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Rapid Access to Dimethylcyclopentadienyltitanium(IV) Amidinate, $(C_5R_5)TiMe_2[NR^1C(R^2)NR^3]$ (R = H and Me; R^2 = Me), Libraries

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Summary: Facile insertion of carbodiimides, $R^1N{=}C{=}NR^3$*, into a* $Ti{-}C_{Me}$ *bond of* $(C_5R_5)TiMe_3$ *(R = H and Me) (**2a** and **2b**, respectively) in pentane solutions at 25 °C provides a wide range of derivatives of* $(C_5R_5)TiMe_2[NR^1C(Me)NR^3]$ *(**1**) in high yield. Low barriers to racemization* (≤ 15 *kcal mol*$^{-1}$*) have been determined for derivatives of **1** where* $R^1 \neq R^3$*, and further, a preliminary screen has found some of these to be Ziegler−Natta catalyst precursors for the polymerization of ethylene upon activation with methylaluminoxane.*

The high activities and stereochemical control exhibited by many d^0 group 4 mono- and biscyclopentadienyl (Cp) metal-based catalysts in the Ziegler−Natta polymerization of α-olefins have generated considerable academic and commercial interest in the search for additional Cp and non-Cp metal complexes that can serve in a similar capacity.[1−3] In this regard, symmetric mono-Cp, mono-*N,N'*-bis(trimethylsilyl)benzamidinate metal complexes of the general structure $(C_5R_5)MX_2[NR^1C(R^2)NR^3]$ (**1**), where M = Ti or Zr; R = H or Me; X = Cl or Me; $R^1 = R^3 = SiMe_3$, and R^2 = Ph, are known to function as Ziegler−Natta catalyst precursors upon activation by methylaluminoxane (MAO).[4] Given this, the next logical step of inquiry would be to systematically vary both the steric and electronic nature of the amidinate organic substituents, R^1, R^2 and R^3, in **1** over a wide range in order to realize the full potential of this class of compound for the polymerization of α-olefins. Nowadays, one attractive approach to achieve this for a large number of derivatives is to identify synthetic methods that are amenable to providing a diverse range of supported amidinate metal complexes in high yield, and preferably, in a few number of steps, for the rapid production and screening of catalytic properties by combinatorial techniques.[5] Herein, we identify one such method that involves facile insertion of carbodiimides, $R^1N{=}C{=}NR^3$, into a $Ti{-}C_{Me}$ bond of the readily available trimethylcyclopentadienyl titanium complexes $(C_5R_5)TiMe_3$ (R = H and Me) (**2a** and **2b**, respectively),[6] to directly provide a range of new derivatives of **1** for M = Ti, R = H or Me, and X = R^2 = Me according to Scheme 1 and Tables 1 and 2. As the series of racemic asymmetric complexes **1b** and **1d−j** represent the first examples of amidinates that possess a chiral titanium metal center and as the configurational stability of Cp-based Ziegler−Natta catalysts are known to directly influence the degree of stereochemical control (i.e., tacticity) that can be achieved in the polymerization of α-olefins,[1] barriers to racemization for these complexes were determined by variable-temperature NMR, which serves to provide insights regarding the influence of steric and electronic effects of R^1 and R^3 on this parameter. Finally, by using a minimal set of conditions under which catalytic activity might be expressed, a preliminary screen found that two members of the library of compounds listed in Table 1, **1a** and **1b**, are indeed active for the polymerization of ethylene in the presence of MAO, with the level of this activity being closely tied to both the steric and electronic nature of the organic substituents on the amidinate ligand. With the availability of polymer-supported carbodiimides,[7] the results reported here now provide a strong foundation and impetus for the directed combinatorial search for new α-olefin polymerization catalyst precursors based on the structure of **1**.

Carbodiimides have previously been shown to insert into a metal−carbon bond of early transition and group 13 organometallic compounds to form amidinate com-

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[1] For a recent review, see: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed., Engl.* **1995**, *34*, 1143−1170.

[2] For recent examples of Cp-based catalyst precursors, see: (a) Amor, F.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **1998**, *558*, 139−146. (b) Sinnema, P.-J.; Liekelema, K.; Staal, O. K. B.; Hessen, B.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1998**, *128*, 143−153. (c) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152−2154. (d) Doherty, S.; Errington, R. J.; Jarvis, A. P.; Collins, S.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1998**, *17*, 3408−3410, and references therein.

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[5] For some recent examples, see: (a) Sigman, M. S.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 4901−4902. (b) Shimizu, K. D.; Cole, B. M.; Krueger, C. A.; Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed., Engl.* **1997**, *36*, 1704−1707. (c) Gilbertson, S. R.; Wang, X. *Tetrahedron Lett.* **1996**, *37*, 6475−6478.

[6] For **2a**, see: Giannini, U.; Cesca, S. *Tetrahedron Lett.* **1960**, *14*, 19−20. Compound **2b** is commercially available from Strem Chemicals, Inc.

[7] (a) Weinshenker, N. M.; Shen, C.-M. *Tetrahedron Lett.* **1972**, *32*, 3281−3284. (b) Drewry, D. H.; Gerritz, S. W.; Linn, J. A. *Tetrahedron Lett.* **1997**, *38*, 3377−3380. (b) Gelbard, G.; Vielfaure-Joly, F. *Tetrahedron Lett.* **1998**, *39*, 2743−2746.

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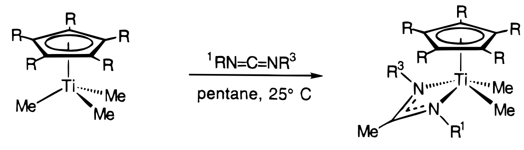
Scheme 1



2a: R = H
2b: R = Me

1

Table 1. Analytically Pure Derivatives of 1 Prepared According to Scheme 1 and Barriers to Racemization at the Coalescence Temperature

	R^1	R^3	$\Delta G_c^‡$ (kcal mol^{-1})	T_c (°C)
R = H				
1a	Cy	Cy		
1b	^{t}Bu	2,6-$Me_2C_6H_3$	12.6	233
R = Me				
1c	Cy	Cy		
1d	^{t}Bu	Et	14.9	308
1e	^{t}Bu	^{i}Pr	14.1	295
1f	^{t}Bu	Cy	15.2	293

Table 2. Additional Derivatives of 1 (R = H) Prepared According to Scheme 1 for Which Barriers to Racemization at the Coalescence Temperature Have Been Measured

	R^1	R^3	$\Delta G_c^‡$ (kcal mol^{-1})	T_c (K)
R = H				
1g	^{t}Bu	Et	12.1	243
1h	^{t}Bu	^{i}Pr	13.7	283
1i	^{t}Bu	Cy	14.7	283
1j	^{t}Bu	Ph	11.0	223

plexes,[8] and as Tables 1 and 2 show, this was also found to be true for **2a** and **2b**, where similar insertion processes occurred rapidly and exothermically with a range of carbodiimides[9] at 25 °C in pentane solution. Importantly, in each case, ^{1}H NMR (400 MHz, benzene-d_6) spectroscopy revealed that the desired amidinate **1** was produced in a near quantitative yield with no evidence of multiple insertions of the carbodiimide having occurred. On a preparative scale, simple removal of the volatiles provided the desired compounds listed in Table 1 in essentially pure form as either dark-red or orange crystalline solids that provided analytically pure samples upon recrystallization from pentane at −35 °C.[10,11] The derivatives listed in Table 2, however, possess physical properties, such as noncrystallinity and/or low thermal stability, which have so far thwarted attempts to secure satisfactory chemical analyses. Nonetheless, for comparison purposes, we feel justified in including this latter group of compounds for discussion, as their ^{1}H NMR spectra are exceedingly clean and strongly supportive of their structural assignments being that of **1**.[11] With regard to the anticipated generality of the reaction shown in Scheme 1, it can be noted that the only limitation that we have encountered so far is with attempts to prepare derivatives of **1** that bear exceedingly bulky organic substituents, such as $R^1 = R^3 = {}^t$Bu or $SiMe_3$. In these instances, the process fails at 25 °C, as insertion is either extremely slow at this temperature or it does not occur at all. Unfortunately, at more elevated temperatures (e.g., ≥50 °C), thermal decomposition of the titanium starting materials now becomes competitive with productive insertion of these bulky carbodiimides.

A common feature of the variable-temperature ^{1}H NMR spectra for all the asymmetric derivatives of **1** documented here is the occurrence of two separate resonances for the diastereotopic methyl groups attached to the chiral titanium center that are observed at the slow exchange limit for racemization.[11] As temperature is increased, these two resonances are observed to first coalesce and then to sharpen to a single strong resonance at the fast exchange limit. Using a standard proceedure,[12] analyses of these spectra yield barriers to racemization at the coalescence temperature, $\Delta G_c^‡$, that are recorded in Tables 1 and 2 for each of the asymmetric complexes. As can be noted upon inspection, all the values so far obtained are associated with barriers that are too low in energy to allow for configurational stability of these complexes at room temperature.[13] Such low observed values for asymmetric derivatives of **1** are in keeping with theoretical calculations of the potential energy surface for [M(bidentate)(unidentate)$_3$] complexes which predict very shallow barriers to racemization for bidentate ligands that have a small bite angle, θ_b, such as that of the amidinate group, where θ_b is known to be in the range 60−62°.[14,15] Upon further analysis of the experimental data, however, two interesting trends can be discerned that bear on the steric and electronic influences of the R^1 and R^3 substituents on the racemization barrier of these compounds. To begin, it can be seen by Table 2 that as the steric bulk of R^3 increases, so does the racemization barrier. An exception to this trend is noted for R^3 = Ph, which has a smaller barrier than the case where R^3 = Et; however, increasing the steric

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(8) (a) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1974**, 1579−1582. (b) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2611−2617. (c) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654−660. (d) Lechler, R.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1989**, *359*, 1−12. (e) Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 5183−5194.

(9) Except for R^3 = Et, which is commercially available, the ^{t}BuN=C=NR^3 derivatives used in this study were conveniently obtained in high yield by tin(II)-mediated heterocumulene metathesis of the corresponding isocyanates R^{3}NCO using commercially available HN(SiMe$_3$)^{t}Bu; see: Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1998**, *120*, 5585−5586.

(10) Representative procedure (conducted in drybox). To a solution of 140 mg (0.89 mmol) of CpTiMe$_3$ (**2a**) in 1 mL of pentane was added a solution of 183 mg (0.89 mmol) of 1,3-biscyclohexylcarbodiimide in 1 mL of pentane by pipet at 25 °C. After ~5 min, the reaction mixture turned red in color, and after 15 min, a brick-red crystalline material began to precipitate from solution. The reaction mixture was left to stir for 18 h, and then the solvent removed in vacuo to provide a brick-red solid, which was recrystallized from pentane at −35 °C to provide 313 mg (97% yield) of **1a** as dark-red crystals: ^{1}H NMR (400 MHz, benzene-d_6) δ 1.05 (s, 6H), 0.9−1.2 (m, 6H), 1.35 (dq, 4H, J = 2.7 Hz, J = 11.5 Hz), 1.5−1.7 (m, 10H), 1.66 (s, 3H), 2.95 (tt, 2H, J = 3.9 Hz, J = 11.4 Hz), 6.30 (s, 5H). Anal. Calcd for $C_{21}H_{36}N_2Ti$: C, 69.22; H, 9.96; N, 7.67. Found: C, 69.10; H, 10.07; N, 7.73. In a similar fashion, **1b** (from **2a**) and **1c**−**f** (from **2b**) were prepared from the corresponding carbodiimides. For ^{1}H NMR spectra of these compounds, see the Supporting Information. Anal. Calcd for $C_{21}H_{32}N_2Ti$ (**1b**): C, 70.00; H, 8.95; N, 7.77. Found: C, 69.52; H, 8.85; N, 8.07. Anal. Calcd for $C_{26}H_{46}N_2Ti$ (**1c**): C, 71.87; H, 10.67; N, 6.45. Found: C, 71.62; H, 10.80; N, 6.47. Anal. Calcd. for $C_{24}H_{44}N_2Ti$ (**1d**): C, 70.57; H, 10.86; N, 6.86. Found: C, 70.51; H, 11.01; N, 6.80. Anal. Calcd for $C_{21}H_{40}N_2Ti$ (**1e**): C, 68.46; H, 10.94; N, 7.60. Found: C, 67.83; H, 10.28; N, 7.65. Anal. Calcd for $C_{20}H_{38}N_2Ti$ (**1f**): C, 67.78; H, 10.81; N, 7.90. Found: C, 67.62; H, 10.76; N, 7.89.

(11) Detailed information is provided in the Supporting Information.

(12) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(13) (a) Veciana, J.; Crespo, M. I. *Angew. Chem., Int. Ed., Engl.* **1991**, *30*, 74−76. (b) Pirkle, W. H.; Welch, C. J.; Zych, A. J. *J. Chromatogr.* **1993**, *648*, 101−109.

(14) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: New York, 1982; pp 52−56.

(15) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300.

size of this aromatic group once more increases barrier height (cf. **1b** vs **1j**). In comparing the Cp and Cp* (C_5Me_5) derivatives, in each case, there is an increase in barrier height on going from the former to the latter with the same R^3 group, but note that now between **1d** and **1f** there is not much change on going from $R^3 = Et$ to $R^3 = Cy$, which suggests that the steric effects of the amidinate substituents quickly become "saturated" in the Cp* series. These steric effects further suggest that the mechanism by which racemization occurs is through a "flipping" of the amidinate group that most likely proceeds via a distorted trigonal bipyramidal state in which steric interactions between R^3 and the cyclopentadienyl group are augmented relative to a preferred square-pyramidal configuration of these complexes.[16] Further, aromatic substituents on the amidinate might lower this barrier by encouraging an unsymmetric mode of amidinate binding, and structural studies are now being pursued in order to verify this.

In a preliminary screen, studies were undertaken to assess the ability of the analytically pure complexes **1a**−**f** to function as Ziegler−Natta catalyst precursors.[17] Gratifyingly, it was found that upon activation by only 80−90 equiv of MAO in toluene, which yielded golden-yellow homogeneous solutions in each case, **1a** was capable of polymerizing ethylene at 25 °C with a modest level of activity (22 kg PE $mol_{cat}^{-1}\ h^{-1}\ atm^{-1}$), whereas **1b**/MAO was substantially less active at 0.1 kg PE $mol_{cat}^{-1}\ h^{-1}\ atm^{-1}$. Unfortunately, none of the Cp* derivatives, **1c**−**f**, were found to be active in this screening.

In conclusion, the present work has served to introduce a new method for the direct production of a subclass of Ziegler−Natta catalyst precursors based on **1** that is characterized by extremely high yields and the absence of problematic side products that might also express catalytic activity. Importantly, this methodology should be quite compatible with libraries of supported carbodiimides to provide a diverse range of supported derivatives of **1** for rapid screening. Although the activity for PE production reported here is only modest for **1a** relative to what can be currently achieved with known d^0 group 4 metal complexes, it is important to point out that our polymerization studies have so far been conducted with only a very limited library of derivatives obtained by classical preparative methods, and we have employed only a simple screen for activity. It can be anticipated, therefore, that much higher activities might be achievable with an expanded library of **1**, higher MAO/**1** ratios, the isolation of discrete "single-site" cationic complexes from **1** possessing noncoordinating anions, and the formation of zirconium-based derivatives of **1** using a reaction analogous to Scheme 1 with known trimethylcyclopentadienylzirconium complexes, $(C_5R_5)ZrMe_3$ (R = H and Me).[1,18] Studies along these lines are now in progress.

Note Added in Proof: The crystal structures of **1a-d** and **1q** have now been determined, and full structural analyses will be detailed elsewhere.

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Supporting Information Available: ^1H NMR spectra of compounds **1b**−**j** in both the fast and slow exchange regions (16 pages). Ordering information is given on any current masthead page.

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[16] A similar amidinate flipping has been observed for the interconversion of diasteromers of the chiral molybdenum complex $(C_5H_5)Mo(CO)_2[N(CH_2Ph)C(Me)N\{(S)\text{-}CH(Et)Ph\}]$; see: Brunner, H.; Agrifoglio, G. *J. Organomet. Chem.* **1980**, *202*, C43−C48.

[17] In a typical procedure, a solution of 20 mg (55 μmol) of **1a** in 1 mL of toluene was rapidly mixed with 50 mL of a 10 wt % solution of MAO (∼80 equiv) in toluene in a pressure-reaction vessel that was charged with ethylene (2 atm). After 10 min, the vessel was quickly vented and the reaction quenched by pouring into a large volume (600 mL) of aqueous 10% HCl. After stirring 1 h, the PE was collected, sequentially washed with water, methanol, acetone, and pentane, and dried at 70 °C (10^{-3} Torr) for 48 h to provide 400 mg of polymer.

[18] For $CpZrMe_3$, see: (a) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732−1736. For Cp^*ZrMe_3, see: (b) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793−799