Binding of a *meso*-Octaethyl Tris(pyrrole)−Mono(pyridine) Ligand to Titanium(III) and Titanium(IV): A Monomeric Titanium(IV) Oxo Bis(pyridine)−Bis(pyrrole) Complex Derived from the C−O Bond Cleavage of Carbon Monoxide

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Summary: The reaction of a Ti−Me species with carbon monoxide occurred with the complete cleavage of the C−O bond and formation of the Ti═O unit, while the [Me−C] fragment homologated a pyrrole to a 4-methylpyridine ring within the meso-octaethyl tris(pyrrole)−mono(pyridine) macrocycle.

The use of macrocycles as ancillary ligands in organometallic chemistry has occurred for a number of reasons,[1] namely (i) the necessity to move away from the almost ubiquitous cyclopentadienyl ligand, expecially in the case of titanium, toward electronically and geometrically more flexible ligands,[2] (ii) the possibility of a better derivatization of the ancillary ligand, (iii) the possibility to generate very reactive organometallic functionalities in a protecting cavity. Some of the most spectacular differences between the [Zr−Cp$_2$] and [Zr−macrocycle] fragments have come recently from Zr−porphyrinogen-based or, to a lesser extent, from Ti−porphyrinogen-based organometallic chemistry.[3] This work led to the discovery of (i) bifunctional carriers of polar organometallics,[3a,4,5] (ii) aliphatic C−H bond activation,[3c] and (iii) the homologation of the porphyrinogen skeleton using carbon monoxide.[3b,d,4b] Such homologation has been used for the synthesis of the title ligand.[3b] The *meso*-octaethyl tris(pyrrole)−mono(pyridine) ligand **1** (Scheme 1), which has no precedent in organometallic and coordination chemistry, except for a single example in the case of hafnium,[3b] may serve as a particularly interesting ancillary ligand in early-transition-metal chemistry. Ligand **1** maintains the conformational peculiarities of *meso*-octaalkylporphyrinogen,[3−5] yet it differs greatly as a result of the following: (i) the change in the overall charge allows one to work with neutral rather than with bimetallic or ion pair complexes; (ii) replacing a pyrrole with a pyridine modifies not only the electronic properties of the ligand but also the size of the cavity, with the pyridine ring becoming a spectator ligand able to protect a coordinatively unsaturated metal. Preliminary results on the organometallic chemistry of titanium associated with **1** emphasize the ligand properties mentioned above.

The organometallic derivatization of **1** is shown in Scheme 1. We have recently reported the synthesis of this ligand and its lithiated form **2**; it is now readily prepared on a large scale.[3b] The reaction of **2** with TiCl$_3$·THF$_3$ led to **3**,[6] whose structure is shown in Figure 1 with some significant structural parameters.[7] Note some of the most chemically appealing structural characteristics of **3**. (i) The η^5:η^1:η^1 bonding mode of the tris(pyrrole) fragment has a Ti−η^5-pyrrole distance (2.088(2) Å) quite close to those in Ti−Cp complexes.[2] This is the first example of a η^5-pyrrolyl anion bonded to titanium. (ii) Facile $\eta^5 \leftrightarrow \eta^1$ rearrangement, which has been observed in the case of zirconium, functions in the case of appropriate electronic demands by the metal during the reaction pathway.[3−5] (iii) The long Ti···N4 distance (2.415(2) Å) suggests the presence of a coordi-

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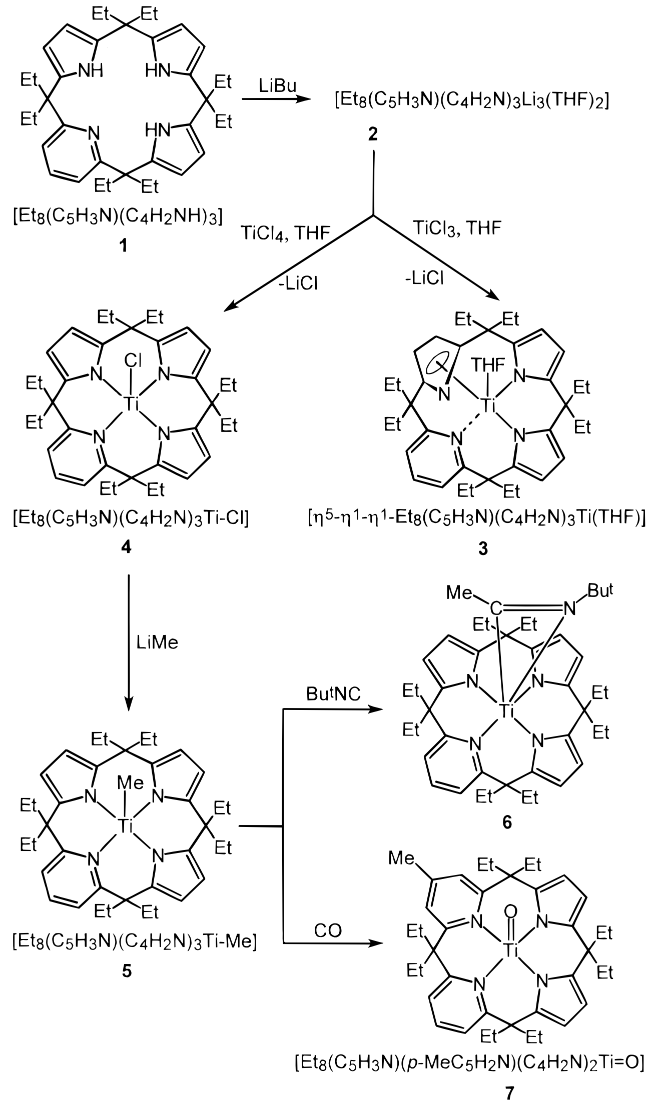
[6] Procedure for **3**: TiCl$_3$(THF)$_3$ (1.23 g, 3.3 mmol) and **2** were added to THF (250 mL). The dark red solution obtained was stirred overnight at room temperature. The solvent was evaporated to dryness, and toluene (200 mL) was added to the brown solid residue. The undissolved white solid, LiCl, was filtered off, and after evaporation the residue was triturated with pentane (50 mL) and the brown solid was filtered and dried in vacuo (77%). Crystals suitable for X-ray analysis were obtained from the recrystallization of the powder in *n*-hexane. Anal. Calcd for **3**, C$_{37}$H$_{49}$N$_4$Ti·C$_4$H$_8$O: C, 73.52; H, 8.58; N, 8.36. Found: C, 73.21; H, 8.56; N, 8.12. μ_{eff} = 1.79 μ_{B} at 290 K.

Scheme 1



natively unsaturated titanium(III), protected by the cavity, a result of the conformation of the ligand.

The bonding mode of ligand **1** to titanium in **3** explains the regiochemistry of the homologation reaction observed in the case of **5**. The formation of **4**[8] and **5**[8] has been achieved using standard procedures. The [Ti–Me] functionality undergoes a migratory insertion reaction with Bu^{t}NC and CO. Although it is difficult to compare the reactions with CO and Bu^{t}NC, since they follow different pathways, both are relatively slow (hours, Bu^{t}NC; days, CO)[9] in THF at room temperature.

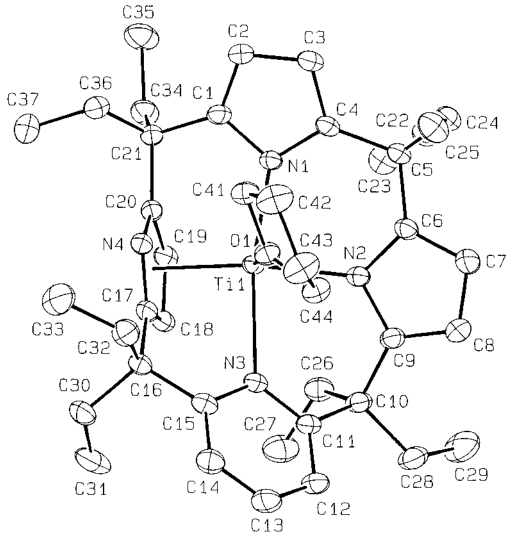


Figure 1. ORTEP view of molecule A of complex **3** (30% probability ellipsoids). Values in brackets refer to molecule B. Selected bond distances (Å) and angles (deg) are as follows: Ti1–O1, 2.109(2) [2.116(2)]; Ti1–N1, 2.136(2) [2.123(2)]; Ti1–N2, 2.108(2) [2.120(2)]; Ti1–N3, 2.415(2) [2.420(2)]; Ti1–N4, 2.337(2) [2.329(2)]; Ti1–C17, 2.343(3) [2.335(2)]; Ti1–C18, 2.423(3) [2.423(2)]; Ti1–C19, 2.461(2) [2.461(4)]; Ti1–C20, 2.409(2) [2.401(2)]; N3–Ti1–N4, 98.0(1) [98.0(1)]; N2–Ti1–N4, 174.1(1) [173.5(1)]; N2–Ti1–N3, 84.8(1) [85.1(1)]; N1–Ti1–N4, 91.0(1) [91.0(1)]; N1–Ti1–N3, 167.6(1) [167.3(1)]; N1–Ti1–N2, 85.4(1) [85.0(1)].

The reaction with Bu^{t}NC leads to the expected η^2-iminoacyl **6**,[4a,8,10,11] which does not evolve further due to its rather low carbenium ion properties, while in the case of carbon monoxide the reaction proceeds further with the homologation of a pyrrole to a pyridine ring.[3b,4a] Such homologation occurs *via* the electrophilic attack of the η^2-acyl (carbenium ion)[12] the electron-rich pyrrolyl anion, followed by complete C═O bond cleavage; thus, a pyridine ring and a titanyl unit are formed (see complex **7**). The complete C═O bond cleavage is relevant in the present case because it is not assisted by a particularly oxophilic metal or by an alkali-metal cation,

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(7) Crystal data for **3**: $C_{41}H_{57}N_4OTi$, M_r = 669.8, monoclinic, space group $P2_1/c$, a = 17.914(2) Å, b = 18.326(2) Å, c = 23.197(3) Å, β = 104.37(1)°, V = 7377.1(15) Å^3, Z = 8, ρ_{calcd} = 1.206 g cm^{-3}, $F(000)$ = 2888, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 22.28 cm^{-1}, crystal dimensions 0.39 × 0.42 × 0.96 mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non-H atoms. All the hydrogen atoms were located from a difference Fourier map and introduced as fixed contributors in the last stage of refinement (U_{iso} = 0.08 Å^2). For 10 013 unique observed reflections ($I > 2\sigma(I)$) collected at T = 295 K on a Siemens AED diffractometer ($6 < 2\theta < 140°$) and corrected for absorption, the current R value is 0.050 (wR2 = 0.128). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. See the Supporting Information for more details.

(8) Syntheses of **4**, **5**, and **6** are reported in the Supporting Information. The X-ray structure of **6** has not been determined.

(9) Procedure for **7**: A red solution of **5** (1.43 g, 2.3 mmol) in benzene (150 mL) was exposed to a CO atmosphere for 4–5 days at room temperature. An orange microcrystalline solid formed. The solvent was evaporated, and the red-orange solid was triturated with n-hexane (100 mL), filtered, and dried in vacuo (70%). Recrystallization of the powder from benzene/hexane gave orange crystals containing benzene of crystallization that were suitable for X-ray analysis. Anal. Calcd for **7**, $C_{39}H_{52}N_4OTi$: C, 73.11; H, 8.18; N, 8.74. Found: C, 73.49; H, 8.05; N, 8.54. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 8.01 (t, C_5H_3N, 1H, J = 7.9 Hz), 7.71 (d, C_5H_3N, 1H, J = 7.9 Hz), 7.56 (d, C_5H_3N, 1H, J = 7.8 Hz), 7.51 (s, C_6H_5N, 2H), 6.08 (m, C_4H_2N, 2H), 5.96 (m, C_4H_2N, 2H), 3.18 (m, CH_2, 2H), 2.73–2.39 (m, CH_2, 4H), overlapping with 2.51 (s, CH_3–pyridine, 3H), 2.14–1.86 (m, CH_2, 8H), 1.34 (m, CH_2, 2H), 0.89–0.55 (m, CH_3, 21H), 0.54 (t, CH_3, 3H). IR (Nujol): 1610 (s), 1077 (s), 968 (s), 747 (s), 686 (s) cm^{-1}.

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as observed elsewhere.[3,4b] Two aspects of the regiochemistry of the reaction are relevant, namely (i) the substitution at the pyridine in the *para* position[3b,4a] and (ii) the formation of a *cis*-bis(pyridine) macrocycle. An explanation of the latter aspect of the regiochemistry comes from the bonding mode of the trianionic ligand observed in **3**, where the η^5-pyrrole is *cis* to the pyridine ring. In the case of zirconium–hafnium[3b] chemistry we argued that electrophilic attack should occur at an η^5- or η^3-pyrrolyl anion which has the appropriate orientation. The formation of the 4-methylpyridine discriminated, probably, between the η^5 and the η^3 bonding mode in favor of the latter one.[3b,4a] Due to the very high fluxionality of the macrocycle ligand, as in the case of *meso*-octaethylporphyrinogen,[3,4] we cannot identify clearly any such η^5–η^3 bonding modes in solution by NMR, even at low temperature. The oxotitanium(IV) functionality is stabilized in **7**[9] by the dianionic bis(pyridine)–bis(pyrrole) macrocycle. The structure is shown in Figure 2 with selected structural parameters.[13]

The coordination polyhedron around titanium is square pyramidal. The metal is displaced by 0.446(1) Å toward the oxygen atom from the N_4 core, which is almost planar, the deviations from planarity ranging from −0.015(2) to 0.015(2) Å. The Ti–O1 vector forms a dihedral angle of 7.6(1)° with the normal to the N_4 core. The macrocycle assumes a conformation so as to have two hydrogen atoms (H291, H381) from two opposite methylene carbons (C29, C38) approaching the oxo group. The geometry of these interactions (O1···H381, 2.32 Å; O1···C38, 3.188(4) Å; O1···H381–C38, 156°; O1···H291, 2.36 Å; O1···C29, 3.234(3) Å; O1···H291–C29, 149°) is consistent with the presence of weak hydrogen bonds. In addition, one hydrogen atom (H311) from the C31 methylene carbon completes the six-coordination around titanium: Ti···H311, 2.37 Å; O1–Ti···H311, 156°. The Ti=O distance is in the range given by the few reports of oxotitanium species.[3b,14]

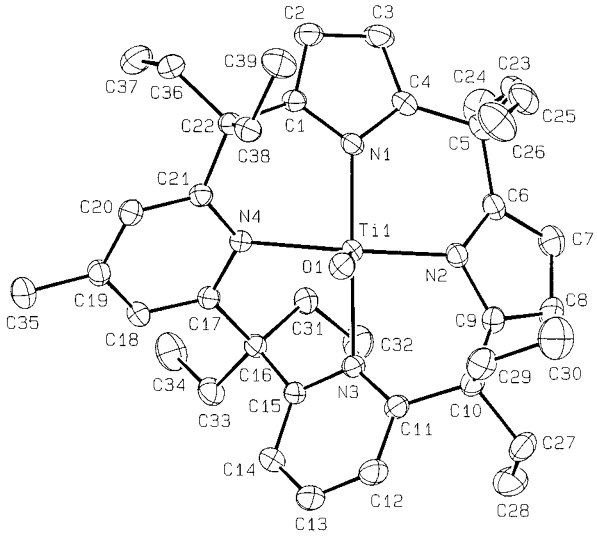

Figure 2. ORTEP view of complex **7** (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) are as follows: Ti1–O1, 1.628(2); Ti1–N1, 2.031(3); Ti1–N2, 2.017(2); Ti1–N3, 2.248(3); Ti1–N4, 2.243(2); N4–C17, 1.360(4); N4–C21, 1.365(2); C17–C18, 1.383(3); C18–C19, 1.392(4); C19–C20, 1.373(5); C20–C21, 1.391(3); N3–Ti1–N4, 90.8(1); N2–Ti1–N4, 154.9(1); N2–Ti1–N3, 84.8(1); N1–Ti1–N4, 83.7(1); N1–Ti1–N3, 156.6(1); N1–Ti1–N2, 90.6(1).

Complex **7** differs from the other M=O derivatives in the porphyrinogen series,[3,4b] in that the Ti=O bond is not associated with an alkali-metal cation; thus, it is present in a neutral form more appropriate for reactivity studies. The chemistry of the M=X functionality (X = O, NR, CR_2) has become, in recent years, particularly relevant for its role in some major metal-assisted processes such as hydrocarbon activation. In those examples the chemical environment of the metal is usually provided by Cp-type ligands.[15] A particularly interesting area of chemistry would involve utilizing easily accessible macrocycles such as **1**. In the meantime, we should emphasize the very unconventional synthetic method of **7**. The use of **1** as an ancillary ligand in organometallic chemistry is being extended to other metals.

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Supporting Information Available: Text giving procedures for **4**–**6**, an ORTEP view of molecule B of complex **3** (Figure S1), and tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for complexes **3** and **7** (21 pages). Ordering information in given on any current masthead page.

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(13) Crystal data for **7**: $C_{39}H_{52}N_4OTi{\cdot}C_6H_6$, M_r = 718.9, triclinic, space group $P\bar{1}$, a = 11.990(2) Å, b = 17.186(3) Å, c = 11.559(2) Å, α = 101.79(2)°, β = 117.78(2)°, γ = 97.83(1)°, V = 1987.8(8) Å^3, Z = 2, ρ_{calcd} = 1.201 g cm^{-3}, $F(000)$ = 772, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 21.01 cm^{-1}, crystal dimensions 0.16 × 0.29 × 0.39 mm. The structure was solved by the heavy-atom method and anisotropically refined for all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps and introduced as fixed contributors in the last stage of refinement (U_{iso} = 0.08 Å^2). For 5557 unique observed reflections ($I > 2\sigma(I)$) collected at T = 295 K on an Enraf-Nonius CAD4 diffractometer ($6 < 2\theta < 140°$) and corrected for absorption the current R value is 0.048 (wR2 = 0.125). All calculations were carried out on an ENCORE E91 computer and on a Quansan Personal Computer equipped with an Intel Pentium processor. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. See the Supporting Information for more details.

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