The Wittig Reaction as a Key Step in the Preparation of Triangular Ligands for the Self-Assembly of Molecular M_4L_4 Tetrahedra

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Abstract: Triangular ligands based on a central C_3-symmetric backbone, ethylene linkages, and catechol ligand units, are prepared by a Wittig approach. The ligands form, in metal-directed self-assembly processes, tetrahedral coordination compounds of the composition M_4L_4.

Key words: Wittig reaction, catechol, ligands, self-assembly, tetrahedra

Metallosupramolecular chemistry provides an opportunity to prepare huge heteronuclear coordination compounds with different structural features in self-assembly processes. Although the self-assembly step is simple, the preparation of the necessary organic ligands is often challenging.[1]

For example, triangular ligand systems with pyridines as metal-binding units at the corners are able to form container molecules as demonstrated by the work of Fujita[2] and Stang.[1a]

Figure 1 presents some ligands with chelating binding sites, which form tetrahedral M_4L_4 complexes in self-assembly processes. The coordination compounds of ligands **A**–**C** are small, providing virtually no internal space for guest uptake.[3,4] Ligand **D**, which is obtained in a simple imine condensation, was introduced by our group and forms an M_4L_4 complex with titanium(IV) ions which possesses a huge cavity and is able to encapsulate organic guest species.[5]

Unfortunately, ligand **D** and its titanium(IV) complex show some disadvantages compared to ligands **A**–**C**. The most important one is the lability of the connecting imine units in the presence of water. However, in order to use such containers for transport processes, phase-transfer catalysis, or to promote chemical reactions, as it was recently demonstrated by Fujita[6] or Raymond,[7] the compounds should be water-stable.

Thus, we have undertaken a study to substitute the imine linkage in ligands like **D** by ethylene units. The new spacers are introduced in a Wittig-type approach followed by hydrogenation of the resulting C=C double bonds. In this paper, we present the synthesis of the ligands and show that they form tetranuclear $[Ti_4L_4]^{8-}$ tetrahedra.

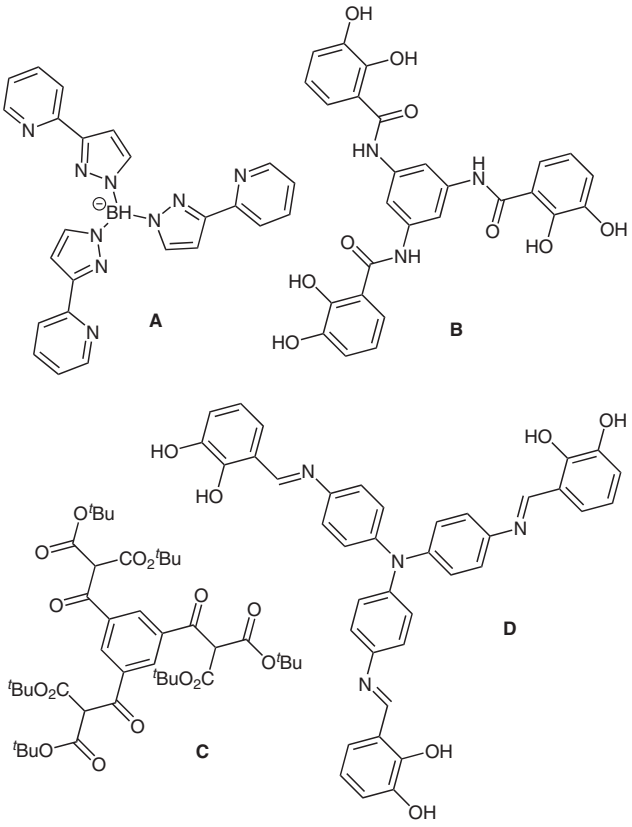

Figure 1 Selected ligands that form M_4L_4 molecular tetrahedra

For the preparation of the ligands by a Wittig approach, two different strategies can be envisaged: (1) A central triangular trisphosphonium salt is transformed into a tris-ylide, which then reacts with three equivalents of 2,3-dimethoxybenzaldehyde. (2) In an alternative protocol, a trialdehyde reacts with three equivalents of 2,3-dimethoxybenzylidene triphenylphosphonium ylide. It will be shown that both reaction sequences are feasible.

[Benzene-1,3,5-triyltris(methylene)]tris(triphenylphosphonium) tribromide (**1**) is easily prepared in a three-step procedure in 26% yield starting from benzene-1,3,5-tricarboxylic acid trimethyl ester.[8] In situ, it is converted into the tris-ylide by deprotonation with potassium *tert*-butoxide in THF and immediately is trapped by the addi-

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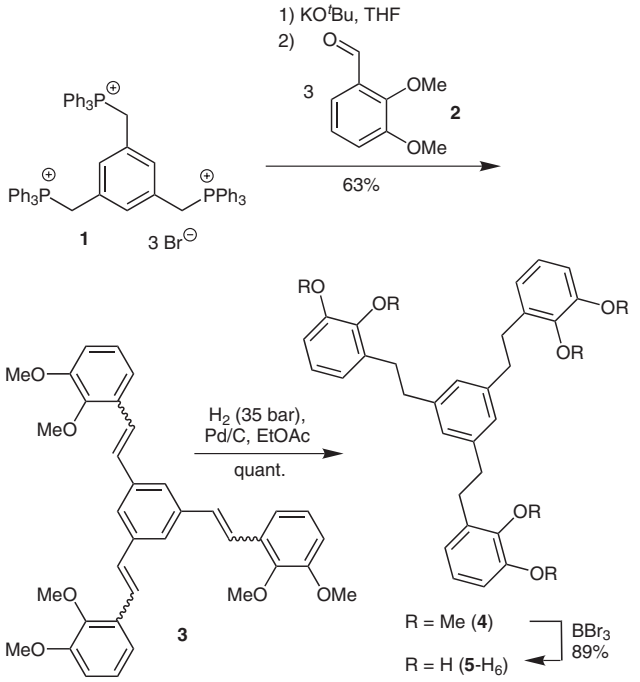
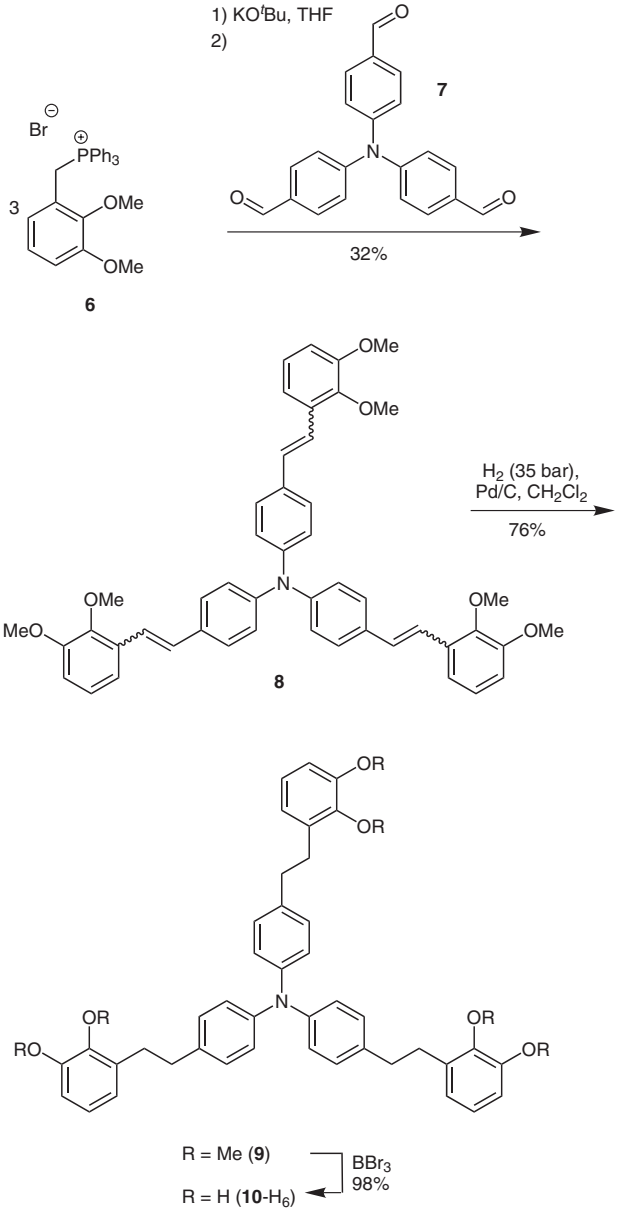


Scheme 1 Preparation of the triscatechol **5**-H_6



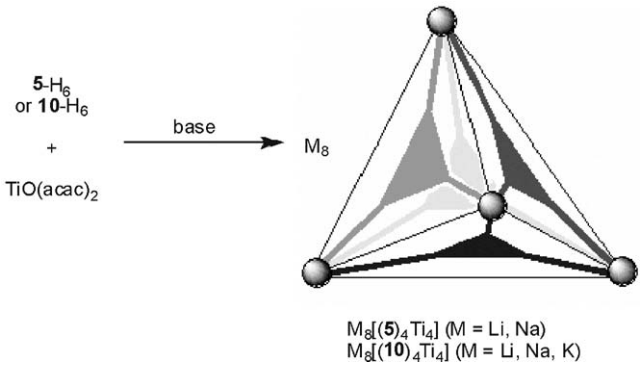
Scheme 2 Preparation of the triscatechol **10**-H_6

tion of three equivalents of 2,3-dimethoxybenzaldehyde (**2**). The trialkene **3** is obtained as a mixture of *E*/*Z* isomers in 63% yield (Scheme 1).

Hydrogenation of the double bonds of **3** at 35 bar using Pd/C in ethyl acetate affords **4** in quantitative yield, which is deprotected to liberate the triscatechol ligand **5**-H_6 in 89% yield. The ligand is characterized by standard techniques (^{1}H NMR, IR, MS, elemental analysis). For example, the ^{1}H NMR spectrum in CD_3OD provides the expected signals of the central benzene ring as a singlet at $\delta = 6.75$ (3 H), the aromatic CH protons of the catechol units at $\delta = 6.54$ (dd, $J = 1.65$, 7.69 Hz, 3 H), 6.47 (t, $J = 7.69$ Hz, 3 H), and 6.42 (dd, $J = 1.65$, 7.69 Hz, 3 H), and the resonance of the alkyl spacer at $\delta = 2.71$ (s, 12 H). MS (EI) shows the molar peak at $m/z = 486$.

In an alternative approach, the (2,3-dimethoxybenzyl)triphenylphosphonium bromide (**6**) is deprotonated with potassium *tert*-butoxide to generate the corresponding ylide. Three equivalents of this ylide react with the trialdehyde **7** (prepared from triphenylamine by Vilsmaier reaction).[9] The trialkene is obtained in 32% and subsequently reduced by hydrogen at 35 bar using Pd/C as the catalyst, resulting in the methylated ligand **9** in 72%. Deprotection with BBr_3 affords the triscatechol **10**-H_6 in 98% (Scheme 2). MS shows the corresponding molar peak at $m/z = 653$. ^{1}H NMR in CD_3OD reveals the doublets of the internal aromatics at $\delta = 7.09$ (d, $^3J = 8.2$ Hz, 6 H) and 6.89 (d, $^3J = 8.2$ Hz, 6 H); resonances of the catechol units are observed at $\delta = 6.62$–6.54 (m, 9 H, CH_{arom}) and the alkyl protons appear at $\delta = 2.83$ (br s, 12 H).

The two ligands **5**-H_6 and **10**-H_6 were applied in coordination studies with titanium(IV) ions using different alkali metal carbonates (for **5**) or hydroxides (for **10**) as the base.



Scheme 3 Formation of tetranuclear complexes with ligands **5**-H_6 and **10**-H_6. The structure of the tetrahedron is only indicated.

The reactions are performed in DMF or methanol and provide the tetranuclear complexes $M_8[(\mathbf{5})_4Ti_4]$ (M = Li, Na) and $M_8[(\mathbf{10})_4Ti_4]$ (M = Li, Na, K) in quantitative yields (Scheme 3).

The complexes are well soluble in DMF or methanol and show reasonable solubility in water. In the latter solvent they possess long-term stability. Elemental analysis indicates the presence of huge amounts of solvent in the solid material (e.g., 50 molecules of water per $Li_8[(\mathbf{5})_4Ti_4]$). This is probably due to the inclusion of the solvents in the interior of the containers as already observed in the crystal structure of the titanium complex of ligand **D**.[5]

^{1}H NMR spectroscopy provides information on the symmetry of the coordination compounds. The very simple spectra show that complexes with high symmetry are formed, indicating the tetrahedral structures (for an example of a spectrum see Figure 2, top).

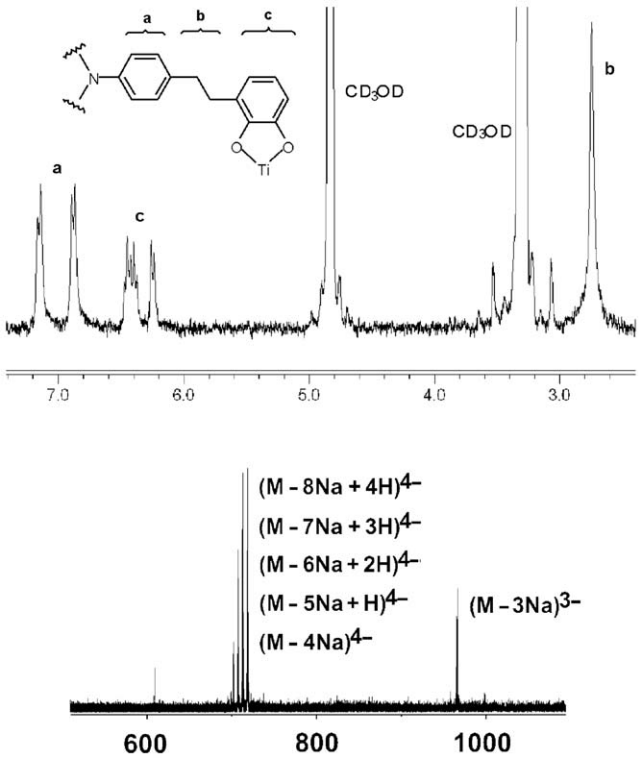


Figure 2 Top: ^{1}H NMR spectrum of $Na_8[(\mathbf{10})_4Ti_4]$ in CD_3OD at room temperature showing the assignment of the signals to the ligand. Bottom: ESI FT-ICR MS of $Na_8[(\mathbf{10})_4Ti_4]$ (**M**) sprayed from methanol.

Diastereotopic behavior is expected for the methylene protons of the alkyl spacers. This is not observed at room temperature due to fast epimerization of the metal complex units. Only in water broad resonances are found for the alkyl protons at room temperature. Cooling a solution of $Na_8[(\mathbf{10})_4Ti_4]$ in CD_3OD in the NMR spectrometer to 220 K does not lead to a splitting of the resonances but significant broadening is observed for the alkyl signals.[10]

The composition of the coordination compounds is shown by ESI FT-ICR MS[11] to be 4:4 complexes. As a representative example Figure 2, bottom shows the spectrum of $Na_8[(\mathbf{10})_4Ti_4]$. Differently charged ions of the M_4L_4 complex can be detected in the negative mode. Substitution of the sodium cations by protons is observed.

In this paper, we have presented the synthesis of two new triscatechol ligands in which the ligand units are connected to the backbone by alkyl spacers. The geometry of the ligands is ideal for the formation of tetrahedral complexes, while steric restrictions prevent the coordination of the three catecholates to only one metal. The preliminary complexation studies show that the supramolecular containers assemble easily and can be characterized by a combination of NMR spectroscopy and mass spectrometry. The obtained complexes are soluble and stable in water and therefore should be ideal candidates for host/guest chemistry in this solvent. This investigation is now in progress in our laboratories.

NMR spectra were recorded on a Varian Mercury 300 or Inova 400 spectrometer. FT-IR spectra were recorded on a Bruker IFS spectrometer. ESI FT-ICR mass spectra were measured on a Bruker Bioapex II FTMS equipped with a 7 Tesla magnet or a Bruker APEX IV Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Melting points: Büchi B-540 (uncorrected). The starting materials **1**,[8] **6**,[12] and **7**[9] were prepared as described before.

1,3,5-Tris(2,3-dimethoxystyryl)benzene (3)

The tris(triphenylphosphonium) tribromide **1** (0.500 g, 0.440 mmol) was dissolved in anhyd THF (20 mL). The solution was cooled to 0 °C and first *t*-BuOK (0.148 g, 1.320 mmol) in THF (10 mL) and after 0.5 h, 2,3-dimethoxybenzaldehyde (**2**; 0.217 g, 1.320 mmol) were added. The mixture was stirred overnight and then poured into H_2O (10 mL). The trialkene was purified by extraction with toluene (3 × 20 mL), drying (Na_2SO_4), and column chromatography (SiO_2; EtOAc–pentane, 1:1). Pure **3** (as a mixture of *E*/*Z* isomers) was obtained after a second chromatographic purification (SiO_2; CH_2Cl_2–pentane, 1:1) as a yellow oil (0.157 g, 63%).

IR ($CHCl_3$): 3527, 2939, 2834, 1584, 1471, 1271, 1224, 1172, 1076, 1007, 895, 752 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6, mixture of isomers): δ = 7.6–6.4 (m, 18 H, $CH_{olefinic}$ + CH_{arom}), 3.9–3.5 (m, 18 H, CH_{alkyl}).

MS (EI, 70 eV): *m*/*z* = 564.3 (M^+).

Anal. Calcd for $C_{36}H_{36}O_6 \cdot 4.5\ H_2O$ (645.74): C, 72.41; H, 6.68. Found: C, 72.50; H, 6.97.

1,3,5-Tris[2-(2,3-dimethoxyphenyl)ethyl]benzene (4)

1,3,5-Tris(2,3-dimethoxystyryl)benzene **3** (157 mg, 0.78 mmol) as well as 10% Pd/C (5 mg) were suspended in EtOAc (5 mL). The mixture was hydrogenated in an autoclave overnight at 35 bar H_2 pressure. The mixture was filtered and the solvent was removed under vacuum. The crude product was purified by column chromatography (EtOAc–pentane, 1:1) to give a viscous oil (0.159 g, quant).

IR ($CHCl_3$): 3492, 3400, 3007, 2936, 2836, 1591, 1476, 1271, 1222, 1172, 1081, 1010, 754, 569, 537 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.98 (t, *J* = 7.9 Hz, 3 H, CH_{arom}), 6.87 (dd, *J* = 1.5, 8.4 Hz, 3 H, CH_{arom}), 6.86 (s, 3 H, CH_{arom}), 6.87 (dd, *J* = 1.7, 7.7 Hz, 3 H, CH_{arom}), 3.78 (s, 9 H, CH_{alkyl}), 3.69 (s, 9 H, CH_{alkyl}), 2.75 (m, 12 H, CH_{alkyl}).

MS (EI, 70 eV): *m*/*z* = 571.2 (MH^+), 435.1 ($C_{28}H_{35}O_4^+$), 419.0 ($C_{27}H_{31}O_4^+$).

Anal. Calcd for $C_{36}H_{42}O_6 \cdot 1.5\ H_2O$ (597.74): C, 72.34; H, 7.59. Found: C, 72.11; H, 7.23.

1,3,5-Tris[2-(2,3-dihydroxyphenyl)ethyl]benzene (5-H_6)

At 4 °C, BBr_3 (2 mL) was added to **4** (0.117 g, 0.210 mol) in CH_2Cl_2 (30 mL). After stirring overnight, MeOH–H_2O mixture (1:1, 5 mL) was added and the product was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed under vacuum to obtain a waxy red solid (0.089 g, 89%).

IR ($CHCl_3$): 3765, 3016, 2931, 2860, 1620, 1359, 1158, 1071, 950, 863, 830, 668, 569, 537 cm^{-1}.

^1H NMR (300 MHz, CD_3OD): δ = 6.75 (s, 3 H, CH_{arom}), 6.54 (dd, *J* = 1.65, 7.69 Hz, 3 H, CH_{arom}), 6.47 (t, *J* = 7.69 Hz, 3 H, CH_{arom}), 6.42 (dd, *J* = 1.65, 7.69 Hz, 3 H, CH_{arom}), 2.71 (s, 12 H, CH_{alkyl}).

MS (EI): *m*/*z* = 486.1 (M^+), 363.1 ($C_{23}H_{23}O_4^+$), 123 ($C_7H_8O_2^+$).

Anal. Calcd for $C_{30}H_{30}O_6 \cdot 4\ H_2O$ (558.62): C, 65.50; H, 6.86. Found: C, 65.49; H, 7.11.

Tris[4-(2,3-dimethoxystyryl)phenyl]amine (8)

The triphenylphosphonium bromide **6** (1.327 g, 2.690 mmol, 4 equiv) and *t*-BuOK (0.403 g, 3.590 mmol, 5.4 equiv) were dissolved in anhyd THF (20 mL). After 1 h, compound **7** (0.222 g, 0.670 mmol, 1 equiv) was added. After stirring overnight at 50 °C, the reaction was quenched with 3 N HCl (2 mL) followed by concd aq NH_3 (1 mL). Filtration, removal of solvent and chromatography (EtOAc–hexane, 2:3) afforded the product as a yellow oil; mixture of *E*/*Z* isomers (0.166 g, 32%).

IR (KBr): 3989, 3931, 3869, 3617, 3566, 3483, 3420, 3369, 3274, 2931, 1590, 1504, 1472, 1424, 1318, 1270, 1220, 1069, 1004, 743 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ (major isomer) = 7.26 (m, 8 H, CH_{arom}), 7.06 (dd, *J* = 8.0, 1.5 Hz, 6 H, CH_{arom}), 6.99 (t, *J* = 8.0 Hz, 6 H, CH_{arom}), 6.78 (dd, *J* = 8.0, 1.5 Hz, 6 H, CH_{arom}), 6.74 (d, *J* = 15.9 Hz, 3 H, CH_{alken}), 6.25 (dt, ^3J = 15.9 Hz, ^4J = 6.9 Hz, 3 H, CH_{alkene}), 3.86 (s, 9 H, CH_{alkyl}), 3.80 (s, 9 H, CH_{alkyl}).

MS (EI): *m*/*z* = 731.4 (M^+), 365.8 ($C_{25}H_{22}NO_2^+$).

Anal. Calcd for $C_{48}H_{45}NO_6 \cdot 0.5$ EtOAc (775.93): C, 77.08; H, 6.62; N, 1.32. Found: C, 77.40; H, 6.37; N, 1.81.

Tris{4-[(2,3-dimethoxyphenyl)ethyl]phenyl}amine (9)

Compound **8** (0.166 g, 0.230 mol) was hydrogenated (30 bar) in an autoclave in CH_2Cl_2 (10 mL) in the presence of 10% Pd/C (5 mg). The mixture was filtered and the solvent removed to obtain a yellow oil (0.134 g, 76%).

IR ($CHCl_3$): 3011, 2936, 2832, 1588, 1505, 1477, 1272, 1220, 1079, 1009, 814, 754 cm^{-1}.

^1H NMR (CD_3OD, 300 MHz): δ = 7.10 (d, *J* = 8.5 Hz, 6 H, CH_{arom}), 6.99 (d, *J* = 8.5 Hz, 6 H, CH_{arom}), 7.03–6.97 (m, 3 H, CH_{arom}), 7.85–6.77 (m, 6 H, CH_{arom}), 3.89 (s, 9 H, CH_{alkyl}), 3.83 (s, 9 H, CH_{alkyl}), 2.98–6.84 (m, 12 H, CH_{alkyl}).

MS (EI): *m*/*z* = 737.3 (M^+), 586.2 ($C_{39}H_{40}NO_4^+$), 573.2 ($C_{38}H_{39}NO_4^+$), 436.2 ($C_{30}H_{31}NO_2^+$), 422.1 ($C_{29}H_{28}NO_2^+$), 271.1 ($C_{20}H_{17}N^+$).

Anal. Calcd for $C_{48}H_{51}NO_6 \cdot 1.5\ H_2O$ (764.95): C, 75.37; H, 7.12; N, 1.83. Found: C, 75.43; H, 7.35; N, 2.15.

Tris{4-[(2,3-dihydroxyphenyl)ethyl]phenyl}amine (10-H_6)

BBr_3 (0.3 mL) was added to the amine **9** (0.124 g, 0.170 mol) in CH_2Cl_2 (15 mL). After stirring overnight, the mixture was quenched by the addition of MeOH (1 mL) in EtOAc (20 mL) at 0 °C. The organic phase was washed with dilute HCl (10 mL) and dried (Na_2SO_4). The solvent was removed to give a dark oil (0.112 g, 98%).

IR ($CHCl_3$): 3539, 3390, 3019, 2936, 1707, 1600, 1505, 1479, 1279, 1217, 1076, 758 cm^{-1}.

^1H NMR (CD_3OD, 300 MHz): δ = 7.09 (d, *J* = 8.2 Hz, 6 H, CH_{arom}), 6.89 (d, *J* = 8.2 Hz, 6 H, CH_{arom}), 6.62–6.54 (m, 9 H, CH_{arom}), 2.83 (br s, 12 H, CH_{alkyl}).

MS (EI): *m*/*z* = 653.4 (M^+), 530.3 ($C_{35}H_{32}NO_4^+$), 394.2 ($C_{27}H_{24}NO_2^+$), 530.3 ($C_{35}H_{32}NO_4^+$), 285.2 ($C_{21}H_{19}N^+$), 246.1 ($C_{18}H_{15}N^+$), 228.1 ($C_{14}H_{14}NO_2^+$), 213.1 ($C_{14}H_{13}O_2^+$), 194.1 ($C_{14}H_{12}N^+$), 110.2 ($C_6H_6O_2^+$), 91.2 ($C_6H_5N^+$).

Anal. Calcd for $C_{42}H_{39}NO_6 \cdot 5\ H_2O$ (698.80): C, 67.82; H, 6.64; N, 1.88. Found: C, 67.53; H, 6.05; N, 1.63.

Complexes of Ligand 5; General Procedure

Ligand **5**-H_6 (0.045 g, 0.092 mmol), $TiO(acac)_2$ (0.024 g, 0.092 mmol) and M_2CO_3 (M = Li, Na, 0.092 mmol) were dissolved in DMF (40 mL) and stirred overnight. The solvent was removed and the residue was dried under vacuum.

$Li_8[(5)_4Ti_4]$

Yield: 0.075 g (quant).

IR (KBr): 3879, 3430, 2920, 2372, 2345, 1662, 1570, 1521, 1441, 1252, 1099, 1062, 1023, 971, 856, 738, 667, 489 cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 6.83 (s, 12 H, CH_{arom}), 6.43 (dd, *J* = 7.8, 1.4 Hz, 12 H, CH_{arom}), 6.35 (dd, *J* = 7.7, 7.8 Hz, 12 H, CH_{arom}), 6.16 (dd, *J* = 7.7, 1.4 Hz, 12 H, CH_{arom}), 2.86 (m, 12 H, CH_{alkyl}), 2.73 (m, 12 H, CH_{alkyl}), 2.50 (m, 24 H, CH_{alkyl}).

MS (ESI–): *m*/*z* = 1065.3 $[M - 6\ Li + 2\ H]^{2-}$, 1062.8 $[M - 7\ Li + 5\ H]^{2-}$, 1059.3 $[M - 8\ Li + 6\ H]^{2-}$, 529.6 $[M - 7\ Li + 3\ H]^{4-}$, 530.1 $[M - 8\ Li + 4\ H]^{4-}$.

Anal. Calcd for $C_{120}H_{96}Li_8O_{24}Ti_4 \cdot 11$ DMF·18 H_2O (3297.33): C, 53.64; H, 6.15; N, 4.50. Found: C, 53.59; H, 5.90; N, 4.48.

$Na_8[(5)_4Ti_4]$

Yield: 0.068 g (quant).

IR (KBr): 3903, 3839, 3751, 3676, 3655, 3629, 3551, 3438, 3278, 2929, 1655, 1637, 473 cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 6.79 (s, 12 H, CH_{arom}), 6.43 (d, *J* = 7.6 Hz, 12 H, CH_{arom}), 6.36 (dd, *J* = 7.6, 7.5 Hz, 12 H, CH_{arom}), 6.18 (d, *J* = 7.5 Hz, 12 H, CH_{arom}), 2.96 (m, 12 H, CH_{alkyl}), 2.74 (m, 12 H, CH_{alkyl}), 2.44 (d, ^3J = 9.1 Hz, 24 H, CH_{alkyl}).

MS (ESI–): *m*/*z* = 1125.3 $[M - 2\ Na]^{2-}$, 1114.8 $[M - 3\ Na + H]^{2-}$, 1103.3 $[M - 4\ Na + 2\ H]^{2-}$, 1092.8 $[M - 3\ Na + 3\ H]^{2-}$, 742.8 $[M - 3\ Na]^{3-}$, 735.5 $[M - 4\ Na + H]^{3-}$, 728.2 $[M - 5\ Na + 2\ H]^{3-}$, 720.5 $[M - 6\ Na + 3\ H]^{3-}$, 545.9 $[M - 5\ Na + H]^{4-}$, 535.1 $[M - 7\ Na + 3\ H]^{4-}$.

Anal. Calcd for $C_{120}H_{96}Na_8O_{24}Ti_4 \cdot 7$ DMF·16 H_2O (2968.93): C, 57.04; H, 6.01; N, 3.30. Found: C 56.89; H, 6.15; N, 3.38.

Complexes of Ligand 10; General Procedure

Ligand **10**-H_6 (0.030 g, 0.046 mmol), $TiO(acac)_2$ (0.012 g, 0.046 mmol) and MOH (M = Li, Na, K, 0.093 mmol) were dissolved in MeOH (40 mL) and stirred overnight. The solvent was removed and the residue was dried under vacuum.

$Li_8[(10)_4Ti_4]$

Yield: 0.043 g (quant).

IR (KBr): 3438, 2923, 1601, 1509, 1450, 1256, 1061, 1026, 847, 738, 622, 487 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.04 (d, *J* = 8.2 Hz, 24 H, CH_{arom}), 6.78 (d, *J* = 8.2 Hz, 24 H, CH_{arom}), 6.37 (d, *J* = 7.7 Hz, 12 H, CH_{arom}), 6.31 (dd, *J* = 7.7, 7.4 Hz, 12 H, CH_{arom}), 6.16 (d, *J* = 7.4 Hz, 12 H, CH_{arom}), 2.65 (br s, 48 H, CH_{alkyl}).

MS (ESI–): *m*/*z* = 1018.5 [M – 8 Li + 4 K + Na + 3 CH_3OH]$^{3-}$, 997.2 [M – 8 Li + 4 K + Na + CH_3OH]$^{3-}$, 991.8 [M – 8 Li + 5 K]$^{3-}$, 970.5 [M – 8 Li + K + 4 Na]$^{3-}$, 965.2 [M – 8 Li + 5 Na]$^{3-}$, 943.9 [M – 4 Li + Na]$^{3-}$, 942.5 [M – 5 Li + Na + H]$^{3-}$, 938.6 [M – 3 Li]$^{3-}$, 782.6 [M – 8 Li + 4 K + 4 CH_3OH]$^{4-}$, 770.7 [M – 8 Li + 3 K + Na + 5 CH_3OH]$^{4-}$, 766.2 [M – 8 Li + 4 K + 4 CH_3OH]$^{4-}$, 762.7 [M – 8 Li + 3 K + Na + 4 CH_3OH]$^{4-}$, 762.5 [M – 7 Li + 3 Na + 6 CH_3OH]$^{4-}$, 759.4 [M – 8 Li + 2 K + 2 Na + 2 CH_3OH]$^{4-}$, 751.0 [M – 8 Li + 2 K + 2 Na + 3 CH_3OH]$^{4-}$, 750.2 [M – 8 Li + 4 K + 2 CH_3OH]$^{4-}$, 746.1 [M – 8 Li + 3 Na + K + 3 CH_3OH]$^{4-}$, 742.2 [M – 8 Li + 4 K + CH_3OH]$^{4-}$, 726.2 [M – 8 Li + 2 K + 2 Na]$^{4-}$, 724.9 [M – 5 Li + H + 3 CH_3OH]$^{4-}$, 722.2 [M – 8 Li + K + 3 Na]$^{4-}$, 720.7 [M – 8 Li + 3 Na + H + CH_3OH]$^{4-}$, 719.2 [M – 8 Li + 4 H + 5 H_2O]$^{4-}$, 718.2 [M – 8 Li + 4 Na]$^{4-}$, 706.4 [M – 5 Li + Na]$^{4-}$, 704.7 [M – 6 Li + Na + H]$^{4-}$, 702.2 [M – 4 Li]$^{4-}$, 700.7 [M – 5 Li + H]$^{4-}$, 699.2 [M – 6 Li + 2 H]$^{4-}$.

Anal. Calcd for $C_{168}H_{132}Li_8N_4O_{24}Ti_4 \cdot 50\ H_2O$ (3738.62): C, 53.97; H, 6.25; N, 1.50. Found: C, 53.65; H, 5.92; N, 1.39.

$Na_8[(10)_4Ti_4]$
Yield: 0.040 g (quant).

IR (KBr): 3407, 2923, 1661, 1506, 1450, 1387, 1320, 1257, 1103, 1060, 1027, 968, 843, 738, 625, 484 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.15 (d, *J* = 7.2 Hz, 24 H, CH_{arom}), 6.88 (d, *J* = 7.2 Hz, 24 H, CH_{arom}), 6.42 (m, 24 H, CH_{arom}), 6.25 (d, ^3J = 6.2 Hz, 12 H, CH_{arom}), 2.75 (s, 48 H, CH_{alkyl}).

MS (ESI–): *m*/*z* = 965.2 [M – 3 Na]$^{3-}$, 718.4 [M – 4 Na]$^{4-}$, 712.9 [M – 5 Na + H]$^{4-}$, 707.7 [M – 6 Na + 2 H]$^{4-}$, 702.2 [M – 7 Na + 3 H]$^{4-}$, 696.2 [M – 8 Na + 4 H]$^{4-}$.

Anal. Calcd for $C_{168}H_{132}N_4Na_8O_{24}Ti_4 \cdot 30\ H_2O$ (3506.70): C, 57.54; H, 5.52; N, 1.60. Found: C, 57.33; H, 5.36; N, 1.94.

$K_8[(10)_4Ti_4]$
Yield: 0.043 g (quant).

IR (KBr): 3756, 3436, 2927, 2345, 1616, 1506, 1448, 1255, 1059, 1029, 841, 732, 626, 573, 474 cm^{-1}.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.15 (d, *J* = 8.2 Hz, 24 H, CH_{arom}), 6.88 (d, *J* = 8.2 Hz, 24 H, CH_{arom}), 6.47 (d, *J* = 7.4 Hz, 12 H, CH_{arom}), 6.43 (dd, *J* = 7.4, 7.7 Hz, 12 H, CH_{arom}), 6.26 (d, *J* = 7.7 Hz, 12 H, CH_{arom}), 2.74 (br s, 48 H, CH_{alkyl}).

MS (ESI–): *m*/*z* = 760.7 [M – 6 K + Na + H + 5 CH_3OH]$^{4-}$, 750.7 [M – 8 K + 4 Na + 4 CH_3OH]$^{4-}$, 741.2 [M – 6 K + Li + H + 3 CH_3OH]$^{4-}$, 740.7 [M – 5 K + H + 2 CH_3OH]$^{4-}$, 736.9 [M – 6 K + Na + H + 2 CH_3OH]$^{4-}$, 731.7 [M – 6 K + 2 H + 2 CH_3OH]$^{4-}$, 721.2 [M – 8 K + 3 Na + H + CH_3OH]$^{4-}$, 711.4 [M – 8 K + Na + Li + 2 H + CH_3OH]$^{4-}$, 702.2 [M – 8 K + 4 Li]$^{4-}$.

Anal. Calcd for $C_{168}H_{132}K_8N_4O_{24}Ti_4 \cdot 35\ H_2O \cdot 35\ CH_3OH$ (3757.69): C, 53.09; H, 5.92; N, 1.41. Found: C, 53.17; H, 5.90; N, 1.99.

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