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Titanocene Imido Complexes: Generation as Reactive Intermediates, Isolation, and Structural Characterization

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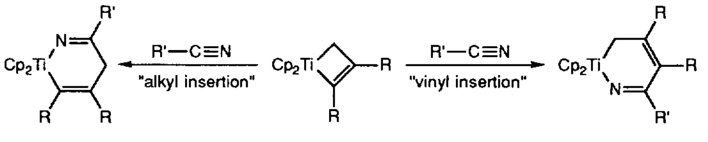
Abstract: Nitriles react with 2,3-dimethyl-1,1-bis(cyclopentadienyl)titanacyclobut-2-ene to afford either azatitanacyclohexadienes or diazatitanacyclooctatrienes. The latter appear to be formed via the intermediacy of butadienylimido complexes, which can be intercepted by the addition of trimethylphosphine. Bis(cyclopentadienyl)titanium bis(trimethylphosphine) undergoes ligand substitution reactions with nitriles. Loss of trimethylphosphine from the 2,4,6-trimethylbenzonitrile complex appears to lead to reductive coupling of the nitrile, affording a dimeric imido complex.

INTRODUCTION

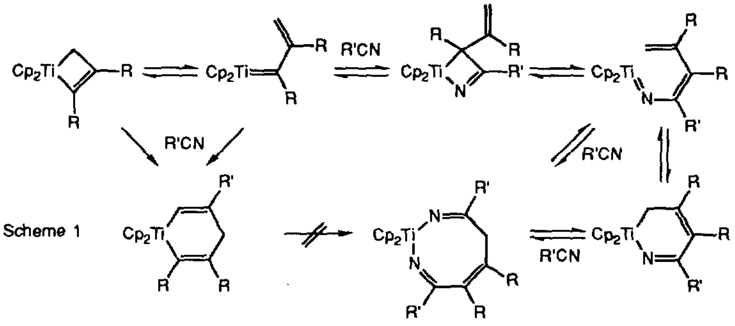
Carbene complexes of the early transition metals play central roles in a number of technologically-important processes, including the Ziegler-Natta-type polymerization of alkenes,[1] the alkene metathesis reaction,[2] and the ring-opening metathesis polymerization of cyclic alkenes,[3] and countless reports of the synthesis, structure, and reactivity of such carbene complexes have appeared over the past several decades. In contrast, the chemistry of early metal complexes bearing metal-heteroatom multiple bonds, including discrete oxide, sulfide, and nitrene complexes, has been comparatively slow in development, although recent years have seen dramatic growth in this area as well.[4]

The group IV metallocenes have been the targets of an extraordinary range of studies, and recent years have seen the generation and trapping or isolation of a number of significant species, including monomeric titanocene and zirconocene oxides[5,6,7] and zirconocene sulfides[7] and nitrene (imido) complexes.[8] Although several monocyclopentadienyl titanium bridging imido complexes have been isolated and structurally characterized,[9] however, titanocene imido complexes remain rare,[10] and to our knowledge no previous reports of their crystallographic characterization have appeared.

We herein report the synthesis of two titanocene imido complexes as reactive but observable intermediates and the isolation and structural characterization of two additional titanocene imido complexes which have arisen in the course of our studies of the reactions of nitriles with titanacyclobutenes. As we previously reported,[11] these reactions favor initial insertion of the nitrile into the sterically more encumbered titanium-sp^2 carbon bond of the metallacycle ("vinyl insertion") in all but the most sterically hindered cases, for which insertion into the titanium-sp^3 carbon bond ("alkyl insertion") is observed.



The complexity of the reaction systems affording these products has rendered detailed kinetic analysis inconclusive. In its place, we have resorted to the generation of a substantial body of circumstantial mechanistic evidence,[12,13] all of which supports a multi-step mechanism for vinyl insertion (Scheme 1) in which electrocyclic ring opening of the titanacyclobutene to the corresponding vinyl carbene complex is followed by [2+2] cycloaddition of the nitrile to the titanium-carbon double bond. The resulting azatitanacyclobutene then undergoes electrocyclic ring opening to the butadienylimido complex, which collapses in a final electrocyclic reaction to afford the vinyl insertion product. The vinyl insertion products readily react with an additional equivalent of nitrile, either through direct insertion into the titanium-carbon bond or through cycloaddition to the corresponding butadienylimido complex, affording diazatitanacyclooctatrienes in high yield. Interestingly, the alkyl insertion products do not afford these complexes, even after prolonged reaction times with excess nitrile.

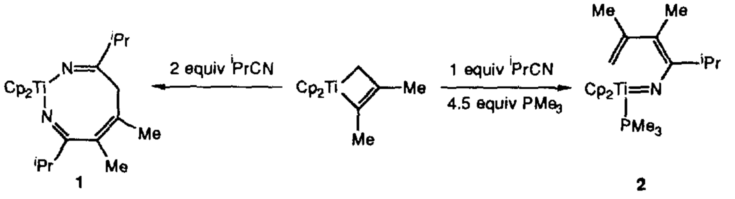


Scheme 1

Each of the proposed mechanistic steps, titanacyclobutene ring opening,[14] [2+2] cycloaddition of nitrile to the titanium-carbon double bond,[10,15] and azatitanacyclobutene ring opening,[15] has been documented in closely related systems. In this manuscript, we report additional studies of the formation of butadienylimido complexes, as well as the synthesis and structures of related titanocene imido complexes.

RESULTS AND DISCUSSION

Treatment of dimethyltitanacyclobutene[16] with two equivalents of isobutyronitrile afforded the diazatitanacyclooctatriene, **1**, in quantitative yield.[11,13] Given our earlier successful trapping of vinylimido complexes as their trimethylphosphine adducts,[10] we treated the dimethyltitanacyclobutene with isobutyronitrile in the presence of excess trimethylphosphine in an attempt to intercept the intermediate butadienylimido complex (cf. Scheme 1). After one hour at 60°C, in addition to the vinyl insertion product and complex **1**, a new complex displaying spectral features consistent with the anticipated butadienylimido complex **2** was formed in ca. 50% yield.[17]



Most characteristic is the ^1H NMR spectrum of **2**, which displays resonances for the terminal methylene protons at 4.98 and 4.92 ppm, analogous to the chemical shifts observed earlier for the vinylimido complexes. Continued heating at 60°C for an additional ten hours resulted in the disappearance of all resonances in the ^1H NMR spectrum of the reaction mixture and the deposition of small, dark single crystals of a new complex, **3**. Although the sparing solubility of this complex precluded solution spectroscopic characterization, mass spectral analysis suggested it was neither the anticipated butadienylimido complex **2** nor the bridging imido dimer anticipated to be formed upon phosphine dissociation from **2**.[8] Fortunately, the complex proved amenable to single crystal x-ray diffraction analysis, which demonstrated the complex to bear an aminofulvene-derived imido ligand (Figure 1).

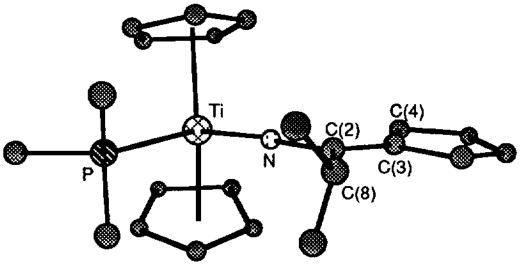


Figure 1. Molecular structure of complex **3**

Imido complex **3**, apparently representing the first crystallographically characterized imido complex of titanocene, displays structural parameters (Table 1) in accord with those anticipated for such a complex. Most suggestive is the near-linear Ti-N-C bond angle, at ca. 168° (average of the observed angles for the two molecules in the asymmetric unit) and the rather short Ti-N bond, at ca. 1.84Å. Interestingly, the short N-C bond (ca. 1.29Å), the somewhat longer than expected C2-C3 bond (ca. 1.43Å), and the near-equivalence of bond lengths within the fulvene ring all suggest that an alternative zwitterionic resonance structure makes a significant contribution to the overall bonding picture.

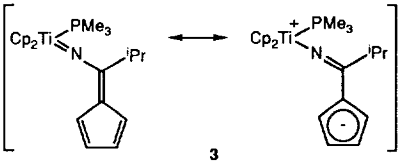


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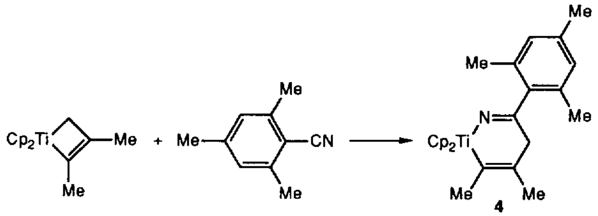
Table 1. Representative Bond Lengths (Å) and Bond Angles (deg) for Complexes **3**, **4**, and **6**.

Complex	**3**[a]	**3**[a]	**4**	**6**
Ti-N	1.833(7)	1.845(9)	1.894(3)	1.810(10)
N-C	1.288(11)	1.298(12)	1.257(5)	1.333(14)
Ti-N-C	172.6(9)	162.7(9)	143.5(3)	164.8(9)

[a] Separate values provided for the two molecules in the asymmetric unit.

The mass spectral data obtained for the bulk product of this reaction are in complete agreement with this structure. The highest mass ion observed (m/z = 312, M-PMe_3+H) results from the same fragmentation as we previously observed for simpler vinylimido complexes.[10] Also consistent with our earlier mass spectral studies is the apparent formation of the phosphine-free imido dimer, with higher mass fragments consistent with formation of this dimer appearing after prolonged heating of the sample in the mass spectrometer inlet port.

Although complex **3** contains the same number of carbon atoms as its putative precursor, **2**, it almost certainly arose through addition of a cyclopentadienyl group to titanium-coordinated isobutyronitrile, rather than as a result of skeletal rearrangement of the butadienylimido complex. In an effort to exploit steric bulk to prevent formation of complexes analogous to **3** and thereby permit isolation of a butadienylimido complex, the reaction of dimethyltitanacyclobutene with 2,4,6-trimethylbenzonitrile was explored. In the absence of trimethylphosphine, a relatively slow reaction occurs at 45°C, affording primarily the alkyl insertion product, **4**, as anticipated given the sensitivity of the nitrile insertion reactions to steric bulk.[11] Also formed with **4** is the apparent tautomeric titanacyclohexa-2,4-diene; although we have earlier noted tautomerization of diazatitanacyclohexadienes,[10] this is the first time we have observed it in a monoaza derivative.



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Recrystallization of complex **4** from toluene afforded single crystals suitable for x-ray diffraction analysis, which confirmed (Figure 2) earlier structural assignments for the alkyl insertion products made on the basis of solution spectroscopic analysis.[11,18] Of particular note in this structure is the rather short Ti-N bond (Table 1), which, at 1.894(3)Å, is only ca. 0.05Å longer than the Ti-N bond in imido complex **3**, and the very wide T-N-C bond angle, at 143.5(3)°. These two somewhat unusual metrical parameters suggest a partial multiple-bonding interaction between titanium and nitrogen, with geometric distortions allowing partial donation of the nitrogen lone pair into the vacant wedge plane orbital of the formally 16-electron complex.

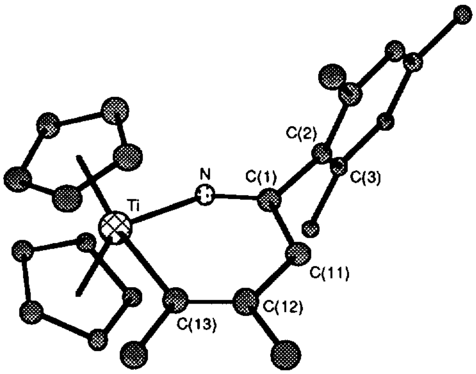
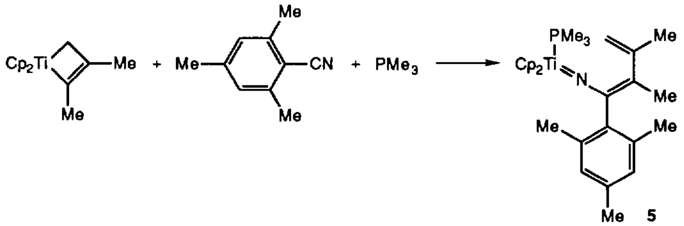


Figure 2. Molecular structure of complex **4**

Repetition of the reaction of dimethyltitanacyclobutene with 2,4,6-trimethylbenzonitrile in the presence of ten equivalents of trimethylphosphine, in contrast, gave, over a shorter period of time and at lower temperature than the phosphine-free reaction, a microcrystalline precipitate of butadienylimido complex **5** in analytically pure form. This complex displays NMR spectral data consistent with the proposed structure, with the terminal methylene proton resonances at 5.96 and 5.20 ppm again proving most diagnostic.



Repeated attempts at recrystallization of butadienylimido complex **5** were unsuccessful. However, a minor contaminant in one preparation was isolated in crystalline form, and x-ray diffraction analysis showed it to be a dimeric imido complex, **6** (Figure 3). This complex, representing the second crystallographically characterized titanocene imido complex, again displays the metrical parameters anticipated for an imido complex (Table 1).

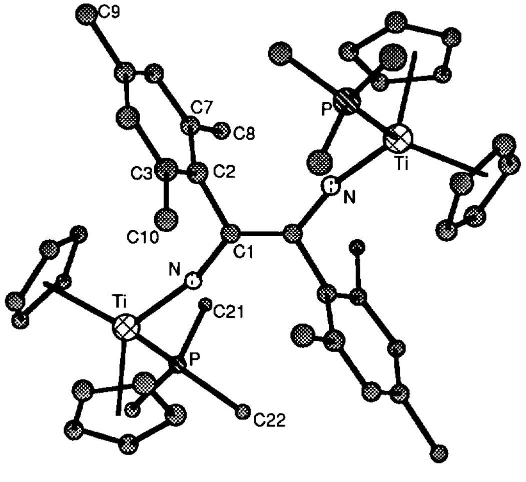


Figure 3. Molecular structure of complex **6**

The formation of imido dimer **6** in this reaction system was most likely the result of reductive coupling of the nitrile by a small amount of low-valent titanocene species present in the original preparation. Related reductive couplings of nitriles by Ti(II) (in the form of its tetramethylethylenediamine complex)[19] and $Cp_2Ti(III)$,[20] as well as by $(C_5Me_5)_2Zr(II)$ (which afforded a mononuclear product),[21] have appeared, but have apparently not been reported for $Cp_2Ti(II)$. To test this hypothesis, we examined the reaction between the bis(trimethylphosphine) complex of titanocene[22] and 2,4,6-trimethylbenzonitrile. The reaction, rapid at room temperature in dry benzene, afforded sparingly soluble **7a** as a nearly black powder displaying elemental analytical data in support of its formulation as $Cp_2Ti(2,4,6\text{-trimethylbenzonitrile})(PMe_3)$. The FAB mass spectrum of **7a** suggested it to be a monomer rather than the anticipated dimer, although the sparing solubility unfortunately precluded solution molecular weight determination. Heating **7a** at 70°C for 14 hours afforded a soluble complex, displaying no evidence of phosphine dissociation (and in fact showing clear spectroscopic evidence for coordinated phosphine), which appears to be dimer **6**.

$$\mathrm{Cp_2Ti(PMe_3)_2 + ArCN \longrightarrow \underset{\mathbf{7a}}{\left[Cp_2Ti(ArCN)(PMe_3)\right]\downarrow} \qquad (Ar = 2,4,6\text{-}Me_3\text{-}C_6H_2)}$$

Isobutyronitrile and *p*-methoxybenzonitrile also reacted readily with the bis(trimethylphosphine) complex of titanocene, affording soluble $Cp_2Ti(PMe_3)$(nitrile) complexes, **7b** and **7c**, consistent with earlier literature reports of the formation of such complexes.[22,23] We have found that these complexes exist in solution in equilibrium with the phosphine-free complexes, with the extent of phosphine dissociation appearing dependent on the steric bulk of the nitrile ($K_{eq} \approx 0.017$ for **7b**, 0.0014 for **7c**). Given this, one might anticipate the 2,4,6-trimethylbenzonitrile complex (**7a**) to dissociate phosphine completely in solution, and the observed reductive coupling of this nitrile may proceed via the phosphine-free complex.

$$\mathrm{Cp_2Ti(PMe_3)_2 + RCN \longrightarrow Cp_2Ti(RCN)(PMe_3) \overset{K_{eq}}{\rightleftharpoons} Cp_2Ti(RCN) + PMe_3}$$

$\mathbf{7b}$ R = ^{i}Pr

$\mathbf{7c}$ R = *p*-MeO-C_6H_4

CONCLUSIONS

Reactions of dimethyltitanacyclobutene with nitriles in the presence of trimethylphosphine as a trapping ligand have provided access to several crystalline titanocene imido complexes, permitting the first determinations of structural details and metrical parameters for such complexes. Bis(cyclopentadienyl)titanium bis(trimethylphosphine) undergoes ligand substitution reactions with nitriles. Loss of trimethylphosphine from the 2,4,6-trimethylbenzonitrile complex appears to lead to reductive coupling of the nitrile, affording a dimeric imido complex.

EXPERIMENTAL

All operations were carried out under a nitrogen or argon atmosphere in dry, deoxygenated solvents, using standard inert atmosphere techniques.[24]

Preparation of 1,1-Bis(cyclopentadienyl)-3,7-diisopropyl-4,5-dimethyl-2,8-diaza-1-titanacycloocta-2,4,7-triene (1). Dimethyltitanacyclobutene (0.113 g, 0.459 mmol) was dissolved in 3 mL of toluene. To this solution was added 85 μL of isobutyronitrile (0.065 g, 0.935 mmol). The dark-red solution was heated at 60°C for 45 min, affording a purple solution. Solvent and excess nitrile were removed in vacuo, affording complex **1** as an orange powder (0.174 g, 98%) in analytically-pure form. ^{1}H NMR (C_6D_6): δ 5.66 (s, 5H, Cp), 5.62 (s, 5H, Cp), 3.17 (d, 1H, $^2J_{HH}$ = 10.2 Hz, CHH), 2.51 (d, 1H, $^2J_{HH}$ = 10.2 Hz, CHH), 2.36 (heptet, 1H, $^3J_{HH}$ = 6.7 Hz, CH), 2.19 (heptet, 1H, $^3J_{HH}$ = 6.7 Hz, CH), 1.63 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.07 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.00 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 0.99 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 0.97 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 174.0 (Ti-N=C), 164.6 (Ti-N=C), 133.8 (=C), 130.9 (=C), 111.5 (Cp), 110.5 (Cp), 48.6 (CH_2), 39.8 (CH), 34.4 (CH), 21.1 (CH_3), 20.8

(CH_3), 20.24 (CH_3), 20.19 (=C-$\underline{C}H_3$), 20.11 (CH_3), 16.0 (=C-$\underline{C}H_3$). MS (70 eV): m/z = 384 (M, 3%), 315 (M-C_4H_7N, 27), 178 (Cp_2Ti, 100), 113 (CpTi, 20), 68 (C_4H_6N, 40), 42 (C_3H_6, 85). Anal. Calcd. for $C_{23}H_{32}N_2Ti$: C, 71.86; H, 8.39. Found: C, 72.06; H, 8.20.

Isobutyronitrile-derived butadienylimido complex 2 and imido complex 3. To a solution of 23.3 mg of dimethyltitanacyclobutene (0.095 mmol) in 0.50 mL of C_6D_6 in a 5 mm NMR tube was added 40.0 μL of trimethylphosphine (0.425 mmol) and 8.8 μL of isobutyronitrile (0.097 mmol). The dark-red solution was heated at 60°C for 1 h, at which time ^{1}H NMR analysis showed conversion to a mixture of the double insertion product, the apparent single vinyl insertion product, and butadienylimido complex **2**, with the latter present as ca. 50% of the product mixture. ^{1}H NMR (C_6D_6): δ 5.68 (br s , 10H, Cp), 4.98 (br s, 1H, =CHH), 4.92 (br s, 1H, =CHH), 2.14 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 0.97 (d, 6H, $^3J_{HH}$ = 5.7 Hz, CH_3), 0.79 (br s, 9H, PMe_3). (Isopropyl methine proton not resolved.) $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.3 (C-N), 107.7 (Cp), 31.3 (CH), 24.0 (CH_3), 22.4 CH($\underline{C}H_3$)$_2$), 19.6 (CH_3), 17.6 (d, $^1J_{CP}$ = 18 Hz, PMe_3). (Olefinic carbons not resolved.) Continued heating for an additional 10 h resulted in the deposition of dark crystals of **3**, isolated by decantation in 12% yield; the mother liquor no longer displayed observable resonances in the ^{1}H NMR spectrum. MS (70 eV): 312 (M-PMe_3+H, 24%), 247 (M-PMe_3-Cp+H, 100), 177 (Cp_2Ti-H, 85), 113 (CpTi, 22), 76 (PMe_3).

X-ray structural analysis of imido complex 3. Crystals obtained as described above proved amenable to x-ray diffraction analysis. Crystal and structure refinement data, resulting from Patterson/direct methods structure solution (PATT routine of SHELXTL PLUS) and full-matrix least squares refinement on F^2, are collected in Table 2 and atomic coordinates are presented in Table 3.

Preparation of 1,1-Bis(cyclopentadienyl)-5,6-dimethyl-3-(2,4,6-trimethylphenyl)-2-aza-1-titanacyclohexa-2,5-diene (4). A solution of 44.2 mg of dimethyltitanacyclobutene (0.179 mmol) and 26.0 mg of 2,4,6-trimethylbenzonitrile (0.179 mmol) in 0.6 mL of C_6D_6 was heated at 45°C for 5 days, at which time NMR analysis indicated quantitative conversion to **4** and its apparent tautomer, the corresponding titanacyclohexa-2,4-diene. After removal of volatiles in vacuo, the crude product was washed with pentane, affording an inseparable mixture of **4** and its tautomer (in a ca. 3:1 ratio) as a red-brown solid, mp 110°C, 170°C, in a combined yield of 76%. IR(KBr): 3100 (mw), 2912 (m), 2836 (m), 1685 (m), 1610 (Mw), 1441 (m), 1320 (mw), 1020 (m), 841 (m), 799 (vs), 640 (m), 543 (mw) cm^{-1}. MS (70 eV): 391 (M, 18%), 178 (Cp_2Ti, 100%), 113 (CpTi, 38%). HRMS: Calcd for $C_{25}H_{29}NTi$: 391.1779. Found: 391.1786. Complex **4**: ^{1}H NMR (C_6D_6): δ 6.70 (s, 2H, ArH), 5.71 (s, 10H, Cp), 3.33 (s, 2H, CH_2), 2.25 (s, 6H, Ar-CH_3), 2.12 (s, 3H, Ar-CH_3), 1.65 (s, 6H, 2xCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 179.8 (Ti-$\underline{C}$=C), 167.0 (C=N), 138.2 (Ar), 136.3 (Ar), 135.2 (Ar), 133.8 (Ar), 121.4 (Ti-C=$\underline{C}$), 109.8 (Cp), 60.6 (CH_2), 25.4 (CH_3), 21.0 (CH_3), 19.7 (Ar-CH_3-*o*), 17.6 (Ar-CH_3-*p*). Tautomer: ^{1}H NMR (C_6D_6): δ 8.57 (br s, 1H, NH), 6.82 (s, 2H, ArH), 5.61 (s, 10H, Cp), 2.18 (s, 6H, Ar-CH_3), 2.13 (s, 3H, CH_3), 1.91 (s, 3H, Ar-CH_3). (Methine and second =C-CH_3 resonances not resolved.) Anal. Calcd for $C_{25}H_{29}NTi$: C, 76.72; H, 7.47; N, 3.58. Found: C, 76.65; H, 7.56; N, 3.50.

Table 2. Crystal and structure refinement data for complexes **3**, **4**, and **6**.

Complex	**3**	**4**	**6**
Empirical formula	$C_{22}H_{30}NPTi$	$C_{25}H_{28}NTi$	$C_{46}H_{60}N_2P_2Ti_2$
Formula weight	387.34	390.38	798.7
Temperature	120(2) K	120(2) K	295 K
Radiation	Cu Kα (rotating anode)	Mo Kα (rotating anode)	Mo Kα
Wavelength	1.54180 Å	0.71073 Å	0.71073 Å
Monochromator	Ni filtered	Zr filtered	graphite
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pmn2_1$	$P2_1/n$	Pbca
a (Å)	12.784(3) Å	8.163(4) Å	10.447(5) Å
b (Å)	17.835(4)	10.855(5)	18.201(13)
c (Å)	9.107(2)	23.024(10)	22.046(4)
β (deg)	-	94.88(4)°	-
Volume (A^3)	2076.4(8)	2033(2)	4192(6)
Z	4	4	4
Density (calcd, Mg/m^3)	1.239	1.276	1.265
Absorption coeff (mm^{-1})	4.23	0.43	-
F(000)	824	828	1696
Crystal size (mm)	0.09 x 0.11 x 0.27	0.16 x 0.20 x 0.60	0.07 x 0.32 x 0.47
Habit	Rectangular rod	Needle	Tablet
Color	Red	Orange	Red-black
Diffractometer	Siemens P4R	Siemens P4R	Enraf-Nonius CAD-4
θ range for data collection	0 to 54.0°	1.78 to 27.56°	-
$2\theta_{max}$	-	-	45°
Index ranges	$0 \leq h \leq 13, 0 \leq k \leq 18, 0 \leq l \leq 9$	$0 \leq h \leq 10, 0 \leq k < 14, -29 \leq l \leq 29$	$0 \leq h \leq 11, 0 \leq k < 19, 0 \leq l \leq 23$
Reflections collected	1420	5014	
Independent reflections	1420	4704 ($R_{int} = 0.0402$)	2732
Data / restraints / parameters	1420 / 108 / 161	4700 / 0 / 114	2732 / 0 / 115
Goodness-of-fit on F^2	0.919	1.027	1.86
Final R indices [$I>2\sigma(I)$]	R1 = 0.0582 wR2 = 0.1368	R1 = 0.0738 wR2 = 0.1604	- -
Final R indices [$I>1.5\sigma(I)$]	- -	- -	R1 = 0.085 wR2 = 0.066
R indices (all data)	R1 = 0.0627 wR2 = 0.1419	R1 = 0.1244 wR2 = 0.2167	- -
Largest diff. peak and hole (eÅ^{-3})	0.658 and -0.307	0.991 and -0.533	0.63 and -0.31
Absolute structure parameter	0.02(2)	-	-

Table 3. Atomic coordinates [x 10^4] for complex **3**.[a]

atom	x	y	z
Ti1	0	4421(1)	4338
P1	0	4460(2)	1523(3)
N11	0	3393(4)	4369(11)
C21	0	2678(5)	4571(12)
C31	0	2364(6)	6013(12)
C41	0	2786(6)	7327(12)
C51	0	2295(7)	8518(15)
C61	0	1573(6)	7942(15)
C71	0	1599(6)	6453(14)
C81	0	2220(7)	3154(16)
C91	994(7)	1795(5)	2916(14)
C111	0	5359(6)	631(16)
C121	1106(6)	3996(5)	641(10)
C141	1863(6)	4324(4)	4126(9)
C151	1605(6)	5053(4)	3748(10)
C161	1200(5)	5399(4)	4991(8)
C171	1189(6)	4871(4)	6147(10)
C181	1619(6)	4202(4)	5592(9)
Ti2	1031(2)	8423(1)	2636(4)
P2	147(4)	9063(2)	460(4)
N12	-165(8)	8224(5)	3700(10)
C22	-834(9)	7917(7)	4588(14)
C32	-552(11)	7488(9)	5855(16)
C42	462(11)	7288(9)	6312(18)
C52	361(10)	6816(10)	7531(20)
C62	-695(12)	6723(10)	7825(19)
C72	-1256(11)	7123(8)	6835(15)
C82	-1984(10)	8038(7)	4187(17)
C92	-2267(19)	8834(9)	3856(33)
C102	-2276(22)	7542(14)	2912(29)
C112	942(15)	9401(11)	-1029(20)
C122	-837(14)	8518(10)	-551(26)
C132	-639(13)	9890(8)	907(22)
C142	707(9)	7306(6)	1257(13)
C152	1543(9)	7661(6)	572(13)
C162	2378(9)	7668(6)	1544(13)
C172	2064(9)	7319(6)	2863(16)
C182	1023(9)	7083(5)	2648(14)
C192	1000(11)	9607(6)	3886(14)
C202	1647(10)	9691(6)	2688(16)
C212	2514(8)	9231(6)	2923(17)
C222	2378(10)	8839(8)	4273(16)
C232	1437(11)	9095(7)	4852(13)

[a] The last digit in an atom name indicates molecule number. Numbers have been skipped in molecule 1 in order to retain numbering conformity with 2. Molecule 2 is disordered across mirror plane.

X-ray structural analysis of 1,1-Bis(cyclopentadienyl)-5,6-dimethyl-3-(2,4,6-trimethylphenyl)-2-aza-1-titanacyclohexa-2,5-diene (4). Single crystals of this complex were obtained in low yield during the attempted recrystallization of complex **5** from toluene/hexanes. Structure solution and refinement were carried out as for complex **3**. Crystal and structure refinement data are collected in Table 1 and atomic coordinates are presented in Table 4.

Preparation of 2,4,6-trimethylbenzonitrile-derived butadienylimido complex 5. 2,4,6-Trimethylbenzonitrile (34.6 mg, 0.238 mmol) was dissolved in a solution of 58.7 mg of dimethyltitanacyclobutene (0.238 mmol) in 0.75 mL of C_6D_6. The red solution was transferred to a 5 mm NMR tube, trimethylphosphine (0.250 mL, 10 equiv) was added, and the tube was flame sealed. The sample was kept at ambient temperature for 3 days, yielding a dark solution and a microcrystalline solid. The mother liquor, which displayed a bluish cast reminiscent of the blue color of the zirconocene complexes reported by Bergman,[8] was decanted, and the solid was washed with hexanes and dried in vacuo, affording the product in analytically-pure form (50 mg, 44%), mp 245-247°C (sealed capillary). IR(KBr): 3086 (w), 2977 (mw), 2915 (m), 1614 (m), 1443 (mw),

Table 4. Atomic coordinates [x 10^4] for complex **4**.

atom	x	y	z	atom	x	y	z
Ti	50(1)	4097(1)	1909(1)	C(13)	-1332(5)	4495(4)	1074(2)
N	1123(4)	2896(3)	1481(1)	C(14)	-2131(5)	4215(4)	-3(2)
C(1)	1094(5)	2367(4)	994(2)	C(15)	-2546(5)	5563(4)	1060(2)
C(2)	2215(5)	1304(4)	894(2)	C(16)	492(6)	6211(4)	2197(2)
C(3)	3880(5)	1543(4)	828(2)	C(17)	1506(6)	5483(5)	2577(2)
C(4)	4941(5)	567(4)	761(2)	C(18)	2681(6)	4894(4)	2256(2)
C(5)	4409(5)	-660(4)	769(2)	C(19)	2389(5)	5277(4)	1671(2)
C(6)	2764(5)	-866(4)	837(2)	C(20)	1044(5)	6095(4)	1633(2)
C(7)	1650(5)	86(4)	898(2)	C(21)	-2697(6)	3783(4)	2186(2)
C(8)	4505(5)	2851(4)	825(2)	C(22)	-1696(5)	4058(4)	2693(2)
C(9)	5600(5)	-1701(4)	707(2)	C(23)	-526(6)	3095(4)	2785(2)
C(10)	-128(6)	-217(5)	974(2)	C(24)	-857(5)	2218(4)	2343(2)
C(11)	-52(5)	2801(4)	482(2)	C(25)	-2174(5)	2638(4)	1969(2)
C(12)	-1183(5)	3879(4)	572(2)				

1272 (m), 1147 (m), 1020 (m), 952 (m), 857 (ms), 809 (s), 789 (s), 557 (m) cm^{-1}. ^{1}H NMR (THF-d_8): δ 6.91 (s, 1H, ArH), 5.96 (br s, 1H. =CH), 5.31 (s, 10H, Cp), 5.20 (br s, 1H, =CH), 2.50 (s, 6H, Ar-CH_3), 2.32 (s, 3H, Ar-CH_3), 2.24 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 1.06 (d, 9H, $^2J_{PH}$ = 7.0 Hz, PMe_3). Anal. Calcd. for $C_{28}H_{38}NPTi$: C, 71.94; H, 8.19; N, 3.00. Found: C, 71.81; H, 8.26; N, 3.03.

X-ray structural analysis of complex 6. Single crystals of this complex were obtained in low yield during the attempted recrystallization of complex **5** from toluene/hexanes. The Patterson function and one cycle of DIRDIF (TEXSAN program suite) revealed all non-hydrogen atoms. The Ti and P atoms were refined anisotropically in the last cycles, and H atoms were included at riding positions with B = 1.2B(C). Crystal and structure refinement data are collected in Table 1 and atomic coordinates are presented in Table 5.

Preparation of Cp_2Ti(2,4,6-trimethylbenzonitrile)(PMe_3) (7a). To 22.1 mg of 2,4,6-trimethylbenzonitrile (0.152 mmol) in 7.5 mL of benzene was added a solution of 50.1 mg (0.152 mmol) of $Cp_2Ti(PMe_3)_2$ in 7.5 mL of benzene. The resulting dark solution was stirred for 2 days at ambient temperature, then frozen and rethawed. The resulting dark precipitate was isolated by filtration, affording sparingly soluble complex **7a** (37 mg, 61%). Anal. Calcd for $C_{23}H_{30}NPTi$: C, 69.17; H, 7.57; N, 3.51; P, 7.76. Found: C, 69.09; H, 7.66; N, 3.57; P, 7.51.

Preparation of Cp_2Ti(isobutyronitrile)(PMe_3) (7b). Addition of 5.6 μL of isobutyronitrile (0.062 mmol) to a solution of 20.3 mg of $Cp_2Ti(PMe_3)_2$ (1 equiv) in 1.0 mL of C_6D_6 cleanly afforded complex **7b**, present in solution in equilibrium with its phosphine-off form. Attempted isolation resulted in decomposition. **7b**: ^{1}H NMR (C_6D_6): δ 4.94 (s, 10H, Cp), 2.73 (m, 1H, J = 6.9 Hz, CH), 1.37 (d, 6H, J = 6.9 Hz, CH_3), 0.85 (br s, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 106.5 (CN), 100.6 (Cp), 22.0 (CH), 19.1 (CH_3), 16 (br, PMe_3). Cp_2Ti(isobutyronitrile): ^{1}H NMR (C_6D_6): δ 5.42 (s, 10H, Cp), 2.07 (m, 1H, J = 6.9 Hz, CH), 0.92 (d, 6H, J = 6.9 Hz, CH_3), 0.85 (br s, PMe_3).

Table 5. Atomic coordinates [x 10^4] for complex **6**.

atom	x	y	z	atom	x	y	z
Ti	7203(2)	5473.4(13)	6208.9(12)	C(11)	9550(13)	5815(8)	6347(6)
P	7736(5)	4109(2)	6314(2)	C(12)	8887(15)	6438(8)	6258(7)
N	6091(10)	5262(5)	5604(4)	C(13)	8376(16)	6410(9)	5675(8)
C(1)	5462(12)	5233(7)	5079(6)	C(14)	8724(16)	5767(9)	5413(7)
C(2)	5900(12)	5832(7)	4625(5)	C(15)	9419(15)	5369(9)	5842(7)
C(3)	5630(13)	6558(7)	4729(6)	C(16)	5571(14)	5279(8)	6971(6)
C(4)	6142(13)	7102(7)	4341(6)	C(17)	5481(14)	6010(8)	6806(6)
C(5)	6889(12)	6904(8)	3877(7)	C(18)	6536(15)	6364(8)	7022(7)
C(6)	7177(15)	6214(8)	3759(7)	C(19)	7269(16)	5888(8)	7344(6)
C(7)	6703(12)	5649(7)	4132(6)	C(20)	6731(15)	5219(8)	7311(6)
C(8)	7061(14)	4847(7)	4037(6)	C(21)	8081(17)	3672(10)	5613(8)
C(9)	7414(16)	7496(9)	3445(7)	C(22)	6483(16)	3540(9)	6605(7)
C(10)	4835(14)	6813(7)	5250(6)	C(23)	9049(17)	3835(9)	6792(8)

Preparation of Cp$_2$Ti(*p*-methoxybenzonitrile)(PMe$_3$) (7c). Addition of 8.2 mg of *p*-methoxybenzonitrile (0.062 mmol) in 0.5 mL of C$_6$D$_6$ to a solution of 20.3 mg of Cp$_2$Ti(PMe$_3$)$_2$ (1 equiv) in 0.5 mL of C$_6$D$_6$ cleanly afforded complex **7c**, present in solution in equilibrium with its phosphine-off form. Attempted isolation resulted in decomposition. **7c**: ^{1}H NMR (C$_6$D$_6$): δ 8.00 (AB, 2H, J = 8.1 Hz, ArH), 6.94 (AB, 2H, J = 8.1 Hz, ArH), 5.02 (s, 10H, Cp), 3.32 (s, 3H, OCH$_3$), 0.80 (br s, PMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 132.4 ($\underline{\text{C}}$-OCH$_3$), 114.3 (aromatic CH), 113.1 (CN or $\underline{\text{C}}$-CN), 106.7 (aromatic CH), 106.2 ($\underline{\text{C}}$-CN or CN), 101.6 (Cp), 54.9 (OCH$_3$), 16 (br, PMe$_3$). Cp$_2$Ti(*p*-methoxybenzonitrile): ^{1}H NMR (C$_6$D$_6$): δ 6.7 (AB, 2H, J = 8.1 Hz, ArH), 5.61 (s, 10H, Cp), 3.46 (s, 3H, OCH$_3$), 0.80 (br s, PMe$_3$). (Other half of AB quartet not resolved.)

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