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Catalyst structural effects in titanocene-catalyzed pinacol coupling: activity, stereoselectivity and mechanistic implications

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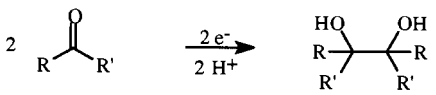
This manuscript is dedicated to Myron Rosenblum, an inspirational mentor and a pioneer in organometallic chemistry, on the occasion of his 75th birthday

Abstract

The effects of catalyst structural variation on the activity and selectivity of titanocene-catalyzed pinacol coupling of cyclohexane carboxaldehyde by Mn/TMSCl have been evaluated. Complexes which have been tested include: Cp_2TiCl_2 (**1**), Cp_2TiBr_2 (**2**), $(C_5Me_5)_2TiCl_2$ (**3**), (1,3-*t*-$Bu_2C_5H_3)_2TiCl_2$ (**4**), (1,3-*t*-$Bu_2C_5H_3$)(Cp)$TiCl_2$ (**5**), *ansa*-[(η^5-tetrahydroindenyl)CH_2CH_2(η^5-tetrahydroindenyl)]$TiCl_2$ (**6**), and *ansa*-[(η^5-Cp)CH_2CH_2(η^5-fluorenyl)]$TiCl_2$ (**7**). Cp_2TiCl_2 (**1**) is the most active (pre)catalyst for pinacol silylether (**8a**) formation, but Brintzinger's complex **6** provides the best DL/*meso* diastereoselectivity (5:1). Complexes **2**, **4** and **7** slowly catalyze the predominant formation of the corresponding pinacol acetal **9a** as a secondary product. Comparative stoichiometric reactions of benzaldehyde/Me_3SiCl with [$Cp_2TiCl{\cdot}MnCl_2(THF)_2{\cdot}Cp_2TiCl$] (**10**) and [$Cp_2TiCl]_2$ (**11**) result in highly diastereoselective pinacol silylether formation with binuclear **11** (29:1), but primarily the production of pinacol acetal (**9b**) from trimetallic **10**, suggesting a dominant role for the binuclear complex (or derived mononuclear species) in the catalytic systems employing Cp_2TiCl_2/M/TMSCl, contrary to previous suggestions.

1. Introduction

The pinacol coupling reaction (Eq. (1)) is an efficient method for generating carbon–carbon bonds with 1,2-difunctionality [1]. Unfortunately, traditional metal reductants for pinacolization (e.g. Na, Mg) display limited functional group tolerance and rarely afford appreciable stereoselectivity.



(1)

Low valent transition metal compounds, employed stoichiometrically or catalytically in combination with a stoichiometric reducing metal, have been shown to induce pinacol coupling of aromatic aldehydes with good D,L-diastereoselectivity. Most of these stoichiometric transition metal reagents have been Ti-based, including $TiCl_3$ [2], Cp_2TiCl_2/RMgX [3] and $[Cp_2TiCl]_2$ [4], which pinacolize aromatic aldehydes with good to excellent DL/*meso* diastereoselectivity.

Some transition metal and lanthanide compounds have been found to catalyze pinacol coupling when combined with a suitable reductant and a silyl halide; these systems include: $TiCl_3(THF)_3$/Zn/Me_3SiCl [5], titanium–Schiff base complexes/Mn/Me_3SiCl [6], $CpV(CO)_4$/Zn/Me_3SiCl [7], and SmI_2/Mg/Me_3SiCl [8]. The Ti-based systems afford moderate to excellent yields and high DL/*meso* diastereoselectivities with aromatic aldehydes. The half sandwich vanadium complex and the SmI_2-based systems couple both aliphatic and aromatic aldehydes, the former to the corresponding acetal pinacol with modest stereoselectivity and the latter to the pinacol silylethers with unreported stereoselectivity.

Metallocene-based *catalytic* systems have been reported recently by three groups (Eq. (2)) [9–11]. An attractive feature of these systems is the potential for tailoring the catalyst to enhance activity and stereoselectivity, including enantioselectivity. Gansauer and co-

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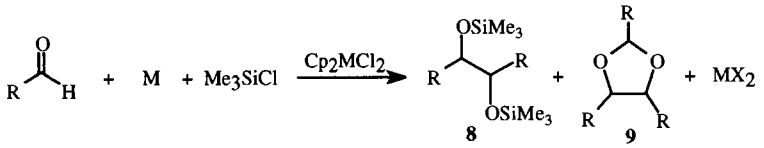
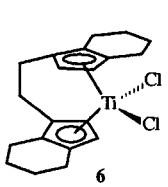
workers found that pinacol coupling of aromatic aldehydes can be achieved in excellent yield and with DL/*meso* ratios of 10–15:1 using titanocene dichloride/Zn–$MgBr_2$/Me_3SiCl [9a]. We reported on the successful pinacol coupling of aromatic *and aliphatic aldehydes* by the system Cp_2TiCl_2/Mn/Me_3SiCl in THF [10]. Moderate to excellent yields and diastereoselectivity are achieved (comparable to the Cp_2TiCl_2/Zn/$MgBr_2$ system), the former decreasing and the latter increasing with the steric bulk of the aldehyde substrate. Hirao and co-workers found that Cp_2VCl_2/Zn/Me_3SiCl catalyzes pinacol coupling of aliphatic aldehydes but with limited DL-stereoselectivity [11]. In contrast, the same group found that aliphatic aldehyde pinacolization using Cp_2TiCl_2/Zn/Me_3SiCl was strongly solvent dependent; in THF, the major product was the pinacol disilylether (**8**) while in DME it was the corresponding pinacol acetal (**9**) [11].



(2)

The effects of varying the metallocene structure on the efficiency and stereoselectivity of pinacol coupling have received little attention. Racemic Brintzinger's complex **6** [12] was shown by Gansauer to catalyze the pinacol reaction of aromatic aldehydes [13] in good yields and with high DL/*meso* selectivity (ca. 20:1). We have found that moderately *enantioselective* pinacolization of benzaldehyde (60% ee) can be effected using non-racemic **6** [10]. In a recent collaborative study with the Halterman group, the pinacolization selectivity of the indenyl and tetrahydroindenyl derivatives, **12** and **13**, was compared [14]; interestingly, the *ansa*-bis-indenyl compound **12** catalyzed the pinacolization of benzaldehyde with slightly higher diastereoselectivity than the tetrahydroindenyl derivative **13** (4.6:1 vs. 3.4:1), but with negligible enantioselectivity compared to 32% ee with **12**, showing the operation of subtle electronic and steric effects on stereoselectivity.



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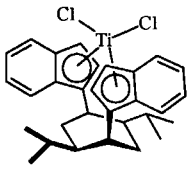
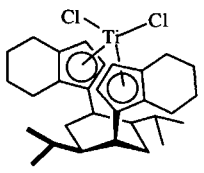
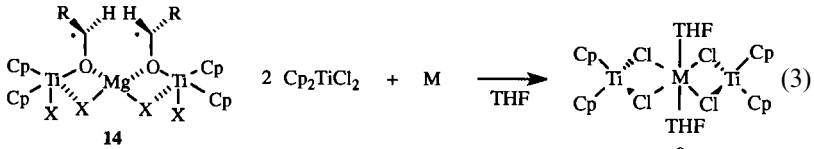


(*1R,2R,4R,5R*)-**12**



(*1R,2R,4R,5R*)-**13**

Mechanistic understanding of (but not speculation about) these metallocene-catalyzed reactions is limited. In the titanocene-based systems, it is generally presumed that reduction of Cp_2TiCl_2 produces an odd electron Ti(III) species which is the active reductive coupling agent. The latter, upon association with the carbonyl substrate induces C–C bond formation (via dimerization) to give a pinacolate which is either hydrolyzed (in the stoichiometric systems) or silylated (in the catalytic systems). However, the identity of the Ti(III) species which is responsible for inducing C–C bond formation and determining the stereoselectivity of the reaction is unclear. The high stereoselectivity observed in the Cp_2TiCl_2/RMgX [3] and Cp_2TiCl_2/Zn/$MgBr_2$/Me_3SiCl [9] systems has been rationalized in terms of a Mg-bridged *trimetallic* intermediate/transition state, **14**, which places the R groups *anti* in the developing pinacolate to reduce the amount of steric hindrance, leading to the DL-pinacol product. The proposed trimetallic species draws precedent from structurally characterized Ti(III) complexes of the type $[Cp_2TiCl(MCl_2)Cp_2TiCl]$ (**10**) (M = Zn, Mg, Mn) which are produced in the reactions of Cp_2TiCl_2 with the corresponding metals (Eq. (3)) [15]. On the other hand, the stoichiometric pinacol coupling effected by $[Cp_2TiCl]_2$ (**11**) has been accounted for by the agency of mononuclear Cp_2TiCl [4]. The sterically crowded environment produced when two Cp_2TiCl(aldehyde) fragments come together (in a *bimetallic* transition state) was considered responsible for the high diastereoselectivity seen.



(3)

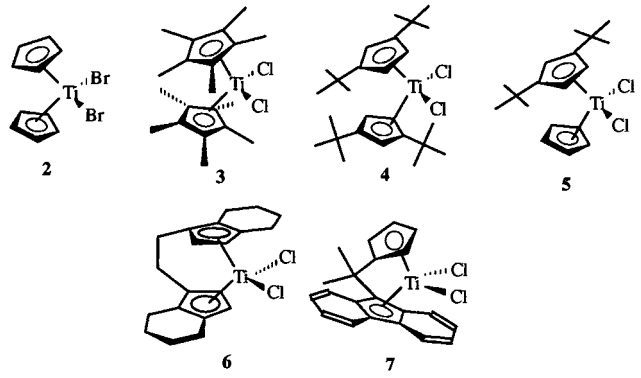
Scattered observations on the effects of the solvent and additives on stereoselectivity, our demonstration of enantioselective pinacol coupling, and the need for improved activity, stereoselectivity and reaction scope

have prompted us to obtain catalyst structure/activity relationships and a better understanding of the pinacolization mechanism, particularly the identity of the product-determining intermediate. Our efforts in this direction are reported herein.

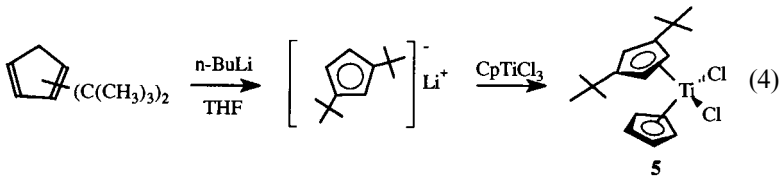
2. Results and discussion

Several titanocene derivatives, i.e. **2**–**7**, were selected to test their effectiveness as (pre)catalysts in the coupling of aliphatic aldehydes. A range of steric, electronic and conformational features of the complexes was represented to assess their influence on the facility and diastereoselectivity of coupling. The limited pinacolization reactivity of aliphatic aldehydes and the variable stereoselectivities achieved in their Cp_2TiCl_2-catalyzed reactions [6,10] provide a convenient and useful testing ground for the evaluation of catalyst structure/activity/selectivity effects.

The dibromide complex **2** was chosen because of its electronic properties vis a vis the chloride derivative **1**. The redox potentials for Cp_2TiBr_2 and Cp_2TiCl_2 [16] suggest that the former should be somewhat more easily reduced but once reduced should be a weaker reductant, and probably a less reactive coupling agent (if inner sphere electron transfer is rate-limiting). On the other hand, the permethylated complex **3** is more difficult to reduce than the parent Cp_2TiCl_2 [17], and hence, the resulting Ti(III) complex should be more reactive than the parent system. Complex **3** is also more sterically demanding, existing exclusively as a monomer (Cp^*_2TiCl) in its reduced state [18], which could have a considerable impact on reactivity and stereoselectivity by limiting access to some bimetallic, but probably not the less crowded trimetallic intermediates. Sterically hindered bis-(η^5-di-*tert*-butylcyclopentadienyl)titanium dichloride (**4**) also exists exclusively in monomeric form in its +3 state [19], but should be somewhat less reducing than Cp^*_2TiCl. The mixed ligand complex **5** is distinctive in having two non-equivalent Cp-type ligands, one of which is bulky and the other which is unhindered. It was hypothesized that in the reduced bi- or trimetallic intermediate derived from **5**, the bulky 1,3-di-*t*-butylcyclopentadienyl ligands would orient *anti* to one another, favoring C_2 symmetric intermediates, and possibly, the C_2 symmetric D,L-products. Conformationally constrained *ansa*-bridged complexes **6** [12] and **7** [20] were studied as well. We anticipated that one conformation of a (*bi* or *tri*)-metallic intermediate might predominate which could favor the formation of a particular diastereomeric pinacolate.

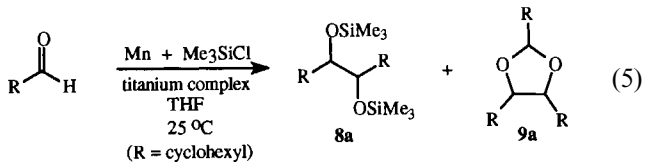


All of the titanocene derivatives, except **5**, were known compounds and were prepared according to the reported methods. Complex **5** was synthesized by treatment of $CpTiCl_3$ with $LiC_5H_3(t\text{-}Bu)_2$ (Eq. (4)). ^{1}H- and ^{13}C-NMR spectra and a high resolution FAB mass spectrum of **5** supported its structural assignment.



(4)

Pinacol coupling reactions catalyzed by complexes **2**–**7** were conducted using cyclohexane carboxaldehyde as the test substrate under our previously developed conditions (Mn/TMSCl/THF, 20 °C, Eq. (5)) [10]. In



(5)

Table 1
Pinacol coupling of cyclohexane carboxaldehyde catalyzed by titanocene derivatives

Catalyst	Conversion (%)	DL/*meso* selectivity	
		Disilylether	Acetal [a]
1	95	2:1[12]	–
2	33	–	6:1
3	40	1:1	–
4 [b]	29	–	6:1
5	10	–	4:1
6	33	5:1	–
7 [c]	20	2:1	2.5:1

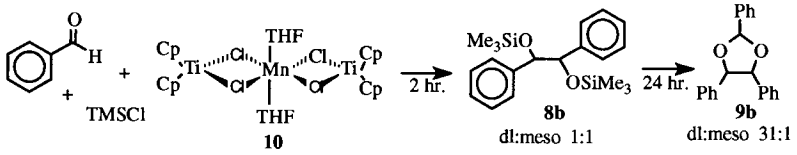
[a] Two *meso* isomers formed.
[b] Reaction run for four days.
[c] Activated Zn used instead of Mn.

each case, the Ti-complex (10 mol%), Mn (five equivalents) and Me_3SiCl (2.5 equivalents) in THF were stirred together for 30 min before the addition of substrate (one equivalent). The reactions were then monitored by GC analysis over 48 h. A simple extractive work-up and NMR and GC/MS analysis revealed that the pinacol disilylether (**8a**) and/or pinacol acetal (**9a**) were formed; the results obtained with complexes **1**–**7** are summarized in Table 1. The stereochemistry of the products was established by NMR and by comparison with authentic samples.

In all cases, the complexes tested were less active than Cp_2TiCl_2, the reactions being incomplete even at 48 h. The (pre)catalysts **1**, **3** and **6** produced the pinacol silylether (**8a**) exclusively, while **2**, **4** and **5** favored selective formation of the pinacol acetal (**9a**). Generally speaking, the faster reactions (with higher conversion) produced **8** while the slower reactions produced **9**. GC monitoring of the reactions which gave the acetal (**9**) indicated that it was a secondary product, derived from subsequent reaction of the initially formed disilylether with additional aldehyde. Experiments to probe the mechanism of this secondary reaction (or to suppress it) were not conducted, but a Lewis-acid promoted process seems likely (e.g. by $MnCl_2$ or Me_3SiCl). The observed pinacol silylether DL/*meso* stereoselectivities (determined by GC/NMR) were poor to moderate (with **6**) as were the acetal stereoselectivities (with **2**, **4**). Although the pinacol D,L-diastereoselectivity observed with **6** and the acetal diastereoselectivity with **2** and **4** were encouraging, the low conversions and long reaction times make these reactions synthetically unattractive. Clearly, the catalyst structure has a strong effect on the pinacolization chemo- and stereoselectivity, but no obvious structure/selectivity correlations emerged from this set of catalysts. Further studies will therefore be necessary to obtain complexes which combine high stereodifferentiating ability with high activity.

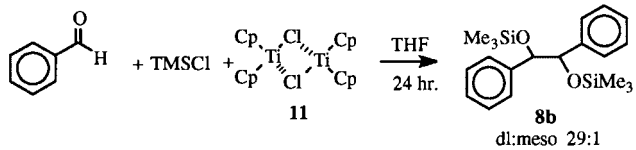
On the mechanistic front, it had been suggested that the reactive titanium species involved in these catalytic reactions was trimetallic, i.e. of the type $[Cp_2TiCl{\cdot}MCl_2(THF)_2{\cdot}Cp_2TiCl]$ (**10**) [3,9]. However, Schwartz's report of *stoichiometric* pinacolization of aldehydes by *binuclear* $[Cp_2TiCl]_2$ (**11**) [4] raises the possibility of the involvement of bimetallic (or monometallic) species in the pinacol formation. To address this issue, the bi- and trimetallic compounds **11** and **10** (M = Mn) were prepared according to literature methods [13,21] and their stoichiometric reactions with benzaldehyde/Me_3SiCl were carried out.

The trimetallic complex **10** was combined in stoichiometric quantity with benzaldehyde and Me_3SiCl in THF (Eq. (6)). Analyzing aliquots by GC, pinacol disilylether (**8b**) was detected after 2 h with a DL/*meso* ratio of 1:1. However, after 24 h no disilylether was detected; pinacol acetal (**9b**) was the only product present with an extraordinary DL/*meso* ratio of 31:1.



(6)

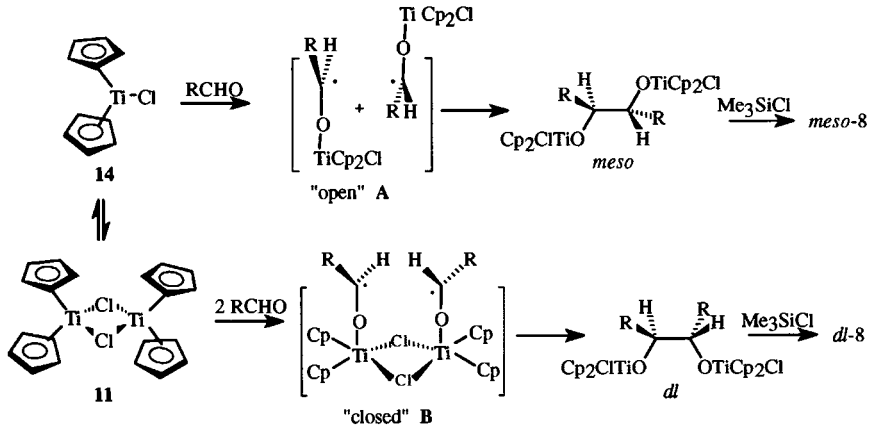
Similarly, bimetallic compound **11** was combined with benzaldehyde and Me_3SiCl in THF at room temperature. After 24 h, only the pinacol silylether (**10**) (and some unreacted aldehyde) were detected by GC, the former with excellent diastereoselectivity (29:1 DL/*meso*); little of the acetal (**9b**) was detected even after 4 days (Eq. (7)).



(7)

The results using stoichiometric quantities of the bimetallic complex **11** are thus similar to those achieved in the catalytic pinacol coupling of benzaldehyde using $Cp_2TiCl_2/M/Me_3SiCl$ (M = Mg, Zn, Mn). In both reactions, the pinacol disilylether (**8b**) was the exclusive product formed with high DL/*meso* diastereoselectivity. Based on these findings, we conclude that the trimetallic complex **10** is not the *primary* product-producing intermediate in the catalytic pinacol reactions employing $Cp_2TiCl_2/M/Me_3SiCl$. Given the similar chemo- and stereoselectivity observed in the catalytic pinacol reaction of benzaldehyde and the corresponding stoichiometric reaction with binuclear $[Cp_2TiCl]_2$(**11**), it is likely that the same intermediate is involved in both of these reactions. We note that although both reactions are highly DL-selective, a significant difference between their stereoselectivities was observed, 13:1 versus 29:1. This difference may reflect some minor involvement of the trimetallic complex **10** (or some other less selective intermediate) in the catalytic reactions. The small but significant effect on pinacolization stereoselectivity of the metal reductant (e.g. Zn, Mg, Mn) and additives (e.g. MgX_2 [9a]) may reflect the small, variable contribution of these trimetallic intermediates to product formation.

In Scheme 1, we suggest a pathway for the DL-selective pinacolization which involves mono- and bimetallic complexes. Reduction (by Mn) of Cp_2TiCl_2 likely pro-



Scheme 1.

duces the relatively unreactive trimetallic complex **10** and bimetallic **11**, which may be in minor equilibrium with its monomer, Cp_2TiCl (**14**) [21]. Although either monometallic **14** or bimetallic **11** could react with aldehyde, C–C bond formation and stereodetermination is best accommodated in a bimetallic transition state, e.g. 'open' **A** or 'closed' **B**. The least hindered *anti* approach in **A** would produce the *meso*-pinacolate (and derived pinacol silylether) while the favored conformation of **B** would afford the DL product. Accordingly, we suggest that the high DL-stereoselectivity observed in the stoichiometric reaction with bimetallic **11** and the catalytic reactions with Cp_2TiCl_2 could be the result of a favored closed transition state **B** which minimizes steric repulsion between the R groups.

Although titanocene derivatives which are active catalysts for the highly stereoselective pinacolization of *aliphatic* aldehydes remain to be found, the present studies have revealed substantial effects of catalyst structure on the chemoselectivity and stereoselectivity of the pinacolization reaction. Perhaps most significantly, evidence has been obtained which points to a dominant role for bimetallic intermediates in titanocene-catalyzed pinacol coupling reactions.

3. Experimental

3.1. General

The organic reactants as well as $(\eta^5\text{-Cp})_2TiCl_2$ and $(\eta^5\text{-Cp})_2TiBr_2$ were obtained commercially. Bis(η^5-di-*t*-butylcyclopentadienyl)titanium dichloride [19], (η^5-Cp)titanium trichloride [22], $[(\eta^5\text{-Cp})_2TiCl\cdot MnCl_2\text{-}(THF)_2\cdot(\eta^5\text{-Cp})_2TiCl]$ [15], $[(\eta^5\text{-Cp})_2TiCl]_2$ [21], and Brintzinger's catalyst [12] were synthesized using reported methods. Isopropylidene(η^5-fluorenyl-η^5-cyclopentadienyl)titanium dichloride (**7**) [20] was provided by Professor Ronald Halterman. THF was distilled under nitrogen from sodium and benzophenone. Glassware was oven-dried and flushed with nitrogen before use. Liquids were transferred using dried syringes, and all sensitive solids were manipulated within the dry box. ^{1}H- and ^{13}C-NMR spectra were obtained using Varian XL-300 or Unity Inova-400 instruments. All NMR samples were dissolved in $CDCl_3$. Hewlett–Packard 5790A and Shimadzu 14A gas chromatographs were used for monitoring reactions. GC/MS were obtained on a Hewlett–Packard 5985 GC/MS instrument.

3.2. Synthesis of (η^5-di-tert-butylcyclopentadienyl)-(η^5-cyclopentadienyl)titanium dichloride (5)

A solution of (η^5-cyclopentadienyl)titanium trichloride (2.36 mmol, 0.517 g) [22] in dry THF (10 ml) was added dropwise to a 10 ml THF solution of Li(di-*tert*-butylcyclopentadienide) (from 1,3-di-*tert*-butylcyclopentadiene [23] (2.36 mmol, 0.420 g) and *n*-butyl lithium (1.6 M in hexanes, 1.48 ml) and stirred for 2 h. The resulting solution was then heated to reflux overnight. The solvent was removed by rotary evaporation and the remaining residue was triturated with a few portions of 1:1 methylene chloride and benzene. The solvent was removed from the red solution by rotary evaporation. Further purification of the residue by flash chromatography with 3:1 petroleum ether–ether as eluant afforded a spectroscopically pure dark-red solid **5** (90% yield). ^{1}H-NMR ($CDCl_3$): δ 1.25 (s, 18H), 6.54 (s, 2H), 6.58 (s, 5H), 6.90 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 28.44 (6C), 113.06 (1C), 114.87 (2C), 117.54 (5C). FABMS; *m*/*e* (relative intensity): 360.1 (M^+, 5.6), 325.1 (M − 35, 100), 295 (M − 65, 28.6), 290 (M − 70, 12.8), 275 (M − 85, 2.6), 260.1 (M − 100, 2.2), 245 (M − 115, 3.0), 176 (M − 184, 2.4).

3.3. Catalytic pinacol reactions of cyclohexane carboxaldehyde using complexes 1–7

To a side arm round bottom flask, was added activated 4Å molecular sieves (one scupula), titanocene

dichloride (0.05 g, 0.20 mmol), and manganese (50 mesh; 0.55 g, 10 mmol) under nitrogen. Dry THF (20 ml) was added and the mixture was stirred for 5 min while changing from red to green. TMSCl (0.63 ml, 5.0 mmol) was added via a syringe followed by cyclohexane carboxaldehyde (2.0 mmol) and the mixture was stirred at 20 °C for 15–48 h. After GC analysis indicated that no further conversion was occurring, the volatiles were removed by rotary evaporation, the residue was triturated with 4:1 petroleum ether–ether, and the washings filtered through Celite. Concentration of the filtrate followed by flash chromatography of the residue over silica gel using petroleum ether–ether as eluant provided the pinacol-bis-silylether (**8a**) and/or the pinacol acetal (**9a**) as colorless oils.

3.3.1. 1,2-Bis(trimethylsiloxy)-1,2-dicyclohexylethane (*8a*)

^{1}H-NMR ($CDCl_3$) major isomer + minor isomer (maj + min): δ 0.8–2.0 (m, 44H), 3.30 (d, $J = 6$ Hz, 4H); maj: 0.10 (s, 18H); min: 0.11 (s, 18H); (in benzene-d_6) maj: 3.34 (d, $J = 4$ Hz, 2H); min: 3.49 (d, $J = 8$ Hz, 2H). ^{13}C-NMR ($CDCl_3$) maj + min: 0.90, 1.09, 26.15, 26.30, 26.63, 29.92, 30.62, 31.88, 39.10, 39.77, 78.30, 78.80. GCMS (12 eV, EI); m/e (relative intensity): GC peak 1: 185.1 ($M^+ - 185.1$, 100), GC peak 2: 185.1 ($M^+ - 185.1$, 100).

3.3.2. 2,4,5-Tricyclohexyl-1,3-dioxolane (*9a*)

^{1}H-NMR ($CDCl_3$): δ 0.8–1.9 (m, 33H), 3.18 (dd, $J = 6$, 9 Hz, 1H), 3.34 (dd, J = 6, 9 Hz, 1H), 4.08 (d, $J = 7.5$ Hz); *meso* 1: δ 0.8–1.9 (m, 33H), 3.58 (d, $J = 5.4$ Hz, 2H), 4.41 (d, $J = 7.2$ Hz, 1H); *meso* 2: δ 0.8–1.9 (m, 33H), 3.64 (d, $J = 5.7$ Hz, 2H), 4.61 (d, $J = 4.8$ Hz, 1H); GCMS (12 eV, EI); m/e (relative intensity): 319 ($M^+ - 1$, 2), 237 ($M^+ - 83$, 85), 208 ($M^+ - 112$, 17), 192 ($M^+ - 112$, 17), 192 ($M^+ - 128$, 11), 109 ($M^+ - 211$, 95).

3.4. Stoichiometric pinacolization using *11*

The reaction was performed within the dry box; aliquots were removed to be analyzed by GC. $[Cp_2TiCl]_2$ (**11**) (0.50 mmol, 0.21 g) and THF (15 ml) were combined in a side arm flask and allowed to stir. TMSCl (1.1 mmol, 0.14 ml) was added followed by benzaldehyde (1.0 mmol, 0.10 ml). The reaction solution was stirred at room temperature (r.t.) for 2–3 days. Aliquots were removed from the reaction and worked up outside the dry box by filtration through Celite and solvent evaporation. The residue was triturated with petroleum ether/ether (4:1) and filtered through Celite again. This filtrate was injected onto the GC and analyzed. NMR and GC/MS analysis indicated that the product was the pinacol silylether (**8b**).

3.4.1. 1,2-Bis(trimethylsiloxy)-1,2-diphenylethane (*8b*)

^{1}H-NMR ($CDCl_3$) min: δ −0.29 (s, 18H), 4.24 (s, 2H), 7.00–7.18 (m, 10H); maj: −0.09 (s, 18H), 4.63 (s, 2H), 7.20, 7.31 (m, 10 H). ^{13}C-NMR ($CDCl_3$) maj + min: δ −0.50, 0.05, 79.38, 79.76, 126.85,127.12, 127.34, 141.80, 143.10. GCMS (12 eV, EI); m/e (intensity): 179.1 ($M^+ - 179.1$, 100) for both GC peaks.

3.5. Stoichiometric pinacolization by *10*

The procedure used in the pinacol reaction with bimetallic **11** was also used with **10** (0.302 mmol, 0.275 g), benzaldehyde (0.60 mmol, 0.10 ml), TMSCl (0.50 mol, 0.10 ml) and THF (15 ml). The reaction mixture was stirred at r.t. for 24 h and monitored by GC. Aliquots were removed from the reaction and worked up outside the dry box by filtration through Celite and solvent evaporation. The residue was triturated with petroleum ether–ether (4:1) and filtered through Celite again. NMR and GC/MS analysis indicated that the product was the pinacol acetal (**9b**).

3.5.1. 2,4,5-Triphenyl-1,3-dioxolane (*9b*)

^{1}H-NMR ($CDCl_3$) DL-isomer: δ 4.95 (d, $J = 8$ Hz, 1H), 4.98 (d, $J = 8$ Hz, 1H), 6.41 (s, 1H), 7.25–7.80 (m, 15 H); *meso*: δ 5.54 (s, 2H), 6.21 (s, 1H), 7.25–7.80 (m, 15H); GCMS (12 eV, EI); m/e (intensity): 196 ($M^+ -$ 106, 100), 180 ($M^+ - 122$, 2), 103 ($M^+ - 199$, 0.2).

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