Reactions of Imines with Half-Open Titanocenes: Substituent Effects and Tandem Couplings with Nitriles and Isonitriles

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The syntheses and characterizations of half-open titanocenes containing bulky Cp ligands are described. Such species include Ti[1,3-$C_5H_3(t\text{-}C_4H_9)_2$](Pdl)($PX_3$) (Pdl = 2,4-$C_7H_{11}$, X = Me; Pdl = C_5H_7, X = Me or Et) and Ti[1,3-$C_5H_3(SiMe_3)_2$](2,4-C_7H_{11})(PMe_3) (C_7H_{11} = dimethylpentadienyl). The structure of Ti[1,3-$C_5H_3(t\text{-}C_4H_9)_2$]($C_5H_7$)$PMe_3$ was determined, and revealed markedly shorter Ti−C bonds for the open dienyl ligand as compared to the cyclic one. The first 2,4-C_7H_{11} complex undergoes a coupling reaction with imines, generating a chiral center with the opposite stereochemistry, as demonstrated by a solid-state structural determination, as occurs in a similar coupling reaction with the Ti(C_5H_5)(2,4-C_7H_{11}) fragment. In addition, mixed coupling reactions can be achieved through the addition of nitriles or isonitriles to the $C_6H_5C(H){=}N(i\text{-}C_3H_7)$-Ti($C_5H_5$)(2,4-$C_7H_{11}$) coupling product. These reactions result in the incorporation of either one equivalent of nitrile ($p\text{-}CH_3C_6H_4CN$) or four equivalents of isonitrile ($p\text{-}CH_3C_6H_4NC$). Structures of both of these species were determined, and a mechanism is proposed for the latter reaction.

Introduction

The coupling reactions of half-open titanocenes with some ketones,[1] isonitriles,[1] and alkynes[2] lead to multiple incorporations of the unsaturated molecules, but intermediate products have not to date been observable. This is perhaps an indication that once the first coupling occurs, the original dienyl fragment is converted to an even more reactive coordinated diene. In contrast, for reactions with imines, one equivalent is incorporated quite rapidly,[1] but the incorporation of a second equivalent can also be achieved, in a reaction which is significantly slower as a presumed result of greater steric demands of the imines which have been employed.[3] As a result, this has led to the possibility of bringing about mixed coupling reactions, in which an imine is first incorporated, followed by a second substrate, such as a ketone or isonitrile. In these reactions, a chiral center is generated selectively at the coupled imine carbon atom, and there is a potential for generating further chiral centers through subsequent reactions.[4] Because it could be possible for highly modified cyclopentadienyl ligands to alter the course of these coupling reactions, we therefore prepared several new half-open titanocenes and examined the effects that bulky substituents have on the coupling processes. In addition, new tandem coupling reactions of an imine with a nitrile or isonitrile were investigated.

Experimental Section

All preparations, reactions, and manipulations of these compounds were carried out under a prepurified nitrogen atmosphere, using either Schlenk techniques or a glovebox. Hydrocarbon, ethereal, and aromatic solvents were dried and deoxygenated by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Spectroscopic data were obtained as previously described.[5] The ^{13}C NMR spectra were not precisely integrated, but numbers of carbon atoms are reported in accord with their assignments. Elemental analyses were obtained from E & R Microanalytical Labs, Robertson Microanalytical Labs, or Desert Analytics. Pentadienyl anions[6] and Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3)[7] (C_7H_{11} = dimethylpentadienyl) were prepared as previously described.

Ti(1,3-*t*-$Bu_2C_5H_3$)(C_5H_7)[$P(CH_3)_3$] 1. To a red solution of Ti(1,3-*t*-$Bu_2C_5H_3$)Cl_3 (3.00 g, 9.05 mmol) in 50 mL tetrahydrofuran (THF) under a nitrogen atmosphere was added activated zinc dust (2.00 g, 30.6 mmol), which led to the formation of a green-blue solution, and the mixture was then stirred overnight. To the aquamarine solution was then added $P(CH_3)_3$ (0.940 mL, 9.08 mmol) and the mixture was stirred for 3 h. The solution was then cooled to −78° and K(C_5H_7) (3.00 g, 28.2

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mmol) in 50 mL of THF was added dropwise via a pressure equalizing addition funnel. The green solution turned violet immediately and was allowed to warm to room temperature, during which time it turned red-brown. The solvent was then removed in vacuo to give a brown-red solid. The solid was extracted with three 100 mL portions of ether and filtered through a Celite pad on a coarse frit. Concentration in vacuo of the red-brown filtrate to approximately 100 mL and cooling to −30° for 3 days gave 1.80 g (55%) of the product as air-sensitive yellow crystals (mp 139−141°). Anal. Calcd. for $C_{21}H_{37}PTi$: C, 68.01; H, 10.49. Found: C, 68.46; H, 10.12. ^{1}H NMR (benzene-d_6, ambient): δ 6.41 (t, 1H, J = 10 Hz, H-3), 6.36 (m, 2H, Cp), 4.74 (q, 2H, J = 10 Hz, H-2,4), 4.23 (t, 1H, J = 2.4 Hz, Cp), 1.83 (t, 2H, J = 8 Hz, H-1,5$_{exo}$), 0.96 (d, 9H, J = 5.4 Hz, $P(CH_3)_3$), 0.73 (s, 18H, $(CH_3)_3C$), −0.87 (q, 2H, J = 8 Hz, H-1,5$_{endo}$). ^{13}C NMR (benzene-d_6, ambient): δ 134.0 (s, 2C, Cp), 112.6 (d, 1C, J = 158 Hz, C-3), 94.2 (dt, 1C, J = 167, 5 Hz, Cp), 93.5 (dt, 2C, J = 158, 9 Hz, C-2,4), 89.8 (dt, 2C, J = 166, 7 Hz, Cp), 52.6 (tt, 2C, J = 148 Hz, J_{C-P} = 8 Hz, C-1,5), 32.4 (s, 1C, $(CH_3)_3C$), 31.3 (q of quintets, 6C, J = 125, 4 Hz, $(CH_3)_3C$), 19.9 (qd, 3C, J = 127 Hz, J_{C-P} = 12 Hz, $P(CH_3)_3$).

Ti(1,3-*t*-Bu$_2$C$_5$H$_3$)(C$_5$H$_7$)[P(CH$_2$CH$_3$)$_3$] 2. To a red solution of Ti(1,3-*t*-$Bu_2C_5H_3)Cl_3$ (3.00 g, 9.05 mmol) in 50 mL THF under a nitrogen atmosphere was added activated zinc dust (2.00 g, 30.6 mmol), leading to the formation of a green-blue solution, which was then stirred overnight. To the aquamarine solution was then added $P(CH_2CH_3)_3$ (1.60 mL, 10.8 mmol) and the mixture was stirred for 3 h. Then the solution was cooled to −78° and $K(C_5H_7)$ (3.00 g, 28.2 mmol) in 50 mL of THF was added dropwise via a pressure equalizing addition funnel. After identical treatment as above, the red-brown filtrate was concentrated to ca. 100 mL, and was cooled to −30° for 3 days to gave 1.48 g (40%) of the product as air-sensitive yellow-brown crystals (mp 119−121°). ^{1}H NMR (benzene-d_6, ambient): δ 6.41 (d, 2H, J = 2.5 Hz, Cp), 6.35 (t, 1H, J = 9.8 Hz, H-3), 4.81 (q, 2H, J = 9.9 Hz, H-2,4), 4.11 (t, 1H, J = 2.5 Hz, Cp), 2.00 (dd, 2H, J = 7, 11 Hz, H-1,5$_{exo}$), 1.38 (m, 6H, $P(CH_2CH_3)_3$), 0.74 (s, 18H, $(CH_3)_3C$), 0.71 (m, 9H, $P(CH_2CH_3)_3$), −0.82 (dd, 2H, J = 7, 11 Hz, H-1,5$_{endo}$). ^{13}C NMR (benzene-d_6, ambient): δ 134.0 (s, 2C, Cp), 111.3 (d, 1C, J = 158 Hz, C-3), 94.9 (dt, 1C, J = 164, 6 Hz, Cp), 93.6 (dd, 2C, J = 156, 10 Hz, C-2,4), 89.9 (dt, 2C, J = 166, 7 Hz, Cp), 54.3 (td, 2C, J = 149, 9 Hz, C-1,5), 32.4 (s, 2C, $(CH_3)_3C$), 31.3 (q of quintets, 6C, J = 125, 5 Hz, $(CH_3)_3C$), 19.1 (t, 3C, J = 131 Hz, J_{C-P} = 7 Hz, $P(CH_2CH_3)_3$), 8.1 (q, 3C, J = 126 Hz, $P(CH_2CH_3)_3$).

Ti(1,3-*t*-Bu$_2$C$_5$H$_3$)(2,4-C$_7$H$_{11}$)[P(CH$_3$)$_3$], 3. To a red solution of Ti(1,3-*t*-$Bu_2C_5H_3)Cl_3$ [8] (3.00 g, 9.05 mmol) in 50 mL THF under nitrogen was added activated zinc dust (2.00 g, 30.6 mmol), after which a green-blue color formed and the mixture was stirred overnight. To the aquamarine solution was added $P(CH_3)_3$ (0.940 mL, 9.08 mmol) and the resulting green solution was stirred for 3 h. The solution was then cooled to −78° and K(2,4-C_7H_{11}) (3.60 g, 26.8 mmol) in 50 mL of THF was added dropwise via a pressure equalizing addition funnel. After identical treatment as in the compound above, the red-brown filtrate was concentrated in vacuo to ca. 50 mL, and was cooled to −90° for over 3 weeks to gave 0.902 g (25%) of the product as an air-sensitive yellow-brown, lumpy solid (mp 55−58°). Anal. Calcd. for $C_{23}H_{41}PTi$: C, 69.68; H, 10.42. Found: C, 69.44; H, 10.31; N, 0.00. ^{1}H NMR (toluene-d_8, ambient): δ 7.38 (t, 1H, J = 2.7 Hz, Cp), 5.80 (s, 1H, H-3), 3.64 (d, 2H, J = 2.6 Hz, Cp), 2.20 (s, 6H, CH_3−Pdl), 1.67 (dd, 2H, J = 4.6, 2.0 Hz, H-1,5$_{exo}$), 1.00 (s, 18H, $(CH_3)_3C$), 0.93 (d, 9H, J = 4.5 Hz, $P(CH_3)_3$), −0.48 (d, 2H, J = 5.9 Hz, H-1,5$_{endo}$). ^{13}C NMR (toluene-d_8, ambient): δ 126.6 (s, 2C, Cp), 111.4 (d, 1C, J = 156 Hz, C-3), 104.7 (s, 2C, C-2,4), 102.3 (dt, 1C, J = 163, 7 Hz, Cp), 99.6 (dt, 2C, J = 171, 5 Hz, Cp), 57.4 (t, 2H, J = 14 Hz, C-1,5), 33.6 (q of quintets, 6C, J = 126, 5 Hz, $(CH_3)_3C$), 32.6 (s, 2C, $(CH_3)_3C$), 31.9 (q of m, 2C, J = 126 Hz, CH_3−Pdl), 20.1 (q, 3C, J = 128 Hz, J_{C-P} = 12 Hz, $P(CH_3)_3$).

Ti{1,3-[(CH$_3$)$_3$Si]$_2$C$_5$H$_3$}(2,4-C$_7$H$_{11}$)[P(CH$_3$)$_3$], 4. A solution of Ti{1,3-$[(CH_3)_3Si]_2C_5H_3$}Cl_3 [9] (1.80 g, 4.95 mmol) in 50 mL THF under nitrogen was stirred with activated zinc dust (0.70 g, 11 mmol) for 24 h. To the blue-green solution, $P(CH_3)_3$ (0.560 mL, 5.41 mmol) was then added at 0°. After overnight stirring, the mixture was cooled to −78° and K(2,4-C_7H_{11}) (2.00 g, 14.9 mmol) in 50 mL THF was added dropwise through a pressure equalizing addition funnel. After identical treatment as in the compound above, the red-brown filtrate was concentrated in vacuo to ca. 50 mL, and was cooled to −30° for 3 days to gave 0.32 g (15%) of the product as air-sensitive orange crystals (mp 160−162°). ^{1}H NMR (benzene-d_6, ambient): δ 7.81 (d, 1H, J = 6.7 Hz, Cp), 6.01 (s, 1H, H-3), 4.09 (d, 2H, J = 1.9 Hz, Cp), 1.98 (s, 6H, CH_3−Pdl), 1.74 (d, 2H, J = 5.3 Hz, H-1,5$_{exo}$), 0.98 (d, 9H, J = 4.9 Hz, $P(CH_3)_3$), 0.10 (s, 18H, $(CH_3)_3Si$), −0.75 (t, 2H, J = 4.9 Hz, H-1,5$_{endo}$). ^{13}C NMR (benzene-d_6, ambient): δ 122.2 (d, 1C, J = 166 Hz, Cp), 113.3 (d, 1C, J = 158 Hz, C-3), 111.4 (d, 2C, J = 170 Hz, Cp), 111.3 (s, 2C, Cp), 102.5 (s, 2C, C-2,4), 54.5 (t, 2C, J = 147 Hz, C-1,5), 31.2 (q, 2C, J = 119 Hz, CH_3−Pdl), 21.0 (q, 3C, J = 137 Hz, $P(CH_3)_3$), 1.5 (q, 6C, J = 117 Hz, $(CH_3)_3Si$).

Ti(1,3-*t*-Bu$_2$C$_5$H$_3$)(NMeCHPhCH$_2$CMe=CHCMe=CH$_2$), 6. To a solution of Ti(1,3-*t*-$Bu_2C_5H_3$)(2,4-C_7H_{11})$[P(CH_3)]_3]$ (0.25 g, 0.63 mmol) in 30 mL THF at −78° under a nitrogen atmosphere was added $C_6H_5C(H)NCH_3$ (0.080 mL, 0.65 mmol). On warming to room temperature a color change from orange to dark red resulted and the mixture was stirred overnight. The solvent was next removed in vacuo and the red sticky residue was extracted with two 30 mL portions of pentane. The extracts were filtered through a Celite pad on a coarse frit. The red filtrate was concentrated in vacuo to ca. 10 mL prior to cooling at −30° for 2 days. Removal of the supernatant via syringe and drying in vacuo gave 0.12 g (42%) of the product as an air-sensitive red microcrystalline powder (mp 92−94°). Anal. Calcd. for $C_{28}H_{41}NTi$: C, 76.51; H, 9.40; N, 3.20. Found: C, 76.39; H, 9.33; N, 3.16. ^{1}H NMR (benzene-d_6, ambient): δ 7.2−7.0 (m, 5H, Ph), 6.02 (t, 1H, J = 3 Hz, Cp), 4.88 (t, 1H, J = 3 Hz, Cp), 4.59 (dd, 1H, J = 7, 11 Hz), 4.13 (t, 1H, J = 3 Hz, Cp), 4.09 (s, 1H, H-3), 3.06 (obscd., 1H), 3.05 (s, 3H, NCH_3), 2.51 (d, 1H, J = 7 Hz), 2.26 and 2.23 (2m, 2H), 2.14 (s, 3H, CH_3−Pdl), 1.94 (s, 3H, CH_3−Pdl), 1.29 (s, 9H, $(CH_3)_3C$), 1.21 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (benzene-d_6, ambient): δ 145.5 (s, 1C, Ph), 142.6 (s, 1C, Cp), 142.5 (s, 1C, Cp), 126−129 (m, 5C, Ph), 122.3 (s, 1C, C-2 or 4), 116.6 (d, 1C, J = 152 Hz, C-3), 107.1 (dt, 1C, J = 165, 7 Hz, Cp), 102.8 (dt, 1C, J = 169, 7 Hz, Cp), 100.6 (dt, 1C, J = 168, 8 Hz, Cp), 92.8 (s, 1C, C-2 or 4), 75.4 (d, 1C, J = 135 Hz, C(H)N), 60.6 (t, 1C, J = 149 Hz, C-5), 48.4 (q, 1C, J = 132 Hz, $N(CH_3)$), 47.0 (t, 1C, J = 127 Hz, C-1), 33.8 (s, 1C, $(CH_3)_3C$), 33.5 (s, 1C, $(CH_3)_3C$), 32.8 (q of quintets, 1C, J = 126, 7 Hz, CH_3−Pdl), 32.0 (q of quintets, 1C, J = 126, 5 Hz, $(CH_3)_3C$), 31.7 (q of quintets, 1C, J = 126, 5 Hz, $(CH_3)_3C$), 29.4 (q of quintets, 1C, J = 126, 7 Hz, CH_3−Pdl).

Ti(C$_5$H$_5$){N(*i*-Pr)CHPhCH$_2$CMeCHCMeCH$_2$C[*p*-CH$_3$-(C$_6$H$_4$)]N}, 8. To a stirred solution of Ti(C_5H_5)(2,4-C_7H_{11})-[$C_6H_5C(H)NCH(CH_3)_2$]^3 (0.40 g, 1.1 mmol) in 50 mL ether under nitrogen at −78° was added *p*-tolunitrile (0.20 mL, 1.7 mmol, 1.5 eq). A rapid color change from dark red to bright red occurred upon the addition. After the mixture was warmed with stirring to room temperature, the solvent was removed in vacuo, yielding a red solid. The solid was in turn extracted with three 50 mL portions of pentane. The extracts were filtered through a Celite pad on a coarse frit. The bright red filtrate was concentrated in vacuo to ca. 20 mL and placed into a −30 °C freezer for 2 days. Removal of the supernatant via syringe and drying in vacuo gave 0.40 g (76%) of the

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Table 1. Crystal, Data, and Refinement Parameters for $C_{21}H_{37}PTi$, $C_{28}H_{41}NTi$, $C_{30}H_{36}N_2Ti$, and $C_{56}H_{63}N_5O_{0.5}Ti$

formula	$C_{21}H_{37}PTi$	$C_{28}H_{41}NTi$	$C_{30}H_{36}N_2Ti$	$C_{56}H_{63}N_5O_{0.5}Ti$
formula weight	736.75	439.5	472.5	862.0
temperature (K)	233	224	298	298
λ, Å	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$
unit cell dimensions				
a, Å	13.403(4)	10.420(4)	12.303(2)	11.286(3)
b, Å	19.143(8)	13.733(4)	26.807(4)	12.832(2)
c, Å	17.708(4)	18.843(7)	15.535(3)	19.672(4)
α	90	69.18(4)	90	79.05(1)
β	108.39(2)	81.24(4)	92.50(3)	82.17(2)
γ	90	89.48(3)	90	67.66(2)
volume (Å^3); Z	4312(2); 8	2488(1); 4	5118(1); 8	2581(1); 2
density (calc)	1.135	1.173	1.226	1.109
abs coeff, cm^{-1}	4.70	3.58	3.54	2.06
θ range	2.1−21.0°	2.0−22.5°	2.0−25.0°	2.1−22.5°
limiting indices	$-1 \le h \le 13$	$-11 \le h \le 11$	$-14 \le h \le 14$	$-1 \le h \le 12$
	$-1 \le k \le 19$	$-13 \le k \le 14$	$0 \le k \le 31$	$-13 \le k \le 13$
	$-17 \le l \le 17$	$0 \le l \le 20$	$0 \le l \le 18$	$-21 \le l \le 17$
reflns collected	5781	6758	5368	7512
indpendent reflns; n: $I > n\sigma(I)$	4620; 2	6527; 2	4467; 2	6328; 2
$R(F)$	0.047	0.077	0.053	0.106
$R(wF^2)$	0.106	0.094	0.090	0.237
max/min diff. Fourier peak (e/Å^3)	0.50/−0.28	0.64/−0.20	0.36/−0.38	0.61/−0.70

product as an air-sensitive red solid (mp 138−140°). Anal. Calcd. for $C_{30}H_{36}N_2Ti$: C, 76.25; H, 7.68; N, 5.93. Found: C, 76.08; H, 7.72; N, 5.86. ^{1}H NMR (benzene-d_6, ambient): δ 7.39−6.98 (9H), 6.69 (s, 1H), 5.77 (s, 5H, Cp), 4.91 (d, 1H, J = 6.2 Hz), 4.69 (s, 1H), 4.49 (s, 1H), 4.07 (septet, 1H, J = 6.5 Hz, $CH(CH_3)_2$), 3.15 (dd, 1H, J = 6, 12 Hz, CHPh), 2.26 (d, 1H, J = 12.4 Hz), 2.08 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 0.70 (d, 3H, J = 6.4 Hz, $CH(CH_3)_2$), 0.66 (d, 3H, J = 6.7 Hz, $CH(CH_3)_2$). ^{13}C NMR (benzene-d_6, ambient): δ 155.8 (s, 1C, C═N), 151.8 (s, 1C, Ph), 138.5 (s, 1C, Ph), 134.0 (s, 1C, Ph), 129−124.5 (9C, Ph), 120.2 (s, 1C, C-2 or 4), 111.2 (s, 1C, C-2 or 4), 109.0 (d of quintets, 5C, J = 171, 7 Hz, Cp), 93.8 (d, 1C, J = 166, C-3), 81.5 (d, 1C, J = 131 Hz, CHPh), 57.2 (d, 1C, J = 135 Hz, $CH(CH_3)_2$), 46.6 (2t, 2C, J = 127 Hz, C-1,5), 30.4 (q, 1C, J = 128 Hz, CH_3−Pdl), 28.8 (q, 1C, J = 127 Hz, CH_3−Pdl), 24.6 (q, 1C, J = 127 Hz, p-CH_3Ph), 22.4 (q, 1C, J = 125 Hz, $CH(CH_3)_2$), 21.2 (q, 1C, J = 125 Hz, $CH(CH_3)_2$).

$Ti(C_5H_5)(2,4\text{-}C_7H_{11})[C_6H_5C(H)NCH(CH_3)_2][4\text{-}CH_3(C_6H_4)\text{-}NC]_4$, 12. A 250 mL flask equipped with a magnetic stirring bar and nitrogen inlet was charged with $Ti(C_5H_5)(2,4\text{-}C_7H_{11})$-$[C_6H_5C(H)NCH(CH_3)_2]$[3] (0.50 g, 1.4 mmol) and 40 mL of THF. The mixture was next cooled to −78° and p-tolylisocyanide (0.91 mL, 7.0 mmol) was added via syringe. A rapid color change from dark red to dark orange occurred. The reaction mixture was allowed to warm to room temperature, after which a reddish-orange mixture remained. The solvent was removed in vacuo to yield an orange-brown solid. Extraction of the solid with a 50:50 ether−pentane mixture and filtration through a Celite pad gave a dark orange filtrate. Placement of the flask into the −30° freezer gave a dark red-orange solid which upon recrystallization gave 0.41 g (35%) of the title compound as a dark red crystalline powder (mp 145−147°). Anal. Calcd. for $C_{54}H_{57}N_5Ti$: C, 78.71; H, 6.97; N, 8.49. Found: C, 78.53; H, 6.98; N, 8.48. ^{1}H NMR (benzene-d_6, ambient, some peaks obscured): δ 7.35−6.52 (21H, Ph), 6.18 (s, 5H, Cp), 5.06 (s, 1H), 3.92 (d, 1H, J = 17.5 Hz), 3.12 (septet, 1H, J = 6.5 Hz), 2.88 (dd, 1H, J = 11, 14 Hz), 2.52 (dd, 1H, J = 6, 15 Hz), 2.35 (d, 1H, J = 17.5 Hz), 2.22 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.43 (d, 3H, J = 6.6 Hz, $CH(CH_3)_2$), 1.40 (s, 3H, CH_3), 0.51 (d, 3H, J = 6.1 Hz, $CH(CH_3)_2$). IR (Nujol mull): 1629 (m), 1601 (w), 1503 (vs), 1348 (m), 1261 (vs), 1099 (vs), 1021 (vs), 865 (w), 802 (vs), 701 (w).

Crystallographic Structural Determinations. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were selected and mounted in thin-walled, nitrogen-flushed, glass capillaries. No absorption corrections were required because ψ-scan data revealed less than a 10% variation in azimuthal scans. Each structure was solved by direct methods, subsequent difference Fourier syntheses, and least-squares refinements. All hydrogen atoms were treated as idealized contributions, and except for **12**, all non-hydrogen atoms were refined anisotropically.

Preliminary photographic data for **1** indicated a monoclinic crystal system and the systematic absences in the diffraction data were uniquely consistent with the reported space group. The asymmetric unit consisted of two independent, but chemically equivalent molecules.

No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **6**. The E-statistics suggested the centrosymmetric alternative ($P\bar{1}$) which was confirmed by the chemically reasonable results of refinement. There are two independent but chemically equivalent molecules in the asymmetric unit. The phenyl rings were fixed as rigid groups in order to keep a reasonable data/parameter ratio.

The photographic data, unit-cell parameters, diffraction symmetry, and systematic absences in the diffraction data of **8** were consistent with either of the monoclinic space groups $C2/c$ or Cc. The E-statistics suggested the centrosymmetric space group which was verified by the chemically reasonable results of refinement.

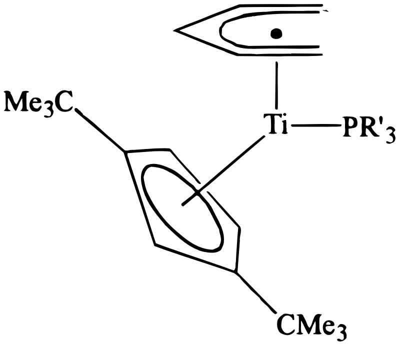
For complex **12**, no evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. E-statistics suggested a centrosymmetric space group and $P\bar{1}$ was chosen. The space group choice was subsequently verified by chemically reasonable and computationally stable results of refinement. After 15 crystals of this sample were screened, the best crystal was selected for data collection. The crystal was a very weak diffractor ($I/\sigma = 3.5$) with broad peak widths. All attempts to grow better crystals of this compound were unsuccessful. The carbon atoms in the phenyl and para-tolyl groups groups were refined isotropically. All phenyl rings and the cyclopentadienyl ring were refined as rigid planar groups to conserve data. There is a partially occupied solvent molecule of diethyl ether in the asymmetric unit and its occupancy refined to 50%. The hydrogen atoms on the solvent molecule were ignored. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

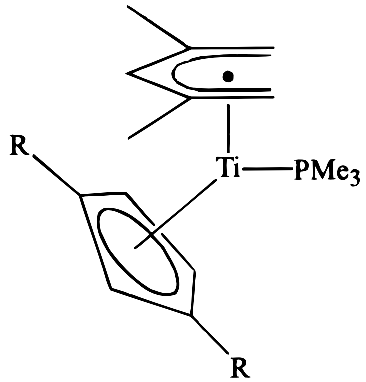
Although half-open titanocenes, M(C_5H_5)(Pdl)(L), have been prepared with a variety of pentadienyl ligands (e.g., Pdl = C_5H_7,[10] 3-C_6H_9,[11] 2,4-C_7H_{11},[10] 6,6-dmch,[4] C_8H_{11}; L = CO, PMe_3, PEt_3; C_6H_9 = methylpentadienyl, C_7H_{11} = dimethylpentadienyl, dmch = dimethylcyclohexadienyl, C_8H_{11} = cyclooctadienyl)[12] and found to have rich and diverse structural natures and chemical reactivities, no efforts have yet been made to explore the potentially significant benefits that might arise from the use of bulkier analogues of the C_5H_5 ligand. It has now been proven possible to make a variety of such species by a procedure essentially identical to that employed for the other half-open titanocenes (eq 1).

$$\mathrm{Ti(1,3\text{-}R_2C_5H_3)Cl_2(THF)_2 + PR_3' + 2KPdl \rightarrow Ti(1,3\text{-}R_2C_5H_3)(Pdl)(PR_3')} \quad (1)$$

where Pdl = C_5H_7, R = CMe_3, R′ = Me (**1**) or Et (**2**); Pdl = 2,4-C_7H_{11}, R = CMe_3 (**3**) or $SiMe_3$ (**4**), R′ = Me.



R′ = Me (1), Et (2)



R = CMe₃ (3), SiMe₃ (4)

The resulting 16 electron complexes are air-sensitive and diamagnetic, as are all previously reported half-open titanocenes.[4,10-12,13] Spectroscopic data for these complexes are consistent with the general structures previously established for half-open titanocenes, e.g., **5**.

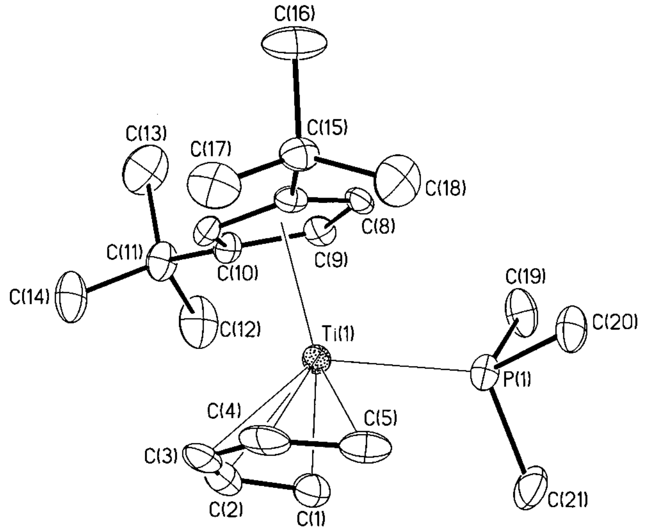
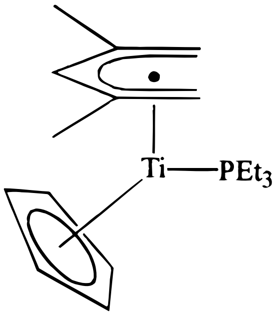


Figure 1. Perspective View of Ti[C_5H_3(*t*-C_4H_9)$_2$](C_5H_7)(PMe_3), **1**.

Confirmation of this assignment has been obtained for **1** (Figure 1 and Table 2). In this case, two independent molecules are found in the unit cell, but there are no significant differences between them.



5

Their PMe_3 ligands have one methyl group rotated around the Ti−P bond by ca. 19.4° away from the center of the open edge of the C_5H_7 ligands, intermediate between the generally observed extremes of 0° and 30° ("90°"). The bulky *t*-C_4H_9 groups are oriented away from the PMe_3 ligand and the open dienyl edge. As in other half-open titanocenes, the M−C(Pdl) bond distances are significantly shorter than those for the aromatic π ligand. The Ti−C bond distances for the open ligands thus average[14] 2.242(2) vs 2.391(1) Å for the cyclic ligands, leading to a remarkable difference of 0.15 Å! These values can be compared to those for Ti(C_5H_5)(2,4-C_7H_{11})(PEt_3) (**5**), 2.240(3) and 2.346(4) Å, respectively. It appears that the bulky *t*-C_4H_9 substituents have selectively weakened the bonding for the cyclic ligand, and although it could be possible that higher thermal libration for the C_5H_5 ligand simply led to a systematic shortening of the apparent Ti−C(C_5H_5) bond lengths in **5**, the Ti−Cp centroid distance here (2.065 Å) is longer than that in **5** (2.049 Å). The Ti−C bonds for the cyclic ligands are not very regular. Those for C(8,9), at the uncrowded end of the ring, are significantly shorter than

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[10] Hyla-Kryspin, I.; Waldman, T. E.; Meléndez, E.; Trakarnpruk, W.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D.; Gleiter, R. *Organometallics* **1995**, *14*, 5030.

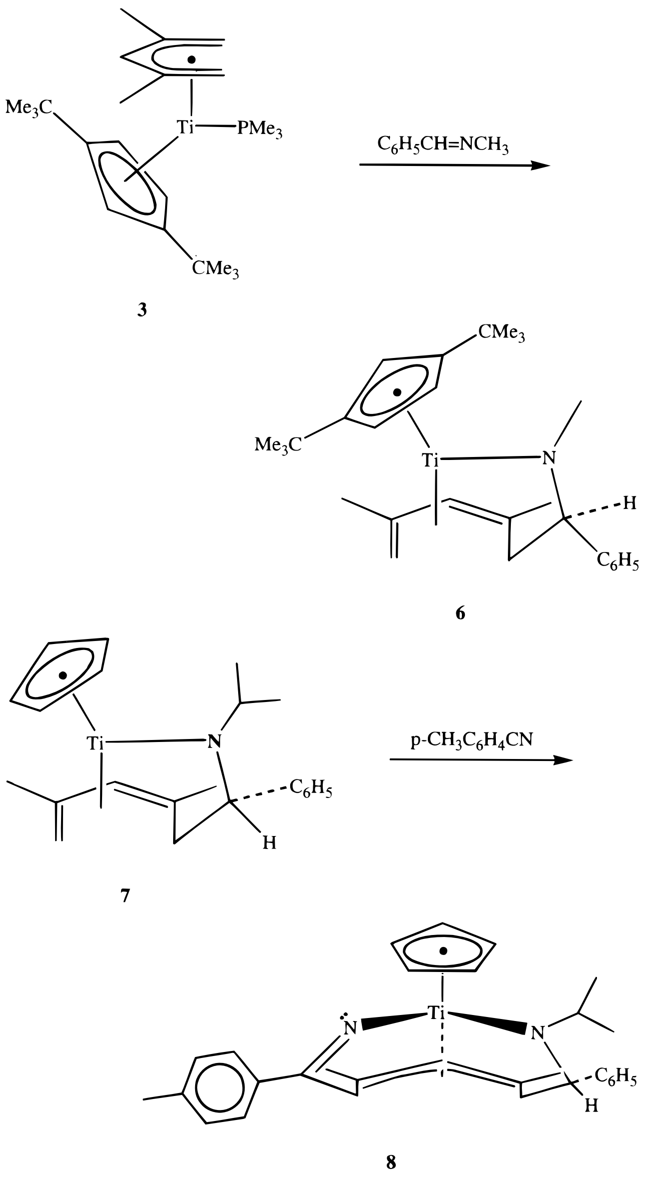
[11] Wilson, A. M. Ph.D. Thesis, University of Utah, Salt Lake City, UT 1994.

[12] Tomaszewski, R.; Hyla-Kryspin, I.; Mayne, C. L.; Arif, A. M.; Gleiter, R.; Ernst, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 2959.

[13] Varga, V.; Polášek, M.; Hiller, J.; Thewalt, U.; Sedmera, P.; Mach, K. *Organometallics* **1996**, *15*, 1268.

[14] The esd's accompanying average values are derived from the esds of the values being averaged, and therefore reflect the uncertainty in the average value, but not the distribution of the individual values.

Scheme 1



those for C(6,7,10), whereas for the C_5H_7 ligand all bonds are fairly similar in length.

As in **5**, the greater girth of the five metal-bonded carbon atoms in the C_5H_7 ligand leads to a much closer approach of the metal center to the C_5H_7 plane, compared to its cyclic counterpart (average 1.562 vs 2.065 Å). The Ti−P vector is nearly parallel to the C_5H_7 plane ($\Delta = 0.8°$), but is significantly tilted relative to the cyclic ligand plane (14.4°). The quaternary carbon atoms of the *t*-C_4H_9 substituents are tilted by an average of 10.1° away from the metal center.

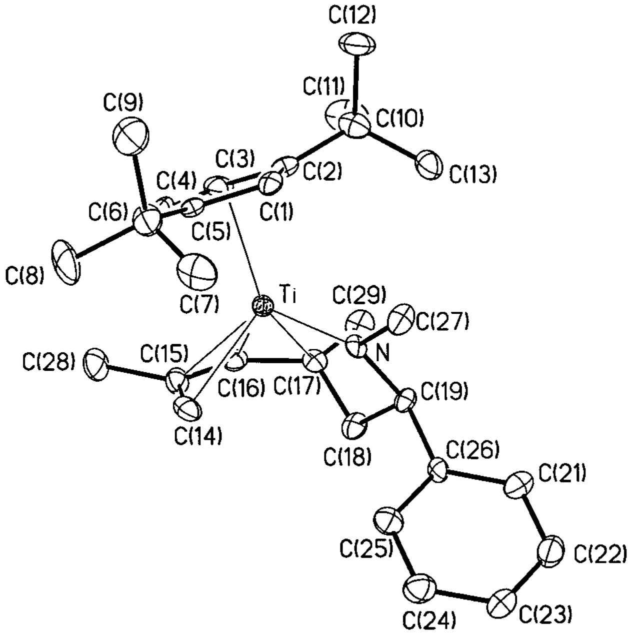


Figure 2. Perspective view of Ti(1,3-*t*-$Bu_2C_5H_3$)(NMeCHPh-$CH_2CMe{=}CHCMe{=}CH_2$), **6**.

The reaction of **3** with $C_6H_5CH{=}NCH_3$ led to incorporation and coupling of a single imine equivalent, yielding **6** (Scheme 1). Unlike the product resulting from the C_5H_5 complex,[1] however, this product could be isolated as a well-behaved crystalline solid. Spectroscopic data for both species clearly revealed that coupling involving only one of the pentadienyl terminal CH_2 groups had occurred, as indicated by a low $J(^{13}C{-}H)$ value (here, 127 vs 149 Hz for the other end), reflecting formal sp^3 hybridization. Because neither the backbone geometry nor the relative configuration for the imine's coupled carbon atom could be determined spectroscopically, a single crystal diffraction study was performed. Two crystallographically independent molecules were found in the unit cell, but any differences between them were observed to be insignificant. The result (Figure 2 and Table 3) revealed that while the original open dienyl fragment has again retained its U conformation, the relative configuration at the imine's coupled carbon atom (C19) has been reversed as compared to that found for the C_5H_5 complex, **7** (Scheme 1). In this case, the phenyl ring is oriented toward the open edge of the original dienyl fragment, rather than away from it. Thus, the stereochemistry generated at the imine carbon atom can be substantially controlled by the choice of the cyclopentadienyl substituents.

In any case, the observed product may be considered to be a 16 electron Ti(Cp)(diene)(amide) complex, given that the bonds about the amide are nearly planar (vide infra), reflecting its formal donation of three electrons. The bonding in the "diene" unit, however, appears more similar to an enediyl coordination mode because the Ti−C(14,17) bonds appear shorter than Ti−C(15,16) bonds, 2.241(4) vs 2.286(4) Å, and the C−C (external) distances appear longer than the C−C (internal) distances, 1.420(6) vs 1.400(9) Å. Actually, the Ti−C(14) and Ti−C(17) bonds appear to differ somewhat, presumably as a result of distortions brought about by the bridge between the enediyl and amide ligands. Some evidence for this can be seen by the 35.7° tilt of C(18) from the diene plane, a much smaller value than would be expected.[5,10,15,16] The amide → Ti interaction appears to involve a 3 electron donation, because the angles about the nitrogen centers average 119.7°, and the average Ti−N distance

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[15] (a) Wilson, D. R.; Ernst, R. D.; Kralik, M. S. *Organometallics* **1984**, *3*, 1442. (b) Arif, A. M.; Ernst, R. D.; Meléndez, E.; Rheingold, A. L.; Waldman, T. E. *Organometallics*, **1995**, *14*, 1761. (c) Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Organometallics* **1987**, *6*, 848.

[16] The sine of the tilt angle is defined by the deviation of the substituent from the diene plane divided by the distance from the substituent to its attached carbon atom in the diene plane. For comparison, the tilt determined from torsion angles (e.g., C15−C16−C17−C18) would be 42.2°.

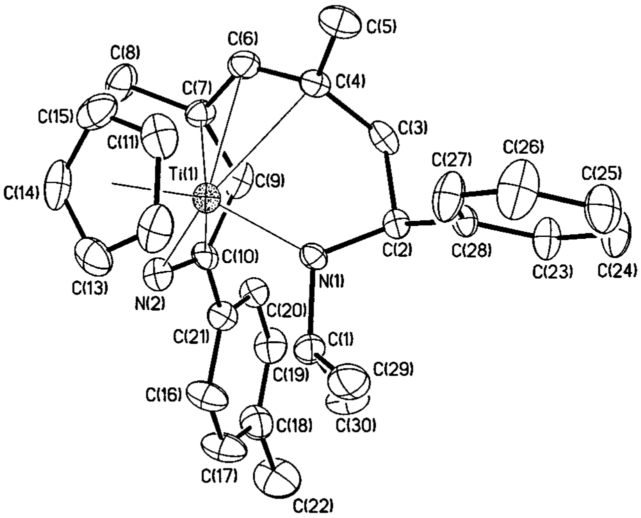

Figure 3. Solid-state structure of Ti(C_5H_5){N(*i*-Pr)-$CHPhCH_2CMeCHCMeCH_2C[p\text{-}CH_3(C_6H_4)]N$}, **8**.

of 1.936(5) Å is similar to values observed for other apparent 3 electron amide → Ti donations, but much shorter than values observed for otherwise similar but bridging amides.[10] The Ti−C(Cp) bonds are longest for the *t*-butyl substituted carbon atoms (2.421(4) Å), shortest for the C(1,1′) atoms (2.362(6) Å), and intermediate for the others (2.389(5) Å). The average C−C distance is 1.409(4) Å. The *t*-C_4H_9 groups experience reasonable (vide supra) tilts of ca. 8.6° out of the Cp plane, away from the metal center.

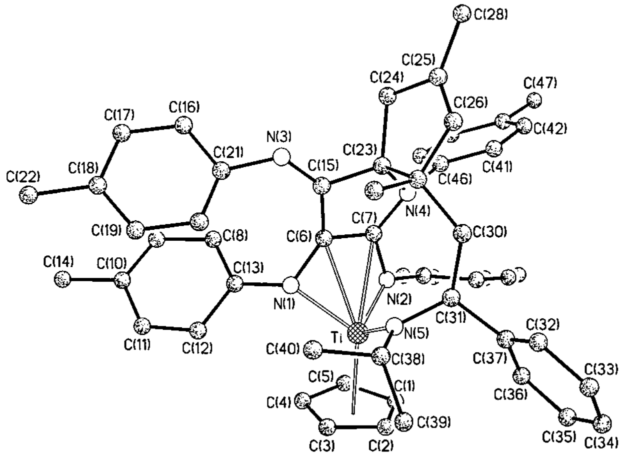

Figure 4. Perspective view of complex **12**, "Ti(C_5H_5)(2,4-C_7H_{11})[$C_6H_5C(H)NCH(CH_3)_2$][$p\text{-}CH_3(C_6H_4)NC$]$_4$."

Table 2. Pertinent Bonding Parameters for Ti[$C_5H_3(t\text{-}C_4H_9)_2$]($C_5H_7$)($PMe_3$)

Bond Distances			
Ti(1)−P(1)	2.529(2)	Ti(2)−P(2)	2.525(2)
Ti(1)−C(1)	2.233(4)	Ti(2)−C(1′)	2.239(5)
Ti(1)−C(2)	2.265(5)	Ti(2)−C(2′)	2.235(5)
Ti(1)−C(3)	2.262(5)	Ti(2)−C(3′)	2.253(5)
Ti(1)−C(4)	2.236(5)	Ti(2)−C(4′)	2.247(5)
Ti(1)−C(5)	2.227(5)	Ti(2)−C(5′)	2.219(4)
Ti(1)−C(6)	2.423(4)	Ti(2)−C(6′)	2.404(4)
Ti(1)−C(7)	2.436(4)	Ti(2)−C(7′)	2.399(4)
Ti(1)−C(8)	2.368(4)	Ti(2)−C(8′)	2.346(4)
Ti(1)−C(9)	2.337(4)	Ti(2)−C(9′)	2.362(4)
Ti(1)−C(10)	2.400(4)	Ti(2)−C(10′)	2.438(4)
C(1)−C(2)	1.424(7)	C(1′)−C(2′)	1.427(7)
C(2)−C(3)	1.417(7)	C(2′)−C(3′)	1.411(7)
C(3)−C(4)	1.403(7)	C(3′)−C(4′)	1.405(7)
C(4)−C(5)	1.402(7)	C(4′)−C(5′)	1.416(6)
Bond Angles			
C(1)−C(2)−C(3)	125.0(5)	C(1′)−C(2′)−C(3′)	126.8(5)
C(2)−C(3)−C(4)	129.6(5)	C(2′)−C(3′)−C(4′)	129.0(5)
C(3)−C(4)−C(5)	126.7(5)	C(3′)−C(4′)−C(5′)	126.2(5)
C(7)−C(6)−C(10)	108.8(4)	C(7′)−C(6′)−C(10′)	109.8(4)
C(6)−C(7)−C(8)	107.6(4)	C(6′)−C(7′)−C(8′)	106.6(4)
C(7)−C(8)−C(9)	108.3(4)	C(7′)−C(8′)−C(9′)	107.6(4)
C(8)−C(9)−C(10)	108.6(4)	C(8′)−C(9′)−C(10′)	109.1(4)
C(6)−C(10)−C(9)	106.8(4)	C(6′)−C(10′)−C(9′)	106.9(3)

Because it was found to be possible to carry out tandem couplings of one equivalent of an imine with a second unsaturated coupling partner (imine, ketone, or isonitrile),[3] it was of interest to determine if this could be extended to nitriles. Such a possibility could not be taken for granted, because a reported mono(nitrile) coupling product appears unreactive under normal conditions to further couplings with either nitriles or ketones.[17] However, in situ generation of a mono(imine) coupling product, followed by addition of an excess of *p*-tolunitrile, was found to lead readily to the desired, mixed coupling product (**8**, Scheme 1). Reactions were observed as well with a variety of other nitriles, but *p*-tolunitrile was found to provide a more nicely crystalline product. As with the other tandem coupling products, NMR spectroscopic data revealed that both open dienyl termini had coupled, as well as the imine's originally unsaturated carbon atom, because $J(^{13}C{-}H)$ values characteristic of sp^3 hybridization were observed (ca. 127, 131 Hz). A single-crystal diffraction study (Figure 3 and Table 4) confirmed this and other expectations. As a starting point the product may be considered to be a 16 electron Ti(C_5H_5)(π-allyl)(π-amide)(σ-imide) species, the π-amide coordination being derived from the original imine, and the σ-imide coordination being derived from the nitrile. The geometry about the amide donor site (N(1)) is nearly trigonal planar, and along with the Ti−N(1) distance of 1.955(3) Å, seems to implicate its participation as a 3 electron donor. The longer Ti−N(2) distance of 2.046(3) Å would then be consistent with 1 electron donation, and from the Ti−N(2)−C(10) angle of 103.0(2)°, it is clear that the lone pair of electrons on N(2) could not be interacting with the metal center (either intra- or intermolecularly), unlike a dimeric mono(nitrile) coupling product.[3] However, the Ti−N(2) distance is still shorter than the Ti−N(amide) bridging distances in the mono(acetonitrile) coupling product, which ranged from 2.117(3) to 2.187(3) Å. In addition, the C(10)−N(2) distance of 1.364(5) Å is notably longer than the bridging imide's average C−N distance of 1.266(3) Å in the dimer. Hence, there could be an additional interaction with the C(10)═N(2) bond. Although its orientation is not optimal for a σ donor interaction of its π cloud to the metal center, some degree of π donation could be occurring, analogous to 4 electron alkyne donation,[18] and could then lead to an 18 electron count. In fact, the Ti−C(10) distance of 2.702(4) Å is significantly shorter than an expected van der Waals separation, although what would normally have been described as a nonbonded Ti−C(9) contact is actually found to be remarkably short, at 2.615(4) Å. The extent to which a (C═N) → Ti interaction (or even

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[17] Tomaszewski, R.; Ernst, R. D. Unpublished results.

[18] Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

Table 3. Pertinent Bonding Parameters for Ti(1,3-*t*-$Bu_2C_5H_3$)(NMeCHPhCH_2CMe=CHCMe=CH_2) (6)

Bond Distances

Ti−N	1.932(5)	Ti′−N′	1.940(8)
Ti−C(1)	2.360(9)	Ti′−C(1′)	2.363(7)
Ti−C(2)	2.423(8)	Ti′−C(2′)	2.399(7)
Ti−C(3)	2.393(8)	Ti′−C(3′)	2.386(10)
Ti−C(4)	2.387(9)	Ti′−C(4′)	2.388(11)
Ti−C(5)	2.428(10)	Ti′−C(5′)	2.434(9)
Ti−C(14)	2.213(8)	Ti′−C(14′)	2.220(8)
Ti−C(15)	2.302(8)	Ti′−C(15′)	2.289(8)
Ti−C(16)	2.282(9)	Ti′−C(16′)	2.271(7)
Ti−C(17)	2.275(10)	Ti′−C(17′)	2.265(7)
C(14)−C(15)	1.430(12)	C(14′)−C(15′)	1.424(13)
C(15)−C(16)	1.390(13)	C(15′)−C(16′)	1.409(12)
C(16)−C(17)	1.446(10)	C(16′)−C(17′)	1.412(13)
C(17)−C(18)	1.506(10)	C(17′)−C(18′)	1.562(15)
C(18)−C(19)	1.535(11)	C(18′)−C(19′)	1.513(11)
C(19)−N	1.488(12)	C(19′)−N′	1.489(10)
C(27)−N	1.472(10)	C(27′)−N′	1.451(10)

Bond Angles

C(14)−C(15)−C(16)	124.8(7)	C(14′)−C(15′)−C(16′)	124.5(9)
C(15)−C(16)−C(17)	130.0(7)	C(15′)−C(16′)−C(17′)	130.5(9)
C(16)−C(17)−C(18)	121.1(7)	C(16′)−C(17′)−C(18′)	119.2(8)
C(17)−C(18)−C(19)	111.9(7)	C(17′)−C(18′)−C(19′)	110.7(7)
C(18)−C(19)−N	105.7(6)	C(18′)−C(19′)−N′	107.5(7)
C(19)−N−C(27)	109.3(6)	C(19′)−N′−C(27′)	108.9(7)
C(19)−N−Ti	119.9(5)	C(19′)−N′−Ti′	119.1(5)
C(27)−N−Ti	129.6(6)	C(27′)−N′−Ti′	131.2(6)
N−C(19)−C(26)	114.2(6)	N′−C(19′)−C(26′)	113.3(6)

Table 4. Pertinent Bonding Parameters for Ti(C_5H_5){N(*i*-Pr)CHPhCH_2CMeCHCMeCH_2C-[*p*-$CH_3(C_6H_4)$]N} (8)

Bond Distances

Ti(1)−C(4)	2.504(4)	Ti(1)−N(1)	1.955(3)
Ti(1)−C(6)	2.352(4)	Ti(1)−N(2)	2.046(3)
Ti(1)−C(7)	2.224(4)	C(2)−C(3)	1.545(5)
Ti(1)−C(10)	2.702(4)	C(3)−C(4)	1.519(5)
Ti(1)−C(11)	2.378(4)	C(4)−C(6)	1.378(5)
Ti(1)−C(12)	2.352(5)	C(6)−C(7)	1.394(5)
Ti(1)−C(13)	2.371(5)	C(7)−C(9)	1.496(5)
Ti(1)−C(14)	2.448(4)	C(9)−C(10)	1.380(5)
Ti(1)−C(15)	2.447(5)	C(10)−N(2)	1.364(5)

Bond Angles

N(1)−Ti(1)−N(2)	100.25(13)	C(4)−C(6)−C(7)	130.0(4)
C(1)−N(1)−C(2)	115.0(3)	C(6)−C(7)−C(9)	122.9(4)
N(1)−C(2)−C(3)	107.7(3)	C(7)−C(9)−C(10)	118.6(4)
C(2)−C(3)−C(4)	114.9(3)	C(9)−C(10)−N(2)	115.1(4)
C(3)−C(4)−C(6)	123.4(4)		

Table 5. Pertinent Bonding Parameters for "Ti(C_5H_5)(2,4-C_7H_{11})[C_6H_5CH=N(*i*-C_3H_7)]-(*p*-$CH_3C_6H_4NC)_4$"

Bond Distances

Ti−N(1)	1.949(8)	C(6)−C(7)	1.400(13)
Ti−N(2)	1.958(9)	C(6)−C(15)	1.52(2)
Ti−N(5)	1.924(10)	C(15)−C(23)	1.469(14)
Ti−C(1)	2.370(12)	C(23)−C(24)	1.60(2)
Ti−C(2)	2.326(12)	C(23)−C(27)	1.571(14)
Ti−C(3)	2.337(13)	C(24)−C(25)	1.541(14)
Ti−C(4)	2.412(12)	C(25)−C(26)	1.264(14)
Ti−C(5)	2.400(11)	C(26)−C(27)	1.50(2)
Ti−C(6)	2.379(13)	C(27)−C(30)	1.558(13)
Ti−C(7)	2.458(12)	C(30)−C(31)	1.59(2)
N(1)−C(6)	1.361(12)	N(4)−C(7)	1.361(13)
N(1)−C(13)	1.404(12)	N(4)−C(23)	1.491(11)
N(2)−C(7)	1.377(12)	N(4)−C(46)	1.464(12)
N(2)−C(53)	1.459(11)	N(5)−C(31)	1.450(13)
N(3)−C(15)	1.245(11)	N(5)−C(38)	1.515(12)
N(3)−C(21)	1.422(12)		

Bond Angles

N(1)−Ti−N(2)	86.6(3)	N(2)−C(7)−N(4)	128.5(9)
N(1)−Ti−N(5)	105.7(3)	N(3)−C(15)−C(6)	135.1(11)
N(2)−Ti−N(5)	111.8(4)	N(3)−C(15)−C(23)	120.4(11)
Ti−N(1)−C(6)	90.1(7)	C(6)−C(15)−C(23)	104.4(9)
Ti−N(1)−C(13)	143.8(8)	N(4)−C(23)−C(15)	105.1(9)
C(6)−N(1)−C(13)	124.1(9)	N(4)−C(23)−C(24)	110.0(8)
Ti−N(2)−C(7)	93.3(6)	N(4)−C(23)−C(27)	112.0(8)
Ti−N(2)−C(53)	142.1(7)	C(15)−C(23)−C(24)	112.7(9)
C(7)−N(2)−C(53)	120.8(9)	C(15)−C(23)−C(27)	114.8(10)
C(15)−N(3)−C(21)	131.1(11)	C(24)−C(23)−C(27)	102.4(9)
C(7)−N(4)−C(23)	108.2(8)	C(23)−C(24)−C(25)	104.5(9)
C(7)−N(4)−C(46)	119.3(9)	C(24)−C(25)−C(26)	109.6(11)
C(23)−N(4)−C(46)	124.5(9)	C(25)−C(26)−C(27)	117.4(12)
Ti−N(5)−C(31)	113.9(6)	C(23)−C(27)−C(26)	103.2(10)
Ti−N(5)−C(38)	131.3(7)	C(23)−C(27)−C(30)	117.8(8)
C(31)−N(5)−C(38)	113.7(9)	C(26)−C(27)−C(30)	108.9(9)
N(1)−C(6)−C(7)	121.0(11)	C(27)−C(30)−C(31)	128.9(9)
N(1)−C(6)−C(15)	132.8(9)	N(5)−C(31)−C(30)	119.4(8)
C(7)−C(6)−C(15)	105.7(10)	N(5)−C(31)−C(37)	115.0(10)
N(2)−C(7)−C(6)	114.8(11)	C(30)−C(31)−C(37)	108.6(9)
N(4)−C(7)−C(6)	112.4(10)		

C−C→Ti agostic interactions[12]) may be taking place is clearly arguable, but it appears reasonable that some interaction will be present as long as an appropriate acceptor orbital is available on the metal center.

Some degree of ambiguity also characterizes the Ti-allyl interaction due to its asymmetry, i.e., respective Ti−C(4,6,7) distances of 2.504(4), 2.352(4), and 2.224(4) Å. However, the respective C(4)−C(6) and C(6)−C(7) bond lengths of 1.378(5) and 1.394(5) Å do not differ noticeably, suggesting a significant degree of η^3 interaction. Perhaps a key indicator of the presence of an η^1 interaction would be significantly differing C−C distances, and a Ti−C(σ-allyl) distance of ca. 2.15 Å, as were observed in some related species formulated as η^1-allyl complexes.[1] Conceivably, the asymmetry experienced here could arise either from geometric constraints imposed on coordination by the chelating nature of the ligands, and/or from a trans weakening influence,[19] because C(4) comes closer to being situated opposite to one of the nitrogen atoms than does C(7). Some evidence for a geometric contribution can be seen in the C(2)−C(3)−C(4) and C(7)−C(9)−C(10) angles, which are significantly larger than expected, whereas the C(9)−C(10)−N(2) angle is significantly smaller than expected.

The Ti−Cp bonding is also somewhat asymmetric, with longer bonds to C(14,15) than to C(11−13) (averages of 2.448(3) vs 2.367(3) Å). The presumed weakening of the Ti−C(14,15) bonds can readily be accounted for as a result of their being situated most nearly opposite to N(1), leading to a competition for π bonding with the metal center.

The course of the tandem imine−isonitrile coupling process is particularly complex, because a total of four equivalents of isocyanide was incorporated. As a result, spectroscopic data provided little information regarding the nature of product that was formed, and the nature of the product could only be elucidated through an X-ray diffraction study. The result may be seen in Figure 4, while important bonding parameters are contained in Table 5. A possible mechanism for the formation of the product is presented in Scheme 2.

As depicted in the scheme, the unsaturated carbon atom of the first equivalent of isonitrile is coupled to the ends of the diene ligand, leading to species **9**. In fact, related species were isolated from coupling reactions utilizing the bulkier *t*-C_4H_9NC ligand.[3] In the present case, however, this species is susceptible to further

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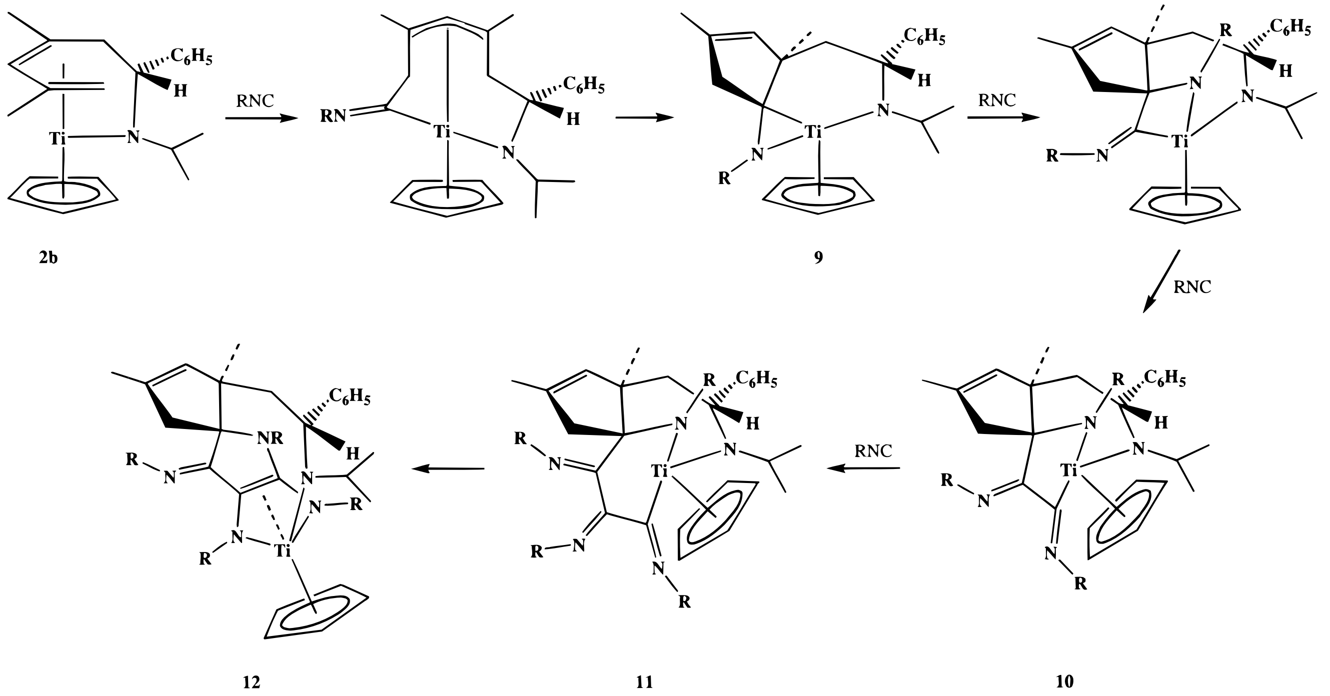
(19) The large N(1)−C(2)−C(28) angle of 117.3(3)° might also indicate some steric problems.

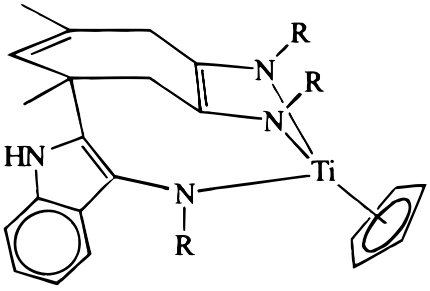
Scheme 2[a]



[a] R = p-CH$_3$C$_6$H$_4$.

reaction, and a second isonitrile inserts in the Ti−C bond formed from the first isonitrile. This results, however, in another Ti−C bond, leading to another insertion, giving an additional Ti−C bond (**10**). A final insertion reaction produces **11**. A formal reductive elimination, forming a C−N bond, then yields the basic skeleton of the final product. Coordination of a diazadiene unit (actually present in more of an enediamide form, vide infra) then completes the reaction. Note that the reductive elimination step creates a five-membered ring (part of a spiro fused ring), which then accounts for the need to have continually inserted additional isonitriles. Through the depicted process one not only constructs a relatively strain-free five-membered ring, but also arrives at a product in which, except for the C$_5$H$_5$ ligand, the titanium center may be regarded as bonding only to electronegative nitrogen donor sites (vide infra).

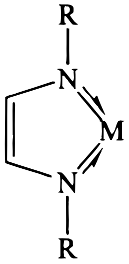
The structure of the product, **12**, is quite similar to that found earlier in another isonitrile coupling product, **13**, in which coordination to a Cp, amide, and diazadiene ligand was also found.



13

In the present case, the coordination involving the Cp and amide ligands is straightforward, and will be considered first. The Ti−N(5) distance of 1.924(10) Å, along with the nearly trigonal disposition of bonds around N(5) (358.9°), point to its role as a 3 electron (π) donor. In fact, this distance is significantly shorter than the Ti−N(1) value of 1.983(5) Å in **13**, perhaps due to the presence of a phenyl substituent on N(1). There is an asymmetry in the Ti−N(5)−C(31,38) angles, however, that indicates that the bridge between the N(5) and diazadiene coordination sites must be somewhat strained. In fact, the C−C−C bond angles within the C(23-C27−30−31)−N(5) chain are all significantly greater than would be expected for their formal sp^3 hybridizations, in accord with this conclusion. In addiion, there is an angle of 18.3° between the C15−C23−N4 and C15−C6−C7−N4 best planes, again appearing to reflect an attempt to "stretch" N(5) out to a more optimal position for bonding to the metal center. One other distortion associated with N(5) appears to be an asymmetry in the Ti−Cp bonding. The Ti−C(4,5) bonds are significantly longer than the others, as an apparent result of their being positioned more nearly opposite N(5), and subsequent competition for π bonding to the metal. Such behavior has also been observed for other related complexes.[3]

As for **13**, the diazadiene coordination is somewhat complex. The sums of the angles about N(1 and 2) equal 358.0 and 356.2°, respectively, indicating a significant approach to sp^2 hybridization, and perhaps then π donation from these two nitrogen centers, each of which could be considered to be a 3 electron donor, as in **14**. The Ti−N(1,2) distances are short enough to provide support for this formulation. Nonetheless, C(6) and C(7) both make close approaches of ca. 2.4 Å to Ti (as in **13**), which also suggests the possibility of a σ donor interaction from the C−C double bond (cf., enediyl complexes). However, even if it were geometrically possible to



14

achieve favorable interactions involving Ti, the olefin, and two π-amide donor sites, this would lead to a 20 electron complex. In all likelihood, partial σ donation from the olefin and π donation from the amide lone pairs are all taking place in competition with each other (and with the Cp ligand). The fact that Ti does not lie in the diazadiene plane either in **12** or **13** provides some support for this formulation. One notable difference between **12** and **13**, however, lies in the presence of a short C7−N2 bond (1.377(12) Å) in the former, suggesting some delocalization in the structure, resulting in partial C7−N2 multiple bonding.

The coupling reactions of metal pentadienyl compounds with imines generate chiral centers, and it has now been demonstrated that the appropriate choice of Cp ligand substituents can allow for the selective isolation of either isomeric coupled species. Subsequently, additional functionalization of the dienyl fragment can be effected with ketones, imines, nitriles, or isonitriles. In these reactions, it has been observed that substituents present in the partner coupling substrates can also influence the course of the reactions. In the cases in which bis(coupling) products are isolated, one obtains organic fragments in which two heteroatoms are separated by seven carbon atoms; related reactions for diene complexes yield similar species, with heteroatoms separated by six carbon atoms.[20] Further efforts to develop the chemistry of these complexes are underway.

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Supporting Information Available: Positional coordinates, anisotropic thermal parameters, additional bonding parameters, and mass spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990463H

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[20] Yasuda, H.; Nakamura, A. *Angew. Chem., Intl. Ed. Engl.* **1987**, *26*, 723.