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Synthesis and characterization of ansa-dimethylsilylbiscyclopentadienyl titanium(II) complexes. Crystal structure of $[Ti\{Me_2Si(C_5H_4)_2\}\{CN(2,6\text{-}Me_2C_6H_3)\}_2]$

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Abstract

The titanium(II) adducts $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2]L_2$ [L = CO (**1**), PMe_2Ph (**2**), CNR (R = 2,6-$Me_2C_6H_3$) (**3**) have been made by the reduction of $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2]Cl_2$ with $HgCl_2$-activated magnesium in THF in the presence of the ligand L. Mixed titanocene adducts $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2]LL'$ (L = CO; L' = PMe_2Ph (**4**), CNR (**5**)) can be prepared by the addition of ligands (PMe_2Ph, CNR) to hexane solutions of $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2](CO)_2$ exposed to sunlight. The crystal structure of **3** has been determined by X-ray diffraction; the phenyl groups of the isocyanide ligand are almost perpendicular to the reflection plane of the cyclopentadienyl groups.

1. Introduction

Bis-cyclopentadienyl derivatives of Group 4d metals in oxidation state II (titanocene and zirconocene), $M(\eta^5\text{-}C_5H_5)_2$, have never been isolated although they have been frequently invoked [1] as intermediate highly active "carbenoid-like" [2] reagents in a wide range of reactions [3–7] with olefins, acetylenes, carbon monoxide, dinitrogen and phosphines and other species such as epoxides, aldehydes and ketones. Many of these reactions gave stable 18-electron adducts $Ti(\eta^5\text{-}C_5H_5)_2L_2$, some of which were used to generate the active $M(\eta^5\text{-}C_5H_5)_2$ [3a–c,5c] species for subsequent reactions.

Carbon monoxide has been most frequently used as the π-acceptor ligand, giving $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ which has been extensively used as a precursor for many other titanocene derivatives [1a,2,5a]. $Ti(\eta^5\text{-}C_5H_5)_2(PMe_3)_2$ [4d] has been shown to be an even more reactive and versatile titanocene source, and the mixed adduct $Ti(\eta^5\text{-}C_5H_5)_2(CO)(PMe_3)$ [4d] is a convenient reagent for more selective reactions. A few monocyclopentadienyl titanium(II) complexes have also been reported [8]. The dimethylsilyl-bridged bis-cyclopentadienyl ligand $[Me_2Si(\eta^5\text{-}C_5H_4)_2]^{2-}$ is a most effective system for stabilizing Group 4d metal complexes in low oxidation states. We describe below the synthesis and characterization of the new titanocene-like complexes $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2]L_2$ [L = CO (**1**); PMe_2Ph (**2**); CN(2,6-$Me_2C_6H_3$) (**3**) and $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2](CO)L$ [L = PMe_2Ph (**4**); CN(2,6-$Me_2C_6H_3$) (**5**) containing this bridged bis-cyclopentadienyl ligand, and the characterization of **3** by an X-ray diffraction study.

2. Results and discussion

The reduction of $Ti[Me_2Si(\eta^5\text{-}C_5H_4)_2]Cl_2$ with $HgCl_2$-activated magnesium in THF at room temperature in the presence of a stoichiometric amount of the appropriate ligand L (L = CNR, PMe_2Ph) or under an

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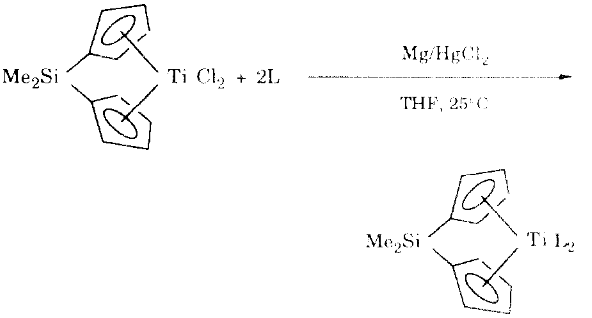
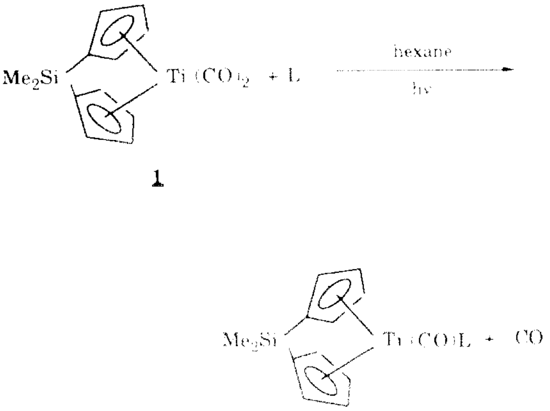
atmosphere of CO, gave the titanium(II) adducts, which were isolated in high yield after evaporation of the solvent and extraction of the crude residue with hexane.



(1)

All these complexes are very air and moisture sensitive; their reactivities decrease in the order CO > CNR > PMe_2Ph, in line with the decreasing π-acceptor character of the ligand. They are very soluble in all common solvents, even aliphatic ones, and react easily with dichloromethane or chloroform to give the dichlorometallocene by oxidative addition.

The addition of 1 equiv. of the ligand L (L = CNR, PMe_2Ph) to irradiated hexane solutions of **1** leads to the mixed titanocene adducts **4** and **5** with evolution of CO.



(2)

L = PMe_2Ph (**4**), $CN(2,6\text{-}Me_2C_6H_3)$ (**5**)

Whereas **4** was isolated as a pure compound in high yield, **5** could only be detected in solution as a minor product always accompanied by large amounts of **1** and **3** as the main products formed by a redistribution reaction. The properties of these mixed complexes are similar to those of the complexes containing two identical ligands; substitution of CO by phosphine would be expected to lead to increasing air sensitivity, but **4** is less oxygen and moisture sensitive than **2**.

All the isolated complexes were identified by elemental analysis, and IR and ^1H, ^{13}C and ^{31}P (**5**) NMR spectroscopy; the data are summarized in Table 1.

TABLE 1. Spectroscopic data for Ti^{II} ansa-metallocene derivatives

Compound	^1H NMR [a]			^{13}C NMR [a]			^{31}P NMR [a]	IR ν(CO)
	C_5H_4	Me_2Si	L	C_5H_4	Me_2Si	L	L	(cm^{-1})
$[Me_2Si(C_5H_4)_2]Ti(CO)_2$	5.13 (t) [b] 4.46 (t) [b]	−0.10 (s)		103.1 [e] 90.8 [f] 76.9 [g]	−6.1	257.1		1980 1905
$[Me_2Si(C_5H_4)_2]Ti(PMe_2Ph)_2$	5.21 (br) 4.44 (br)	−0.09 (s)	1.08 (br) 7.30–7.00 (br)	102.4 [e] 90.4 [f] 81.3 [g]	−5.9	128.9–126.1 22.5		
$[Me_2Si(C_5H_4)_2]Ti[CN(2,6\text{-}Me_2C_6H_3)]_2$	5.81 (t) [c] 5.05 (t) [c]	0.21 (s)	2.17 (s) 6.68 (m)	106.2 [e] 92.3 [f] 80.9 [g]	−5.4	18.9 130.1–124.6 (i)		2044 1938
$[Me_2Si(C_5H_4)_2]Ti(CO)(PMe_2Ph)$	5.23 (m) 5.17 (m) 4.75 (m) 4.62 (m)	−0.08 (s) 0.18 (s)	1.02 (d) [d] 7.28–7.00	109.1 [h] 94.2 [h] 93.6 [h] 91.4 [h] 79.0 [h]	−6.9 −4.3	290.6 [j] 142.2–127.9 [k] 20.4 (d) [k,l]	34.8 (s)	1860
$[Me_2Si(C_5H_4)_2]Ti(CO)[CN(2,6\text{-}Me_2C_6H_3)]$	5.63 (m) 5.37 (m) 4.89 (m) 4.76 (m)	0.00 (s) 0.14 (s)	2.15 (br) 6.65 (br)					

[a] Benzene-d_6. [b] J_{H-H} = 2.26 Hz. [c] J_{H-H} = 2.20 Hz. [d] J_{P-H} = 5.13 Hz. [e] $C_{2,5}$ (C_5H_4). [f] $C_{3,4}$ (C_5H_4). [g] C_1 (C_5H_4). [h] C_{1-5} (C_5H_4). [i] Shift for CN not observed. [j] CO. [k] PMe_2Ph. [l] J_{P-C} = 17.7 Hz.

The IR spectra of all these complexes show characteristic absorptions reported for the silyl-bridged bis-cyclopentadienyl ligand [10]. Two IR bands are observed for ν(CO) and ν(CN) stretching frequencies respectively, in complexes **1** and **3**. The expected decrease in the electron donor character of the silyl bis-cyclopentadienyl ligand due to the electron withdrawing ability of the vacant 3d silicon orbitals results only in a very small displacement to higher frequencies compared with bands from the unsubstituted cyclopentadienyl ring in $Ti(\eta^5\text{-}C_5H_5)_2L_2$ (L = CO, CNR) [1a, 4a]; the differences are < 10 cm^{-1}. The observed values for ν(CO) are almost exactly the same as those reported for $Ti[(CH_2)_2(C_5H_4)_2](CO)_2$ [11] for which the reverse behaviour would have been expected; this behaviour is probably attributable to structural rather than electronic factors. Complex **4**, containing mixed ligands, shows one ν(CO) absorption clearly displaced to a lower frequency (1860 cm^{-1}) compared with that for the di-carbonyl complex **1** due to the increase in electron density at the metal centre when CO is substituted by a less π-electron acceptor ligand, as noted previously for similar metallocene complexes containing mixed ligands (PMe_3 [4d], CNR [7e]).

The ^{1}H NMR spectra of **1**, **2** and **3** show the expected two pseudotriplets for the cyclopentadienyl ring protons of an AA'BB' spin system and one singlet for the protons of both equivalent methyl silyl groups, demonstrating the presence of a plane of symmetry bisecting the two substituents located on the reflection plane of the rings. When both ligands on this plane are different, as in complexes **4** and **5**, the cyclopentadienyl ring protons appear as four multiplets corresponding to an ABCD spin system. Furthermore, for these compounds, the two methyl silyl groups are inequivalent, and give two different singlets. The same effect is also observed in the ^{13}C NMR spectra, but all the ^{1}H and ^{13}C NMR signals are displaced to higher fields compared with those for the dichloro or dialkyl titanium (IV) [12] complexes containing the same cyclopentadienyl ligand.

The expected pseudo-tetrahedral structure of these compounds was confirmed by the X-ray diffraction study of complex **3**.

2.1. Crystal structure of $[Ti\{Me_2Si(C_5H_4)_2\}\{CN(2,6\text{-}Me_2C_6H_3)\}_2]$ (3)

The molecular structure of $[Ti\{Me_2Si(C_5H_4)_2\}\{CN\text{-}(2,6\text{-}Me_2C_6H_3)\}_2]$ (**3**) is shown in Fig. 1, with the atomic labelling scheme. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2 and selected bond distances and bond angles in Table 3.

It can be seen that the "ansa" ligand acts as a

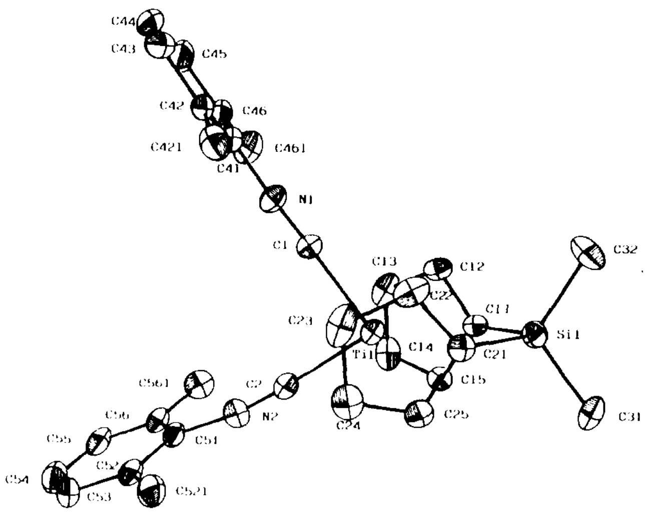


Fig. 1. ORTEP view of $[Ti\{Me_2Si(C_5H_4)_2\}\{CN(2,6\text{-}Me_2C_6H_3)\}_2]$ (3) with atom labelling scheme.

TABLE 2. Atom coordinates with estimated standard deviations.

Atom	x	y	z	B (Å^2)
Ti1	0.05778(8)	0.21964(6)	0.35019(5)	3.70(2)
Si1	−0.0244(1)	0.3736(1)	0.4703(1)	4.75(3)
N1	−0.0585(4)	0.1637(3)	0.1706(2)	5.0(1)
N2	0.2355(4)	0.0542(3)	0.3145(3)	5.5(1)
C1	−0.0174(4)	0.1845(3)	0.2358(3)	4.4(1)
C2	0.1730(4)	0.1156(3)	0.3291(3)	4.4(1)
C11	0.0858(4)	0.3684(3)	0.3842(3)	3.8(1)
C12	0.0588(5)	0.3631(3)	0.2961(3)	4.8(1)
C13	0.1519(6)	0.3202(4)	0.2548(3)	6.3(1)
C14	0.2348(5)	0.2998(4)	0.3138(4)	6.0(1)
C15	0.1978(5)	0.3271(3)	0.3930(4)	4.5(1)
C21	−0.0618(4)	0.2535(3)	0.4641(3)	4.3(1)
C22	−0.1310(4)	0.2097(4)	0.4012(3)	5.4(1)
C23	−0.0962(6)	0.1206(4)	0.3945(4)	4.3(1)
C24	−0.0063(6)	0.1057(4)	0.4524(4)	6.5(2)
C25	0.0177(5)	0.1866(4)	0.4931(3)	4.9(1)
C41	−0.1136(5)	0.1400(3)	0.0964(3)	4.8(1)
C42	−0.2166(5)	0.0869(3)	0.1024(4)	5.4(1)
C43	−0.2695(6)	0.0659(4)	0.0273(5)	7.8(2)
C44	0.2249(7)	0.0944(4)	0.0494(4)	8.3(2)
C45	−0.1259(7)	0.1472(4)	−0.0537(4)	7.7(2)
C46	−0.0689(6)	0.1705(4)	0.0196(3)	5.7(1)
C51	0.2969(4)	−0.0194(4)	0.2854(3)	4.7(1)
C52	0.2739(5)	−0.1021(4)	0.3223(3)	5.2(1)
C53	0.3356(6)	−0.1742(4)	0.2907(4)	6.6(2)
C54	0.4206(6)	−0.1651(4)	0.2288(4)	7.3(2)
C55	0.4397(5)	−0.0825(4)	0.1933(4)	6.5(1)
C56	0.3787(5)	−0.0070(4)	0.2204(3)	5.1(1)
C421	0.2581(5)	0.0544(4)	0.1874(4)	6.2(2)
C461	0.0416(6)	0.2245(5)	0.0164(4)	7.5(2)
C521	0.1855(6)	−0.1113(4)	0.3908(4)	6.5(2)
C561	0.3982(6)	0.0819(5)	0.1814(4)	7.1(2)
C31	0.0362(6)	0.4003(4)	0.5756(4)	7.2(2)
C32	−0.1490(6)	0.4460(5)	0.4430(5)	8.5(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as: $(4/3)\,[a^2\,B_{1,1} + b^2\,B_{2,2} + c^2\,B_{3,3} + ab(\cos\gamma)\,B_{1,2} + ac(\cos\beta)\,B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

TABLE 3. Selected bond distances (Å) and bond angles (°) [a]

Ti–C(1)	2.064(5)	Ti–C(2)	2.064(5)
Ti–C(11)	2.307(5)	Ti–C(21)	2.312(5)
Ti–C(12)	2.306(5)	Ti–C(22)	2.308(5)
Ti–C(13)	2.381(5)	Ti–C(23)	2.403(6)
Ti–C(14)	2.420(6)	Ti–C(24)	2.453(6)
Ti–C(15)	2.364(5)	Ti–C(24)	2.349(5)
C(11)–C(12)	1.424(7)	C(21)–C(22)	1.427(7)
C(11)–C(15)	1.428(7)	C(21)–C(25)	1.425(7)
C(12)–C(13)	1.402(8)	C(22)–C(23)	1.393(8)
C(13)–C(14)	1.363(8)	C(23)–C(24)	1.392(8)
C(14)–C(15)	1.378(8)	C(24)–C(25)	1.395(8)
N(1)–C(1)	1.170(6)	N(2)–C(2)	1.185(6)
N(1)–C(41)	1.375(6)	N(2)–C(51)	1.383(6)
Si(1)–C(11)	1.852(5)	Si(1)–C(21)	1.846(5)
Si(1)–C(31)	1.841(6)	Si(1)–C(41)	1.375(6)
Cp(1)–Ti	2.034	Cp(2)–Ti	2.041
C(1)–Ti–C(2)	86.2(2)	Ti–C(1)–N(1)	178.9(4)
C(1)–N(1)–C(41)	176.3(5)	Ti–C(2)–N(2)	176.9(4)
C(2)–N(2)–C(51)	170.3(5)	C(11)–Si(1)–C(21)	94.5(2)
C(31)–Si(1)–C(32)	111.9(2)		
C(1)–Ti–C(2)	86.2	C(1)–Ti–Cp(1)	106.0
C(1)–Ti–Cp(2)	105.2	C(2)–Ti–Cp(1)	107.3
C(2)–Ti–Cp(2)	105.9	Cp(1)–Ti–Cp(2)	135.2

[a] Cp(1) is the centroid of C(11)...C(15); Cp(2) is the centroid of C(21)...C(25).

chelating system, leading to pseudotetrahedral coordination around the Ti atoms if the centroids of the two Cp rings are assumed to be coordination sites. The other two positions are occupied by the carbon atoms of the isocyanide ligands.

The angles are quite close to the ideal tetrahedral values except for that of the isocyanide carbon atoms C(1)–Ti–C(2), which is very small, *viz.* 86.2°, and that between the centroids Cp(1)–Ti(1)–Cp(2), which, in contrast, is much larger, *viz.* 135.2°.

This type of distortion has been found in other similar structures [9,12]. However in the present case the difference between both angles is very large. This could be taken as indicating that the small size and the linear nature of the isocyanide group allows the carbon atoms to be closer than in the case of other ligands, except in the case of [Ti{$Me_2Si(C_5H_4)_2$}Cl(PMe_2Ph)] [9b], for which there is a similar difference.

A more open angle between the rings does not mean, however, that the metal–ring interaction is weaker; the distances from Ti to the Cp centroids are 2.034 and 2.041 Å, respectively, for rings 1 and 2, these distances being slightly smaller that those observed for similar compounds.

The rings are essentially planar, although Ti–C(ring) distances show significant differences. The Ti atom lies closer to the carbon atoms directly bonded to silicon. Therefore, the metal atom is significantly incorporated into the sandwich system. Distances from Ti to the bridgehead carbon atoms are Ti–C(11) 2.307(5) Å and Ti–C(21) 2.312(5) Å. These distances are clearly smaller than the average values observed for similar titanium (IV) compounds [12] (2.392 Å), and a value of 2.354 Å has been found for a Ti^{III} derivative [9b].

Comparison of the distances from Ti to each of the carbon atoms of the Cp rings suggest that, in this case, the pentahapto coordination is highly distorted, since the distances Ti(1)–C(11), Ti(1)–C(12) in Cp(1) and Ti(1)–C(21), Ti(1)–C(22) in Cp(2) are significantly smaller than the other three. Shorter Ti–C distances correspond to larger C–C ring distances, and larger Ti–C distances to smaller C–C ring distances. Such a situation has been observed previously [12].

The Si atom shows almost tetrahedral coordination, which is again determined by the bridge with a C(11)–Si–C(21) angle of 94.5(2)° and a C(31)–Si–C(32) angle of 111.9 (2)°.

The Si–C distances are, however, fairly regular, ranging between 1.852(5) Å and 1.840(7) Å. The Si atom is shifted out of the planes of the rings and are located at 0.683(2) Å from the Cp(1) mean plane and 0.652 (2) Å from the Cp(2) main plane, which implies a distortion of the sp^2 hybridization of the bridgehead carbon atom. The angle between the ring planes is 51.9(2)°.

Ti–C(1) and Ti–C(2) distances (2.064(5) Å) are in both cases shorter than those corresponding to a single Ti–C bond as observed in titanium(IV) compounds [12]. The N(1)–C(1) (1.170(6) Å) and N(1)–C(2) (1.185(6) Å) distances correspond with that expected for triple bonding, and the slight differences in values of Ti–C(1)–N(1) (178.9(4)°), Ti–C(2)–N(2) (176.9(4)°) and C(1)–N(1)–C(41) (176.3(5)°), C(2)–N(2)–C(51) (170°) confirm the bonding situation of the isocyanide ligands, this being the main difference between the two ligands.

The N(1)–C(41) (1.375(6) Å) and N(2)–C(51) (1.383 (6)) Å distances are shorter than expected for a single N–C bond, indicating a delocalized multiple bond.

The phenyl rings have normal C–C distances, with mean values of 1.385 Å (C(41)–C(46)) and 1.386 Å (C(51)–C(56)). These phenyl rings are planar, and perpendicular to the plane defined by Si(1)–Ti(1), N(1), C(1) and N(2), C(2); the dihedral angles are 97.7 (1)° and 102.4 (1)°, with an angle of 101.9 (2)° between the two rings.

3. Experimental section

All manipulations were performed under dinitrogen or argon by use of Schlenk and high vacuum line techniques or a glove box Model HE 63P (PEDATROL). Solvents were purified by distillation from an appropriate drying/deoxygenated agent (sodium/benzophenone for THF, sodium for toluene, and sodium/potassium alloy for hexane). $Ti[Me_2Si(C_5H_4)_2]Cl_2$ [12] and $CN(2,6\text{-}Me_2C_6H_3)$ [13] were prepared by published procedures. Mg, $HgCl_2$ (Ventron) and PMe_2Ph (Strem Chemicals) were obtained commercially. NMR spectra were recorded on Varian FT-80 and Varian Unity FT-300 instruments (^1H and ^{13}C chemical shifts are referenced to Me_4Si). IR spectra were recorded (as Nujol mulls) on a 883 Perkin-Elmer spectrophotometer. Elemental C, H, N analyses were carried out with a Perkin-Elmer 240B microanalyser.

3.1. Synthesis of $[Ti\{Me_2Si(C_5H_4)_2\}(CO)_2]$ (1)

$Ti[Me_2Si(C_5H_4)_2]Cl_2$ (0.5 g, 1. 64 mmol) was added under argon to a mixture of 0.4 g (16.66 mmol) of magnesium turnings and 20 mg (0.075 mmol) of $HgCl_2$ in tetrahydrofuran (THF). The argon atmosphere was replaced by a CO atmosphere and the mixture stirred for 12 h. The solvent was removed *in vacuo* and the residue extracted with 100 ml of hexane. The extract was filtered, and a black-brown microcrystalline solid separated as the solvent was removed *in vacuo*. Recrystallization from hexane at −30°C gave crystals of **1**. Yield 0.402 g (84.7%).

Anal. Found: C, 57.67; H, 4.71. $C_{14}H_{14}O_2SiTi$ calcd.: C, 57.93; H, 4.83%. IR: ν(CO) 1980 and 1905 cm^{-1}. ^1H NMR (C_6D_6, 300 MHz, 25°C): δ −0.10 (s, 6H, Me_2Si); 4.46 (t, 4H, $J = 2.26$ Hz, C_5H_4); 5.13 (t, 4H, $J = 2.26$ Hz, C_5H_4). ^{13}C NMR (C_6D_6, 75.5 MHz, 25°C): δ −6.1 (Me_2Si); 76.9 $[C_1(C_5H_4)]$; 90.8 $[C_{3,4}(C_5H_4)]$; 103.1 $[C_{2,5}(C_5H_4)]$; 257.1 (CO).

3.2. Synthesis of $[Ti\{Me_2Si(C_5H_4)_2\}(PMe_2Ph)_2]$ (2)

A solution of 0.5 g (1.64 mmol) of $Ti[Me_2Si(C_5H_4)_2]Cl_2$ in 30 ml of tetrahydrofuran (THF) was treated under argon with 0.4 g (16.66 mmol) of magnesium turnings, 20 mg (0.075 mmol) of $HgCl_2$, and 0.46 ml (3.28 mmol) of PMe_2Ph and stirred. A red-brown solution was formed in 12 h. The solvent was evaporated *in vacuo* and the residue extracted with 50 ml of toluene. After filtration the extract was concentrated and kept at −30°C to give **2** as a microcrystalline red solid, which was recrystallized from toluene. Yield 0.613 g (73.4%).

Anal. Found: C, 65.39; H, 6.88. $C_{28}H_{36}P_2SiTi$ calcd.: C, 65.88; H, 7.06%. ^1H NMR (C_6D_6, 300 MHz, 25°C): δ −0.09 (s, 6H, Me_2Si); 1.08 (br, 12H, CH_3–P); 4.44 (m, 4, C_5H_4); 5.21 (br, 4, C_5H_4); 7.00–7.30 (br, 10 H, Ph). ^{13}C NMR (C_6D_6, 75.5 MHz, 25°C): δ −5.9 (Me_2–Si); 22.5 (d, CH_3–P); 81.3 $[C_1(C_5H_4)]$; 90.4 $[C_{3,4}(C_5H_4)]$; 102.4 $[C_{2,5}(C_5H_4)]$; 126.1–128.9 (Ph).

3.3. Synthesis of $[Ti\{Me_2Si(C_5H_4)_2\}\{CN(2,6\text{-}Me_2C_6H_3)\}_2]$ (3)

The procedure described for **2**, but starting with 0.43 g (3.28 mmol) of $CN(2,6\text{-}Me_2C_6H_3)$ gave compound **3** as violet-brown crystals. Yield 0.667 g (82.1%).

Anal. Found: C, 72.51; H, 6.41; N, 5.63 $C_{30}H_{32}N_2SiTi$ calcd.: C, 72.58; H, 6.45; N, 5.64%. IR. ν(C≡N): 2044 and 1938 cm^{-1}. ^1H NMR (C_6D_6, 300 MHz, 25°C): δ 0.21 (s, 6H, Me_2–Si); 2.17 (s, 12 H, Me–Ph); 5.05 (t, 4H, $J = 2.2$ Hz, C_5H_4); 5.81 (t, 4H, $J = 2.2$ Hz; C_5H_4); 6.68 (m, Ph). ^{13}C NMR (C_6D_6, 75.5 MHz, 25°C): δ −5.4 (Me_2–Si); 18.9 (CH_3–Ph); 80.9

TABLE 4. Crystal and experimental data for determination of the structure of $[Ti\{Me_2Si(C_5H_4)_2\}\{CN(2,6\text{-}Me_2C_6H_3)\}_2]$ (3)

Crystal data	
Formula	$TiSiN_2C_{30}H_{32}$
Crystal habit	Prismatic
Symmetry	Orthorhombic, $P2_12_12_1$
Crystal colour	Red-brown
Unit cell determination	Least-squares fit from 25 reflections
Unit cell dimensions	11.437(1), 14.932(2), 15.748(3)
Packing V (Å^3); Z; D_c (g cm^{-3})	2.689; 4; 1.226
M; F(000): μ (cm^{-1})	496.58; 1048; 3.764
Experimental data	
Technique	Four-circle diffractometer Enraf Nonius, CAD4 with bisecting geometry; graphite oriented monochromator, MoKα, w/θ scans: $\theta_{max} = 27°$
Number of reflections:	
Measured	3391
Independent	3311
Observed	1998 ($I > 2\sigma(I)$)
Range of *hkl*	h 0–14; k 0–19; l 0–20
Standard reflections	2 reflections every 120 min; Total loss of gain in intensity was 13.5% in 74.9 h; corrections were made with the DECAY program

$[C_1(C_5H_4)]$; 92.3 $[C_{3,4}, (C_5H_4)]$; 106.2$[C_{2,5}, (C_5H_4)]$; 124.6–130.1 (Ph).

3.4. *Synthesis of $[Ti\{Me_2Si(C_5H_4)_2\}(CO)(PMe_2Ph)]$ (4)*

A hexane solution (30 ml) containing 0.25 g (0.86 mmol) of $Ti[Me_2Si(C_5H_4)_2](CO)_2$ (**1**) and 0.12 ml (0.36 mmol) of PMe_2Ph was irradiated in a photoreactor (Phillips HPK 125 W) for 12 h. The resulting solution was concentrated to 10 ml and kept at −40°C. Complex **4** separated as dark-brown crystals, which were dried *in vacuo*. Yield 0.204 g (59.3%).

Anal. Found: C, 62.87; H, 6.15. $C_{21}H_{25}POSiTi$ calcd.: C, 63.00; H, 6.25%. IR ν(CO): 1860 cm^{-1}. ^1H NMR (C_6D_6, 300 MHz, 25°C): δ −0.08 (s, 3H, Me–Si); 0.18 (s, 3H, Me–Si); 1.02 (d, 6H, J = 5.13 Hz, CH_3–P); 4.62 (m, 2H, C_5H_4); 4.75 (m, 2H, C_5H_4); 5.17 (m, 2H, C_5H_4); 5.23 (m, 2H, C_5H_4); 7.00–7.28 (m, Ph). ^{13}C NMR (C_6D_6, 75.5 MHz, 25°C): δ −6.9, −4.3 (Me_2–Si); 20.4 (d, J = 17.7 Hz, CH_3–P); 79.0, 91.4, 93.6, 94.2, 109.1 $[C_{1-5}(C_5H_4)]$; 127.9–142.2 (Ph); 290.6 (CO). $^{31}P\{^1H\}$ NMR (C_6D_6, referenced to H_3PO_4 in D_2O): δ 34.8 (s).

3.5. *Reaction of $[Ti\{Me_2Si(C_5H_4)_2\}(CO)_2]$ with $CN(C_6H_3Me_2)$ under irradiation*

A solution of 30 ml of hexane containing 0.25 g (0.86 mmol) of $Ti[Me_2Si(C_5H_4)_2](CO)_2$ (**1**) and 0.11 g (0.86 mmol) of $CN(C_6H_3Me_2)$ was irradiated in a photoreactor (Phillips HPK 125 W) over 12 h. A violet solution was obtained and this was evaporated to dryness to give a mixture of $Ti[Me_2Si(C_5H_4)_2](CO)_2$ (**1**), $Ti[Me_2Si(C_5H_4)_2][CN(2,6\text{-}Me_2C_6H_3)]_2$ (**3**), and the complex $[Ti\{Me_2Si(C_5H_4)_2\}(CO)\{CN(2,6\text{-}Me_2C_6H_3)\}]$, which was identified by ^1H NMR spectroscopy (C_6D_6, 300 MHz, 25°C): δ 0.00 (s, 3H, Me–Si); 0.14 (s, 3H, Me–Si); 2.15 (br, 6H, CH_3–Ph); 4.76 (m, 2H, C_5H_4); 4.89 (m, 2H, C_5H_4); 5.37 (m, 2H, C_5H_4); 5.63 (m, 2H, C_5H_4); 6.65 (br, 3H, Ph).

3.6. *Crystal structure data for complex $[Ti\{Me_2Si(C_5H_4)_2\{CN(2,6\text{-}Me_2C_6H_3)\}_2]$ (3)*

Crystallographic data and experimental details of the structure determination are given in Table 4.

Data were collected at room temperature from a crystal sealed in a Lindeman glass capillary under dry N_2. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structures were solved by a combination of direct methods and Fourier synthesis and refined (on F) by full matrix least-squares calculations. All the non hydrogen atoms were refined anisotropically. The hydrogen atoms were found in the difference synthesis map; those in the methyl groups were placed in calculated positions and included in the last refinement with fixed thermal parameters equivalent to those of the atoms to which they are attached. Final values of R = 0.049 and R_w = 0.050 with $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and $w = 4F_o^2/[\sigma(F_o)^2]^2$ were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from International Tables [14]. Calculations were performed with the SDP package [15], and the programs MULTAN [16] and DIRDIF [17] on a Microvax II computer.

A list of structure factors is available from the authors.

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