space group would then be either $P2_1/m$ or $P2_1$.

Data were collected for the entire copper sphere ($2\theta = 55°$). Direct methods (MULTAN 78) were first attempted in the centric space group, and a solution was obtained with the two W atoms lying in a mirror plane. The two peaks were also located in a Patterson syntheses. Refinement and Fourier techniques progressed normally, with all atoms in the pyridine and five neopentoxy ligands being easily located (with one apparently disordered OC_2CMe_3).

At this point it was noted that there was also an apparent disorder in the acetylenic ligand and also that several of the atoms did not "settle down" as would be expected. Since the Patterson map is consistent with either $P2_1$ or $P2_1/m$, an attempt was made to refine the structure in the noncentric setting. This proved to be the correct space group as the residuals rapidly decreased and the apparent disorder in the acetylenic ligand and bridging neopentoxy ligand were no longer present. In spite of resolving the disorder, it was difficult to obtain convergence because of the large correlations between similar atoms on either side of the molecular plane. It is to be noted in the tables provided in the supplementary material that several of the carbon atoms lie at unrealistic distances [the extreme being 1.80 for C(34)–C(35)]. While convergence may indeed have been obtainable at some stage, it was felt the increased precision would not justify the expense since the molecular parameters of interest were not shifting significantly. Although some of the hydrogen atoms were visible in a difference Fourier, no attempt was made to locate or refine them, instead using idealized fixed hydrogen contributions. Psi scans indicated no absorption correction was necessary.

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Registry No. $W_2(ONp)_6(py)_2$, 88608-50-8; $W_2(ONp)_6(py)(\mu\text{-}C_2Ph_2)$, 104872-65-3; $PhC{\equiv}CPh$, 501-65-5; $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$, 104872-66-4; $EtC{\equiv}CEt$, 928-49-4; $W_2(ONp)_6(Py)_2(\mu\text{-}C_2H_2)$, 104779-53-5; $HC{\equiv}CH$, 74-86-2; $[(t\text{-}BuO)_3W{\equiv}CMe]_2$, 86669-24-1; $MeC{\equiv}CMe$, 503-17-3; $W_2(ONp)_6(py)_2(\mu\text{-}C_2Me_2)$, 104870-71-5; $W_3(\mu_3\text{-}CEt)(ONp)_9(py)$, 104779-54-6; $[(t\text{-}BuO)_3W{\equiv}CEt]_2$, 104779-55-7; $(t\text{-}BuO)_3W{\equiv}CPh$, 82228-87-3.

Supplementary Material Available: VERSORT and ORTEP drawings and complete listings of atomic positional parameters, anisotropic thermal parameters, bond distances, and bond angles (19 pages); listings of F_o and F_c values (42 pages). Ordering information is given on any current masthead page. The complete structural reports are available in microfiche form only from the Indiana University Library at 2.50 per copy. Request MSC Report No. 84040 for $W_2(ONp)_6(py)_2(\mu\text{-}C_2H_2)$ and 84029 for $W_2(ONp)_6(py)(\mu\text{-}C_2Et_2)$.

Diamagnetic Isocyanide Complexes of Titanium, Zirconium, and Hafnium

Lawrence B. Kool,[1a,b] Marvin D. Rausch,*[1b] Max Herberhold,[1a] Helmut G. Alt,*[1a] Ulf Thewalt,[1c]
and Brigitte Honold[1c]

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-8580 Bayreuth, Federal Republic of Germany,
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, and Sektion für
Röntgen- und Elektronenbeugung, Universität Ulm, D-7900 Ulm, Federal Republic of Germany

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Isocyanide complexes of the type $Cp_2M(CO)(L)$ (Cp = η^5-cyclopentadienyl, L = *tert*-butyl isocyanide, M = Ti, Zr, Hf; L = 2,6-dimethylphenyl isocyanide, M = Ti, Zr; L = methyl isocyanide, M = Ti) and $(Ind)_2Ti(CO)(L)$ (Ind = η^5-indenyl, L = *tert*-butyl isocyanide) were prepared and characterized by their IR, ^1H and ^{13}C NMR, and mass spectra. These are the first examples of diamagnetic isocyanide complexes of group 4 elements. The crystal structure of $Cp_2Ti(CO)(CN\text{-}t\text{-}Bu)$ (1) was determined by X-ray diffraction using 1414 reflections that were refined to a final R index of 0.077. The crystals were monoclinic, space group $P2_1/c$, with unit cell parameters $a = 6.559$ (2) Å, $b = 14.236$ (3) Å, and $c = 16.631$ (4) Å, $\beta = 100.81$ (3)°, and $Z = 4$. The molecular structure is typical of compounds of the type Cp_2TiXY, with pseudotetrahedral geometry.

Introduction

Numerous examples of transition-metal isocyanide complexes now exist.[2] Surprisingly, however, no diamagnetic isocyanide complexes of group 4 metals are known.[3] This may be due to the tendency of isocyanide ligands to form polymeric or polynuclear products when treated with low-valent early transition-metal complexes. As part of our continuing program to synthesize and study the chemistry of low-valent group 4 metallocene derivatives, we have undertaken the development of synthetic routes to diamagnetic group 4 metallocene isonitrile complexes. In this paper we report on the synthesis and spectral properties of the first diamagnetic isocyanide complexes of group 4 metals and on the crystal structure of $Cp_2Ti(CO)(CN\text{-}t\text{-}Bu)$ (1).

Results and Discussion

When *tert*-butyl isocyanide was added to THF solutions of $Cp_2M(CO)_2$ (M = Ti, Zr and Hf)[4] at −78 °C and the solutions then allowed to slowly warm to ambient temperature, the isocyanide complexes 1–3 were obtained as pure, crystalline solids.

The crude reaction products (before crystallization) contained small amounts of the dicarbonyl starting materials. Experiments run in pentane or at higher tem-

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(1) (a) University of Bayreuth. (b) University of Massachusetts. (c) University of Ulm.

(2) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. See also references cited therein.

(3) Several examples of paramagnetic isocyanide complexes of titanium(III) have been previously described: Floriani, C.; Fachinetti, G. **1974**, 1954. de Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *166*, 193.

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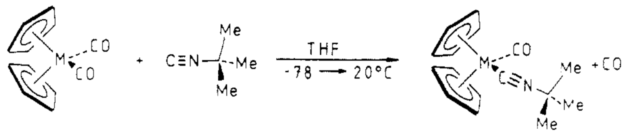
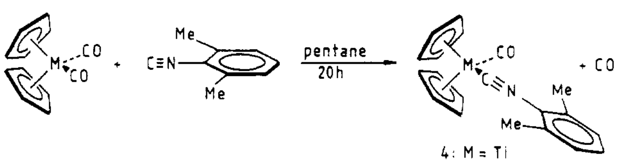


1: M = Ti
2: M = Zr
3: M = Hf

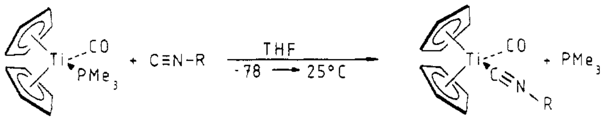
peratures resulted in the formation of poorly soluble polymeric products which were difficult to characterize. Complex **1** could be obtained in analytically pure form through recrystallization. Due to their extreme sensitivity complexes **2** and **3** could not be obtained analytically pure, being contaminated with small quantities of the dicarbonyl precursors. It was not possible to displace the second CO ligand of **1–3** with excess isocyanide even under photochemical conditions.

Addition of 2,6-dimethylphenyl isocyanide to Cp$_2$M(CO)$_2$ (M = Ti and Zr) in pentane afforded the related complexes **4** and **5**. In contrast to the *tert*-butyl isocyanide ligand, minimal polymerization occurred with 2,6-dimethylphenyl isocyanide, presumably because of the steric requirements of the two ortho methyl groups.



4: M = Ti
5: M = Zr

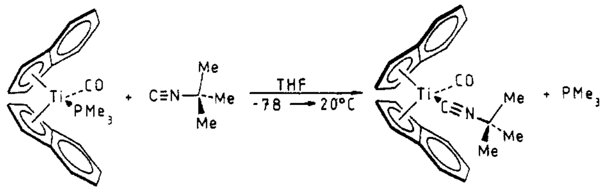
Reactions of the mixed-ligand complex Cp$_2$Ti(CO)(PMe$_3$)[5,6] with methyl isocyanide and *tert*-butyl isocyanide provided **6** and **1** in excellent yields.



6: R = Me
1: R = t-Bu

The PMe$_3$ ligand is more easily displaced than CO, making this route to isocyanide complexes more convenient, since the products are contaminated with unreacted dicarbonyl starting materials. The route provides higher yields and more facile crystal formation. Unfortunately the zirconium and hafnium analogues could not be obtained from Cp$_2$M(CO)(PMe$_3$) (M = Zr, Hf)[6] due to the formation of insoluble oligomeric or polymeric materials.

The indenyl complex (Ind)$_2$Ti(CO)(CN-*t*-Bu) (**7**) was obtained in high yield from (Ind)$_2$Ti(CO)(PMe$_3$)[6] and *tert*-butyl isocyanide.



7

Treatment of the permethylated complex (C$_5$Me$_5$)$_2$Ti(CO)$_2$[4] with various isocyanides did not provide (C$_5$Me$_5$)$_2$Ti(CO)(CNR) even under photochemical conditions. Attempts to isolate related complexes from reactions of isocyanides with Cp$_2$Ti(PMe$_3$)$_2$[7] and Cp$_2$Zr(PMe$_3$)$_2$[8] have thus far been unsuccessful, although IR and NMR spectral evidence indicates the formation of isocyanide-containing products.

Table I. IR and NMR Spectral Data of Complexes 1–7

	IR,[a] cm^{-1}		^{1}H NMR,[b] ppm	
compd	ν(CO)	ν(CN)[c]	δ(CP) or δ(Ind)	δ(CNR)
Cp$_2$Ti(CO)(CN-*t*-Bu)[d] (1)	1850	2170	4.81 (s, 10 H)	1.07 (s, 9 H)
Cp$_2$Zr(CO)(CN-*t*-Bu) (2)	1838	2185	5.53 (s, 10 H)	1.12 (s, 9 H)
Cp$_2$Hf(CO)(CN-*t*-Bu) (3)	1810	2192	5.50 (s, 10 H)	1.14 (s, 9 H)
Cp$_2$Ti(CO)(CNC$_6$H$_3$Me$_2$)[e] (4)	1862	2020	4.80 (s, 10 H)	2.00 (s, 6 H) 6.64 (m, 3 H)
Cp$_2$Zr(CO)(CNC$_6$H$_3$Me$_2$)[f] (5)	1842	2010	5.35 (s, 10 H)	2.13 (s, 6 H) 6.65 (m, 3H)
Cp$_2$Ti(CO)(CNMe) (6)	1840	2093	4.83 (s, 10 H)	2.28 (s, 3 H)
(Ind)$_2$Ti(CO)(CN-*t*-Bu) (7)	1855	2173	5.01 (m, 3 H) 7.10, 6.74 (m, 4 H)	0.95 (s, 9 H)

[a] KBr pellet. [b] Toluene-d_8, −20 °C. [c] Free CN-*t*-Bu, ν(CN) 2138 cm^{-1} (neat); free CNC$_6$H$_3$Me$_2$, ν(CN) 2110 cm^{-1} (KBr), free CNMe, ν(CN) 2161 cm^{-1} (neat). [d] ^{13}C NMR (toluene-d_8, −20 °C): δ 92.8 (Cp), 58.9 and 30.5 (*t*-Bu), 273.6 (CO). [e] ^{13}C NMR (toluene-d_8, −20 °C): δ 92.9 (Cp), 18.6 (Me), 130.3, 129.8, 127.8, 125.0 (C$_6$H$_3$Me$_2$), 220.0 (CN), 259.3 (CO). [f] ^{13}C NMR (toluene-d_8, −20 °C): δ 95.6 (Cp), 18.8 (Me), 128.2, 128.1, 127.9, 123.8 (C$_6$H$_3$Me$_2$), 237.3 (CN), 268.0 (CO).

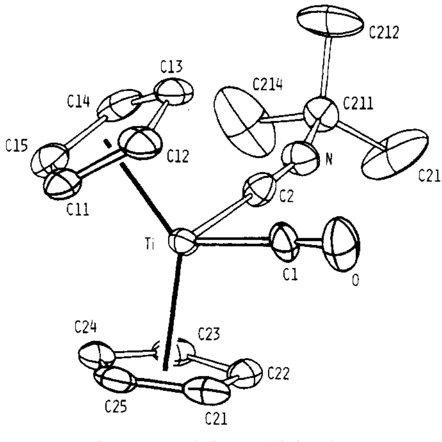


Figure 1. ORTEP drawing of Cp$_2$Ti(CO)(CN-*t*-Bu) (1) showing 30% probability thermal ellipsoids and the atomic numbering scheme.

The IR and ^{1}H NMR spectra of **1–7** are summarized in Table I. A comparison of the IR spectra of **1–3** reveals that the carbonyl stretching frequency ν(CO) is gradually lowered on proceeding down the series, due to increased M→CO back-bonding. In contrast, the isocyanide

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Table II. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for Cp$_2$Ti(CO)(CN-*t*-Bu) (1)^a

	Bond Distances		
Ti-C1	1.993 (10)	Ti-Z1	2.036 (12)
Ti-C2	2.112 (9)	Ti-Z2	2.037 (10)
C1-O	1.161 (13)	C11-C12	1.416 (16)
		C12-C13	1.439 (15)
C2-N	1.161 (12)	C13-C14	1.431 (17)
N-C211	1.469 (12)	C14-C15	1.429 (16)
C211-C212	1.499 (16)	C15-C11	1.418 (15)
C211-C213	1.501 (21)		
C211-C214	1.535 (22)	C21-C22	1.432 (14)
		C22-C23	1.444 (16)
Ti-C11	2.388 (11)	C23-C24	1.429 (15)
Ti-C12	2.371 (11)	C24-C25	1.419 (16)
Ti-C13	2.350 (11)	C25-C21	1.427 (17)
Ti-C14	2.358 (11)		
Ti-C15	2.386 (12)		
Ti-C21	2.371 (10)		
Ti-C22	2.362 (10)		
Ti-C23	2.370 (10)		
Ti-C24	2.380 (10)		
Ti-C25	2.379 (10)		
	Bond Angles		
C1-Ti-C2	92.6 (4)	Ti-C2-N	177.0 (8)
Z1-Ti-Z2	138.5 (4)	C2-N-C211	159.8 (10)
C1-Ti-Z1	103.6 (5)	N-C211-C212	107.1 (9)
C1-Ti-Z2	103.4 (4)	N-C211-C213	108.6 (9)
C2-Ti-Z1	103.5 (4)	N-C211-C214	107.3 (9)
C2-Ti-Z2	106.1 (4)	C212-C212-C213	113.3 (11)
		C212-C211-C214	107.8 (11)
Ti-C1-O	176.0 (8)	C213-C211-C214	112.5 (12)
		C-C-C^b	108.0 (9)

^{a} Z1 and Z2 are the centers of the C11- and C21-containing Cp rings, respectively. ^{b} Average for Cp rings.

stretching frequencies, ν(CN), show the opposite trend. A comparison of 4 and 5 also indicates increased M→CO back-bonding when M = Zr. The ν(CO) values of the titanium complexes 1, 4, and 6 decrease in the order L = 2,6-dimethylphenyl isocyanide > *tert*-butyl isocyanide > methyl isocyanide, due to increased Ti→CO back-bonding.

The ^{1}H NMR spectra of 1–6 indicate stronger deshielding of the cyclopentadienyl ring protons as compared to the corresponding Cp$_2$M(CO)(PMe$_3$) (M = Ti, Zr, Hf) analogues.[6] The ^{1}H and ^{13}C NMR spectra confirm the composition of 1–7, and the mass spectra are also consistent with a mononuclear structure.

The expected pseudotetrahedral geometry of the complexes was confirmed by determining the crystal and molecular structure of 1 by X-ray diffraction. Suitable crystals were grown from pentane solution at −78 °C. The molecular structure is illustrated in Figure 1, and bond distances and angles are listed in Table II.

The methyl C atoms of the *tert*-butyl group show rather high thermal motion. The shape and orientation of the respective temperature ellipsoids is consistent with a limited rotation of the *tert*-butyl group around the N–C211 axis. The molecule possesses a pseudotetrahedral structure which is typical for Cp$_2$TiXY complexes and is independent of the oxidation state of the titanium atom. The Ti–C(carbonyl) distance of 1.993 (10) Å is close to the Ti–C(carbonyl) distances found in other titanium complexes: 2.030 (11) Å in Cp$_2$Ti(CO)$_2$[9] and 1.963 (5) Å in Cp$_2$Ti(CO)(PMe$_3$)[6]. It is clearly shorter than the Ti–C(isocyanide) distance of 2.112 (9) Å.

Experimental Section

General Data. All operations were performed under argon atmosphere. Pentane, toluene, and THF were dried over Na/K alloy and freshly distilled. The complexes Cp$_2$Ti(CO)$_2$,[4] Cp$_2$Zr(CO)$_2$,[4] Cp$_2$Hf(CO)$_2$,[4] Cp$_2$Ti(CO)(PMe$_3$),[6] and (Ind)$_2$Ti(CO)(PMe$_3$)[6] as well as methyl isocyanide[10] were prepared according to literature procedures. Mass spectral values are based on ^{48}Ti, ^{90}Zr, and ^{180}Hf isotopes, respectively. *tert*-Butyl isocyanide and 2,6-dimethylphenyl isocyanide were used as received from Fluka Chemical Co.

^{1}H and ^{13}C NMR spectra were recorded at 90 and 22.5 MHz on a Fourier transform JEOL FX 90 Q spectrometer and are reported in δ values downfield from SiMe$_4$. The internal standard is the residual methyl proton resonance occurring at δ 2.09 for toluene. The internal standard for ^{13}C spectra is the resonance at δ 20.4 for toluene.

IR spectra were obtained in KBr by using a Perkin-Elmer 297 spectrometer. Electron-impact mass spectra were recorded on a Varian CH7 mass spectrometer at 70 eV. Elemental analyses were performed by Pascher Laboratories, Bonn, West Germany.

Cp$_2$Ti(CO)(CN-*t*-Bu) (1). Method 1. A sample of Cp$_2$Ti(CO)(PMe$_3$)[6] (480 mg, 1.70 mmol) in 50 mL of THF in a Schlenk tube was cooled to −78 °C, and *tert*-butyl isocyanide (0.38 mL, 3.4 mmol) was added via syringe. After being slowly warmed to room temperature over a 90-min period, the solution was deep red-brown. After concentration under reduced pressure to ca. 10 mL and storage at −78 °C, the supernatant solution was decanted from air-sensitive, analytically pure brown-black crystals of 1 (440 mg, 90%). Anal. Calcd. for C$_{16}$H$_{19}$NOTi (289.24): C, 66.44; H, 6.62; N, 4.84. Found: C, 66.18; H, 6.78; N, 4.96. Mass spectrum (70 eV): *m/e* 289 (M$^+$), 261 (M$^+$ − CO), 206 (M$^+$ − CNCMe$_3$).

Cp$_2$Ti(CO)(CN-*t*-Bu) (1). Method 2. A solution of Cp$_2$Ti(CO)$_2$[4] (480 mg, 2.05 mmol) in 50 mL of THF was cooled to −78 °C and treated with *tert*-butyl isocyanide (2 mL, 20 mmol). The solution was allowed to warm to room temperature and stirred for 20 h. During this time, slow, steady gas evolution was apparent. The solvent was removed in vacuo from the red-brown solution. The residue was extracted with pentane; the pentane solution was filtered and cooled to −78 °C. Compound 1 was obtained as an air-sensitive brown-black crystalline solid (460 mg, 78%).

Cp$_2$Zr(CO)(CN-*t*-Bu) (2). The same procedure was employed as that given above as method 2. Cp$_2$Zr(CO)$_2$[4] (340 mg, 1.23 mmol), *tert*-butyl isocyanide (0.13 mL, 1.1 mmol), and 50 mL of THF were used. After the reaction was complete, the solution was light yellow-orange. Complex 2 was obtained as an air-sensitive, crystalline orange-brown solid (350 mg, 86%). Mass spectrum (70 eV): *m/e* 332 (M$^+$), 303 (M$^+$ − CO), 248 (M$^+$ − CNCMe$_3$).

Cp$_2$Hf(CO)(CN-*t*-Bu) (3). Method 2, given above, was used. Cp$_2$Hf(CO)$_2$[4] (420 mg, 1.15 mmol) and *tert*-butyl isocyanide (0.13 mL, 1.1 mmol) were dissolved in 50 mL of THF. As the solution warmed, it turned red, then orange, and finally light yellow. Complex 3 was obtained as a very air-sensitive, crystalline red solid (310 mg, 64%). Mass spectrum (70 eV): *m/e* 421 (M$^+$), 393 (M$^+$ − CO), 338 (M$^+$ − CNCMe$_3$).

Cp$_2$Ti(CO)(CNC$_8$H$_9$) (4). A solution of Cp$_2$Ti(CO)$_2$[4] (780 mg, 3.3 mmol) and 2,6-dimethylphenyl isocyanide (0.87 g, 6.6 mmol) in 100 mL of pentane was stirred for 20 h at room temperature. During this period gas evolved and the solution became deep red-brown. The solution was filtered through filter aid, concentrated to ca. 50 mL, and cooled to −20 °C. The supernatant solution was decanted from shiny, brown-black, air-sensitive crystals (800 mg, 72%). A second crop was obtained after further concentration and cooling (combined crops: 1.10 g, 98%). Anal. Calcd for C$_{20}$H$_{19}$NOTi (337.26): C, 71.23; H, 5.68; N, 4.15. Found: C, 71.58; H, 6.16; N, 4.64. Mass spectrum (70 eV): *m/e* 337 (M$^+$)

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Table III. Crystallographic Data for the X-ray Diffraction Study of $Cp_2Ti(CO)(CN\text{-}t\text{-}Bu)$ (1)

Crystal Parameters

cryst system: monoclinic
space group $P2_1/c$
$a = 6.559$ (2) Å
$b = 14.236$ (3) Å
$c = 16.631$ (4) Å
$\beta = 100.81$ (3)°
$V = 1525$ (1) Å^3
$Z = 4$
ρ(calcd) = 1.259 g cm^{-3}
abs coeff $\mu = 5.0$ cm^{-1}
$T = 20$ °C

Measurement of Intensity Data

diffractometer:	Phillips-PW 1100
radiation:	Mo Kα ($\lambda = 0.71069$ Å, graphite monochromator)
scan type:	θ–2θ; θ(max) = 25°
reflcns collected:	2681
reflcns used in the refinement	1414; $F_0 \geq 1.5\sigma(F_0)$
Lp correction used	
$R = R_w - 0.077$	
max of remaining electron density:	0.52 e Å^{-3}

309 (M^+ - CO), 206 (M^+ - CN - C_8H_9).

$Cp_2Zr(CO)(CNC_8H_9)$ (5). The procedure reported above for complex 4 was employed, with the following quantities: $Cp_2Zr(CO)_2$[4] (830 mg, 3.0 mmol), 2,6-dimethylphenyl isocyanide (390 mg, 3.0 mmol) and 100 mL of pentane. Complex 5 was obtained as pyrophoric, dark red-brown crystals (1.12 g, 98%). Anal. Calcd for $C_{20}H_{19}NOZr$ (380.62): C, 63.11; H, 5.03; N, 3.68. Found: C, 63.29; H, 6.15; N, 4.71. Mass spectrum (70 eV): *m/e* 379 (M^+), 351 (M^+ - CO), 296 (M^+ - $CNCMe_3$).

$Cp_2Ti(CO)(CNMe)$ (6). The procedure reported as method 1 for complex 1 was employed by using $Cp_2Ti(CO)(PMe_3)$[6] (730 mg, 2.59 mmol), 30 mL of THF and methyl isocyanide (0.11 mL, 2.6 mmol). After 3.5 h the solution was red-brown. The solvent was removed in vacuo, and the residue was washed with pentane. The residue was extracted with toluene, the solution was filtered and concentrated, and a layer of pentane was added. After the solution was cooled to −78 °C, the supernatant was decanted from red-brown crystals of 6 (540 mg, 84%). Anal. Calcd for $C_{13}H_{13}NOTi$ (247.13): C, 63.18; H, 5.30; N, 5.67. Found: C, 62.90; H, 5.21; N, 5.58. Mass spectrum (70 eV): *m/e* 247 (M^+), 219 (M^+ - CO), 206 (M^+ - CNMe).

$(Ind)_2Ti(CO)(CN\text{-}t\text{-}Bu)$ (7). A solution of $(Ind)_2Ti(CO)(PMe_3)$ (310 mg, 0.81 mmol) in 10 mL of THF was cooled to −78 °C and *tert*-butyl isocyanide (0.1 mL, 0.9 mmol) was added via syringe. The solution was allowed to warm to room temperature over a 90-min period, and the solvent was removed in vacuo. The residue was extracted with pentane, filtered, concentrated to ca. 15 mL, and cooled to −78 °C. Complex 7 was obtained as fine, chocolate-brown needles (270 mg, 87%). Anal. Calcd for $C_{24}H_{23}NOTi$ (389.3): C, 74.04; H, 5.95; N, 3.60: Found: C, 74.36; H, 5.98; N, 3.48. Mass spectrum (70 eV): *m/e* 403 (M^+ + 14).

Structure Determination and Refinement of $Cp_2Ti(CO)(CN\text{-}t\text{-}Bu)$ (1). The crystals were not of high quality. A fragment with the dimensions 0.2 × 0.3 × 0.3 mm was sealed in a Lindemann glass capillary. Crystal data and intensity parameters for $C_{16}H_{19}NOTi$ (M_r 289.21) are presented in Table III. Systematic absences (*h*0*l* absent if *l* odd; 0*k*0 absent if *k* odd) indicated space group $P2_1/c$. All calculations were performed on a DEC VAX-780 computer using the SHELX76-system[13] and locally written programs. The Ti atom was located by Patterson synthesis; the remaining non-hydrogen atoms were found in ΔF syntheses; H atoms could not be located. The refinement was carried out by using anisotropic temperature factors and unit weights. The final R index was 0.077 ($R = [\sum(|F_o| - |F_c|)/\sum|F_o|]$). Scattering factors for neutral atoms were taken from ref 11. Corrections for anomalous dispersion effects[12] were applied. The atomic parameters are given in Table IV.

Table IV. Atomic Parameters for $Cp_2Ti(CO)(CN\text{-}t\text{-}Bu)$ (1) with Estimated Standard Deviations

atom	x	y	z	U_{eq}, Å^2
Ti	0.1462 (2)	0.0623 (1)	0.2365 (1)	0.036 (1)
O	−0.1709 (11)	−0.0447 (6)	0.3246 (4)	0.083 (10)
C1	−0.0602 (13)	−0.0034 (7)	0.2905 (5)	0.048 (9)
C2	−0.0842 (14)	0.1461 (6)	0.1646 (5)	0.047 (9)
N	−0.2145 (12)	0.1887 (6)	0.1234 (4)	0.058 (8)
C211	−0.3192 (15)	0.2479 (7)	0.0557 (5)	0.052 (10)
C212	−0.4289 (24)	0.1832 (10)	−0.0094 (7)	0.112 (19)
C213	−0.4631 (29)	0.3138 (12)	0.0882 (8)	0.147 (24)
C214	−0.1500 (26)	0.2998 (15)	0.0209 (11)	0.162 (29)
C11	0.3650 (15)	−0.0602 (7)	0.2033 (5)	0.056 (10)
C12	0.1626 (18)	−0.0974 (7)	0.1977 (7)	0.065 (11)
C13	0.0320 (16)	−0.0476 (8)	0.1323 (6)	0.067 (12)
C14	0.1559 (19)	0.0204 (8)	0.1001 (6)	0.067 (12)
C15	0.3637 (17)	0.0122 (7)	0.1446 (6)	0.059 (11)
C21	0.2384 (17)	0.1002 (7)	0.3775 (6)	0.062 (11)
C22	0.1304 (14)	0.1790 (6)	0.3361 (5)	0.050 (9)
C23	0.2573 (17)	0.2153 (7)	0.2810 (6)	0.059 (11)
C24	0.4388 (15)	0.1579 (8)	0.2887 (6)	0.061 (11)
C25	0.4268 (16)	0.0872 (7)	0.3478 (6)	0.060 (11)

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Registry No. 1, 104738-32-1; 2, 104738-33-2; 3, 104738-34-3; 4, 104738-35-4; 5, 104738-36-5; 6, 104738-37-6; 7, 104738-38-7; $Cp_2Zr(CO_2)$, 59487-85-3; $Cp_2Ti(CO)(PMe_3)$, 56770-61-7; $Cp_2Hf(CO)_2$, 59487-86-4; $Cp_2Ti(CO)_2$, 12129-51-0; $(Ind)_2Ti(CO)(PMe_3)$, 104738-39-8; *tert*-butyl isocyanide, 7188-38-7; 2,6-dimethyl phenyl isocyanide, 2769-71-3; methyl isocyanide, 593-75-9.

Supplementary Material Available: A table of final anisotropic thermal parameters (1 page); a listing of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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