups, the corresponding metalated derivative $E_2M_tCl_2$ (**9**) is formed rapidly and completely (Scheme 1). These metalations represent an extraordinarily expeditious route to metallocene and nonmetallocene procatalysts for olefin polymerization.[12] In a one-flask operation M_tCl_4 dispersed in a hydrocarbon medium at −78 °C is treated with 2 equiv of *n*-butyllithium to form $Bu_2M_tCl_2$ (**1**), and shortly thereafter 2−3 equiv of E−H (**8**) is added and the mixture warmed to 20 °C or higher.[13] The solvent is removed under reduced pressure, and $E_2M_tCl_2$ extracted away from the LiCl byproduct with hot toluene in a Soxhlet apparatus. In most cases $E_2M_tCl_2$ (**9**) can be recovered from the toluene extract essentially quantitatively and pure by NMR spectral criteria.

The titanium, zirconium, and hafnium derivatives of $Bu_2M_tCl_2$ all reacted readily in toluene at −78 °C with freshly distilled cyclopentadiene or substituted cyclopentadienes (**10**) to provide quantitatively the corre-

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[3] Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

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[5] Eisch, J. J.; Boleslawski, M. P. *J. Organomet. Chem.* **1987**, *334*, C1.

[6] Eisch, J. J.; Shi, X.; Lasota, J. *Z. Naturforsch.* **1995**, *50b*, 342.

[7] Eisch, J. J.; Shi, X.; Alila, J. R.; Thiele, S. *Chem. Ber./Recl.* **1997**, *130*, 1175.

[8] The butyl groups are lost as a mixture of butane and 1-butene, which were identified in the condensed ether solvent at −78 °C, by a combination of ^1H and ^{13}C NMR and IR spectral analysis as well as the chemical trapping of 1-butene with Br_2.

[9] Eisch, J. J.; Shi, X.; Owuor, F. A. *Organometallics* **1998**, *17*, 5219.

[10] The 1-butene evolved was trapped by passing through a CCl_4 solution of Br_2 and the 1,2-dibromobutane identified by NMR spectroscopy.

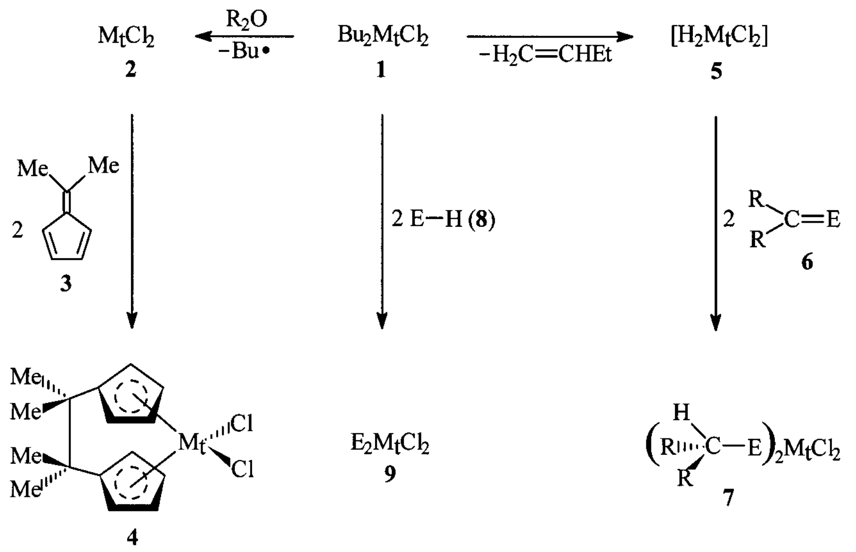
[11] Eisch, J. J.; Owuor, F. A.; Shi, X. *Organometallics* **1999**, *18*, 1583. The hydrometalating action of $Bu_2M_tCl_2$ (**1**) on organic substrates could conceivably occur via two routes: (1) dissociation by elimination of 1-butene into $H_2M_tCl_2$ and subsequent hydrometalation and/or (2) direct transfer of an $H-M_t$ bond to the organic substrate via a six-membered ring complex of **1** with the substrate. Which mechanism prevails remains to be determined.

[12] Such procatalysts must be admixed with a cocatalyst, such as R_nAlX_{3-n} or MAO, to produce the olefin polymerization catalyst containing the crucial $C-M_t$ bond.

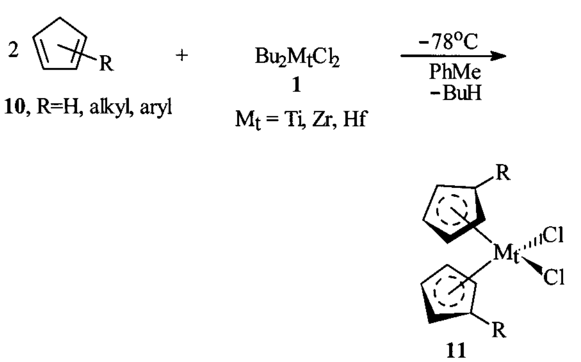
[13] With indenes and amines (R_2NH), prolonged reaction times at 20 °C or heating is required to attain higher yields of $E_2M_tCl_2$. With 1-alkynes, such as phenylacetylene, the metalation reaction with Bu_2ZrCl_2 took place smoothly and cleanly in hexane. Proof of metalation was obtained by treating such a reaction mixture with D_2O and isolating $PhC\equiv CD$. In toluene, however, even at low temperatures the reaction between phenylacetylene and Bu_2ZrCl_2 gives only a mixture of cyclotrimers and polymer. Heating should be minimal, since it promotes the decomposition of $Bu_2M_tCl_2$ into M_tCl_2.

10.1021/om0104621 CCC: $20.00

Scheme 1



sponding metallocene dichlorides (**11**) (eq 1).[14a] With indene, the reaction with **1** to produce bis(indenyl)metal



(1)

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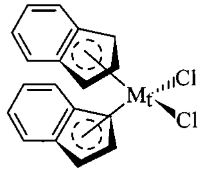
dichlorides (**12**) proceeded less readily and both prolonged stirring at 20 °C and heating in hexane at 65 °C was necessary to give yields of metallocenes ranging upward of 75% of **12**.[14b] Likewise, 1-alkynes such as



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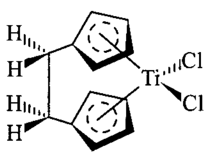

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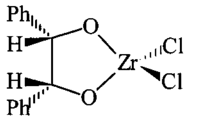

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phenylacetylene reacted cleanly in hexane at 20 °C to give high yields of $(RC{\equiv}C)_2M_tCl_2$. On the other hand, reaction of **1** under various conditions with fluorene failed to give any significant amounts of the expected bis(9-fluorenyl)metal dichloride.

Two classes of diprotic Brønsted acids proved to be particularly advantageous substrates for reaction with these novel $Bu_2M_tCl_2$ metalating agents. First, as demonstrated specifically with Bu_2TiCl_2, an intramolecular bis-metalation of the isomeric 1,2-dicyclopentadienylethanes with Bu_2TiCl_2 led smoothly to the *ansa*-metallocene dichloride **13**.[15] Second, 1,2-diols such as *meso*-hydrobenzoin react readily with Bu_2ZrCl_2 to form the cyclic *ansa*-nonmetallocene derivative **14**.[16] The success of such bis-metalations may well prove applicable to the synthesis of heteroatom-tethered transition-metal procatalysts of constrained geometry.[17] Accordingly, our efficient metalations with $Bu_2M_tCl_2$ reported here offer a novel and facile access to both *ansa*-metallocenes and a number of transition-metal procatalysts of constrained geometry.

Finally, the ready reaction of hydroxy Brønsted acids (**15**), such as alcohols or phenols, with $Bu_2M_tCl_2$ (**1**)

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(14) (a) A typical procedure for the preparation of zirconocene dichloride is as follows: A suspension of 20 mmol of $ZrCl_4$ in 150 mL of hexane or toluene, under argon and cooled to −78 °C, was treated slowly with 40 mmol of BuLi in hexane. The stirred light brown mixture of Bu_2ZrCl_2 and LiCl was warmed to 20 °C over 8 h. The mixture was recooled to −78 °C and then treated with 2.5 equiv of freshly distilled cyclopentadiene. After 1 h at −78 °C and 4 h at gentle reflux, the cooled mixture was filtered to remove the LiCl. LiCl was extracted with portions of pentane−methylene chloride (3:1 v/v), and the combined filtrate and extracts were freed of volatiles under reduced pressure. The residue consisted of pure zirconocene dichloride (>95%). ^1H and ^{13}C NMR data for the metallocene dichlorides obtained (**10**, R = H): Ti, 6.59 and 120.1 ppm; Zr, 6.50 and 116.0 ppm; Hf, 6.40 and 114.5 ppm. (b) Other modifications of solvent, temperature, or possible catalysts have proved ineffectual or deleterious: (1) heating **1** and indene in refluxing heptane (bp 98 °C) led to lower yields of **12** because of the thermal decomposition of $Bu_2M_tCl_2$ (**1**) to M_tCl_2 (**2**);[9] (2) even dissolution of **1** in toluene at 25 °C accelerated the alkylative reduction of **1** to **2**, possibly due to the π-basicity of toluene promoting the reductive elimination of the butyl groups from **1**; (3) in CH_2Cl_2, with or without an additional Lewis acid such as $MeAlCl_2$, the yield of **12** dropped markedly, most likely because of the known cationic polymerization of indenes by Lewis acids: Sigwalt, P. *J. Polym. Sci.* **1961**, *52*, 15.

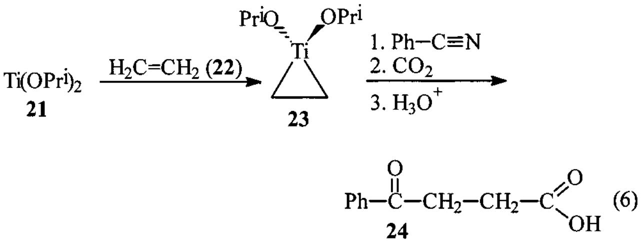
(15) The isomeric 1,2-dicyclopentadienylethanes were prepared according to the literature method: Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159. Compound **13** was obtained as dark red crystals (80%). ^1H NMR ($CDCl_3$): 6.87 (4H); 6.05 (4H); 3.22 (4H).

(16) Interaction of a hexane−benzene suspension of 10 mmol of **1** (M_t = Zr), containing the LiCl byproduct, with 1 equivalent of *meso*-hydrobenzoin at 50 °C under argon for 1 h led to gas evolution. The warm suspension was filtered to remove the LiCl, and then the residual LiCl was extracted further with warm benzene. Solvent removal from the combined filtrate and extracts left a 95% yield of **14** as a colorless solid. ^1H NMR (C_6D_6): δ 4.06 (H), 6.89 (5H). ^{13}C NMR: δ 54, 127.3, 128.1, 128.4, 128.7. IR (mineral oil mull): no O−H absorption in the 3300−3500 cm^{-1} region. The ^1H NMR peaks of *meso*-hydrobenzoin occur at δ 1.23, 4.31, and 6.77−6.90 and the ^{13}C peaks at δ 79.1, 128.5, 128.7, 129.0, and 129.3.

(structure **14** and eq 2) and the slower reaction with secondary amines (**16**) (eq 3) provide a reliable and convenient preparation of group 4 metal complexes bearing different ligands, such as **17** and **18**, which ligands can be selectively displaced by reaction with a main-group organometallic reagent. Such derivatives as **17** and **18** can be directly combined with MAO or an aluminum alkyl to generate a modified olefin polymerization catalyst system,[12] or they can be treated with 2 equiv of *n*-butyllithium in THF to effect selective loss of the chloride ligands and the formation of the labile complexes **19** and **20** (eqs 4 and 5). Just as the $Bu_2M_tCl_2$ derivatives themselves, **19** and **20** decompose cleanly above −78 °C to the corresponding group 4 derivatives $(RO)_2M_t$ and $(R_2N)_2M_t$. Such so-called transition-metal carbenoids have been shown to add readily to C═C, C═O, and related linkages in a process termed epimetalation[18] and have shown great promise in organic synthesis.[19−21] As an illustration of the great utility of epimetalation in synthesis, consider the conversion of ethylene (**22**), via its epimetalation adduct **23**, into **24** by means of two different insertions of reagents into its vicinal C−Ti bonds (eq 6).[19]

$$\underset{\mathbf{18}}{(R_2N)_2M_tCl_2} \xleftarrow[\substack{-BuH\\ \text{eq. 3}}]{2\,R_2NH\,(\mathbf{16})} \underset{(\mathbf{1})}{Bu_2M_tCl_2} \xrightarrow[\substack{-BuH\\ \text{eq. 2}}]{2\,ROH\,(\mathbf{15})} \underset{\mathbf{17}}{(RO)_2M_tCl_2} \qquad (2,3)$$

$$\underset{\mathbf{20}}{Bu_2M_t(NR_2)_2} \xleftarrow[\substack{-LiCl\\ \text{eq. 5}}]{\mathbf{18}} \substack{2\,BuLi\\ -78\,^{\circ}C} \xrightarrow[\substack{-LiCl\\ \text{eq. 4}}]{\mathbf{17}} \underset{\mathbf{19}}{Bu_2M_t(OR)_2} \qquad (4,5)$$



The preparation of titanium(II) isopropoxide (**21**) free of any undesirable $LiOPr^i$ byproduct[22a] illustrates the ease and efficiency of the method.[22b] To a solution of 1 equiv of $TiCl_4$ in anhydrous toluene at −78 °C and under argon is added 2 equiv of BuLi in hexane in order to form Bu_2TiCl_2. After 30 min of stirring at −78 °C, 2 equiv of anhydrous isopropyl alcohol in hexane is slowly added to produce $Cl_2Ti(OPr^i)_2$.[23] After 30 min of stirring and warming to 0 °C, the mixture is recooled to −78 °C and then treated with an additional 2 equiv of BuLi to yield $Bu_2Ti(OPr^i)_2$. After subsequent warming to 20 °C the mixture turns black, signaling the formation of $Ti(OPr^i)_2$. The volatiles are removed under reduced pressure, and anhydrous, deoxygenated toluene is added. The LiCl is filtered off to provide a toluene solution of black $Ti(OPr^i)_2$, free of any byproduct lithium salts. Here again, all of the foregoing chemical transformations can be conducted in a one-flask operation.

In summary, by the metalating action of group 4 metal derivatives of the type $Bu_2M_tCl_2$ on various Brønsted acids, a wide array of both metallocene and nonmetallocene olefin polymerization procatalysts has become readily accessible and a highly convenient route to subvalent transition-metal carbenoid reagents for organic synthesis has been established.

Acknowledgment. Our research on this topic over the past decade has been supported at various times by Akzo Corporate Research America, the U.S. National Science Foundation, Solvay, SA, Brussels, Belgium, and the Alexander von Humboldt Stiftung, Bonn, Germany. Technical advice and assistance have been provided by Mr. John N. Gitua.

OM0104621

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(17) Heteroatom-tethered constrained-geometry catalysts are covered in the following Dow European patent application: Stevens, J. C.; Timmers, F. C.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Patent EP-416-815-A2, March 13, 1991.

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(19) Eisch, J. J.; Gitua, J. N.; Otieno, P. O.; Shi, X. *J. Organomet. Chem.* **2001**, *624*, 229.

(20) Kulinkovich, O. G.; Meijere, A.d. *Chem. Rev.* **2000**, *100*, 2789.

(21) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835.

(22) (a) Although $Ti(OPr^i)_2$ can be and indeed has been generated from the action of 2 equiv of *n*-butyllithium on $Ti(OPr^i)_4$ at −78 °C in hexane, toluene, or THF,[19] the generated byproduct, 2 equiv of $LiOPr^i$, is soluble in the hydrocarbon or ether medium and hence cannot be separated from the $Ti(OPr^i)_2$ reagent. The $LiOPr^i$ can by its strongly basic character interfere with the reactions of $Ti(OPr^i)_2$ with unsaturated organic substrates. (b) The sequence of steps described here starts with 20 mmol of $TiCl_4$ dissolved in 80 mL of THF, which at −78 °C under argon is treated with 40 mmol of *n*-butyllithium in 25 mL of hexane.

(23) Titanium(IV) compounds bearing different ligands, such as $ClTi(OPr^i)_3$ and $Cl_2Ti(OPr^i)_2$, have previously been shown to be readily prepared by a redistribution reaction between appropriate molar ratios of $TiCl_4$ and $Ti(OPr^i)_4$ at 0 °C: Reetz, M. T.; Westermann, J.; Steinbach, R.; Wenderoth, B.; Peter, R.; Ostarek, R.; Maus, S. *Chem. Ber.* **1985**, *118*, 1421. The method for preparing $Cl_2Ti(OPr^i)_2$ reported here does not require the synthesis of the $Ti(OR)_4$ component beforehand and hence is easily extensible to the preparation of other $Cl_2Ti(OR)_2$ species by simply treating Bu_2TiCl_2 with 2 equiv of the requisite alcohol, ROH.