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Synthesis and Structural Characterization of 1,2,4-Diazaphospholide Complexes of Titanium(IV) and Titanium(III)

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Supporting Information

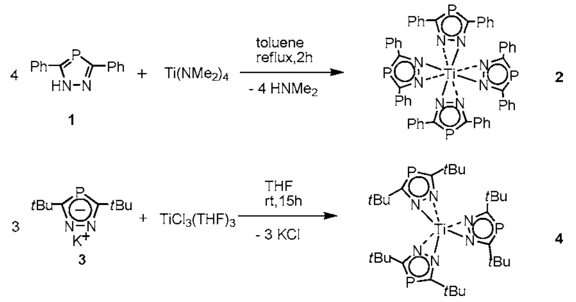
ABSTRACT: Two 1,2,4-diazaphospholide complexes of [Ti(η^2-3,5-Ph$_2$dp)$_4$] and paramagnetic [Ti(η^2-3,5-*t*Bu$_2$dp)$_3$] were prepared by the reaction of tetrakis(dimethylamido)titanium(IV) with 3,5-diphenyl-1,2,4-diazaphophole, H[3,5-Ph$_2$dp], or by the treatment of 3,5-*tert*-butyl-1,2,4-diazaphopholide potassium, K[3,5-*t*Bu$_2$dp], with titanium trichloride. Complexes can be viewed as the core of P($\sigma^2\lambda^3$)-functionalized metallodendrimers, in which the metal atoms are exclusively η^2(N,N) bonding to the 1,2,4-diazaphospholides while P atoms ($\sigma^2\lambda^3$) with electron lone pairs are located on the periphery of the molecules.

Metallodendrimers represent a new class of dendrimers in which metal ions have been incorporated into the different sites of the dendritic structure: the core unit, the branches, the branching centers, or the periphery of the dendrimers.[1] Advantages to using metallodendrimers with catalysts on the periphery include their increased multivalency (higher local concentration), which allows for enhanced reaction rates, and the possibility of separating the catalysts from the reaction medium, for example, through precipitation or ultrafiltration using membrane reactors.

The modified ligands (or coordination compounds) containing low-coordination P atoms ($\sigma^2\lambda^3$) are stronger π acceptors toward low-valent transition metals than, for example, tertiary phosphanes.[2,3] The complexes bearing such ligands (or coordination compounds) have demonstrated to be highly active and selective catalysts in different organic transformations.[3,4] The 1,2,4-diazaphospholides (dp) are a mixed N−P($\sigma^2\lambda^3$) heteroaromatic system[5a,b] and have been recently applied to the preparation of the corresponding complexes[5c−e,6] in which P atoms ($\sigma^2\lambda^3$) have donor lone pairs available.[6] Subsequent work has shown that the metal 1,2,4-diazaphospholides played an important role as efficient ligands in the palladium-catalyzed Heck reaction, where bimetallic complexes may form with P−Pd π-back-bonding.[7] Impetus was provided by the results[6,7] that 1,2,4-diazaphospholide complexes may provide a unique molecular environment, especially in the higher local concentration of low-valent P($\sigma^2\lambda^3$) on the periphery of the molecule, for the coordinated catalysts[7] or for the redox-active species.[6f] Herein, we describe the synthetic approach to the dendritic core structures of 1,2,4-diazaphospholide titanium(IV) and titanium(III) with an exclusive η^2(N,N) coordination. B3LYP/6-311G* and B3LYP/LANL2DZ calculations were used to rationalize the bonding structures of the complexes.

The reaction of Ti(NMe$_2$)$_4$ and [3,5-Ph$_2$dp]H (**1**)[8] in toluene at reflux afforded [Ti(η^2-3,5-Ph$_2$dp)$_4$]·3THF (**2**·3THF, where THF = tetrahydrofuran) as a red solid (60%), while the treatment of TiCl$_3$(THF)$_3$[9] and [3,5-*t*Bu$_2$dp]K (**3**)[6a] in ether smoothly led to complex [Ti(η^2-3,5-*t*Bu$_2$dp)$_3$] (**4**) as blue-purple crystals (75%), as shown in Scheme 1. **2** is well soluble in THF and warm toluene, while **4** is soluble in common organic solvents.[10]

Scheme 1. Synthesis of Complexes 2 and 4



An X-ray crystal structure determination of **2** and **4** was carried out.[10,11] Both **2** and **4** can be regarded as possible cores of dendritic titanium 1,2,4-diazaphospholides with endo bidentate η^2(N,N) coordination (Figures 1 and 2). The ligands at titanium(IV) in **2** arrange in closer tweezer arms with dihedral angles of 78.8°. With a dihedral angle of 178.5° between the plane defined by the atoms N1, N2, and Ti and the plane of the heterocyclic core (N1, N2, C1, C2, and P1), the observed conformation involving the donation of the in-plane N atom lone pairs to the metal center is similar to that found in the η^2(*N,N*)-pyrazolato (pz) titanium complex [Ti(η^2-3,5-Ph$_2$pz)$_4$] (**5**).[12] Such similarity likely stems from the phosphorus conjugative ability to be comparable to that of carbon.[13] Compound **2** does not attain coordination saturation in a 16-electron system, presumably attributed to the steric

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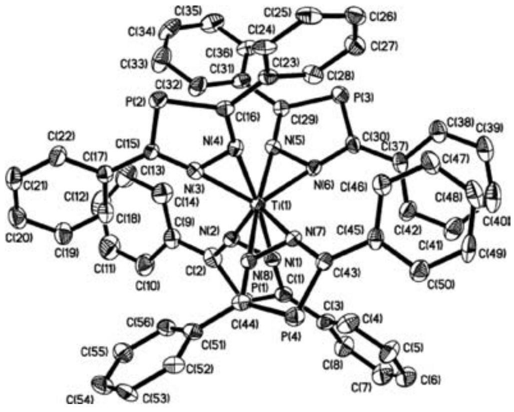

Figure 1. Molecular structure of **2**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti(1)−N(1) 2.071(5), Ti(1)−N(2) 2.058(5); N(3)−Ti(1)−N(4) 38.02(17).

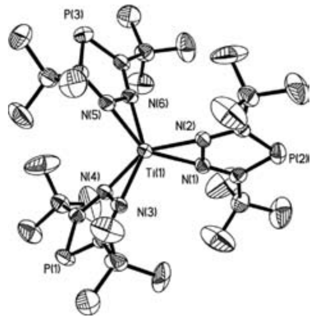

Figure 2. Molecular structure of **4**. H atoms are omitted for clarity. Two of the *t*Bu groups are disordered. Selected bond lengths [Å] and angles [deg]: Ti(1)−N(1) 2.045(4), Ti(1)−N(2) 2.048(4); N(3)−Ti(1)−N(4) 39.26(16).

demand of the ligands. The Ti−N bond lengths are between 2.042(5) and 2.093(5) Å, which fall in the expected range of Ti−N distances associated with the titanium complex Ti[NN(H)Ph](*t*Bubpy)(dpma) [Ti−N 2.073(4) Å].[14] The N−N bond lengths range between 1.340(6) and 1.362(6) Å, comparable to that found in the dianion radical 1,2,4-diazaphospholide potassium complex [N(1)−N(2) 1.351(8) Å].[6f] The N−Ti−N angles within each η^2-1,2,4-diazaphospholide range from 37.78(17) to 38.44(18)°.

The crystal structure of **4** shows that 1,2,4-diazaphospholides are coordinated to Ti^{III} atoms with nearly perfect η^2 geometry, with Ti−N bond lengths ranging from 2.024(5) to 2.048(4) Å, comparable to those found in $[Ti(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_3]$ [Ti−N 2.048(3) Å].[15] The N−Ti−N angles within each η^2-1,2,4-diazaphospholide are also very similar, and vary from 39.13(17) to 39.39(17)°, but are slightly wider that those found in **2**.

The $^{31}P\{^1H\}$ NMR resonance of **2** (THF-d_8, 23 °C) is observed at 145.3 ppm, which is significantly shifted downfield relative to the corresponding signals of the free heterocyclic ligand H[3,5-Ph_2dp] (^{31}P δ = +74.3 ppm),[8] the potassium salt K[3,5-Ph_2dp] (^{31}P δ = +67.19 ppm),[6a] and the 1-methyl-1,2,4-diazaphosphole (^{31}P δ = +93.8 ppm),[16] clearly assigned to the electron-withdrawing character of the Ti^{IV} ion. However, the $^{31}P\{^1H\}$ NMR resonance of **4** (C_6D_6, 23 °C) is observed at 66.9 ppm, which is only shifted downfield about 1.5 and 16.2 ppm relative to the corresponding signals of the free heterocyclic ligand H[3,5-$t\text{Bu}_2$dp] (^{31}P δ = +65.4 ppm)[8b] and potassium salt K[3,5-$t\text{Bu}_2$dp] (^{31}P δ = +50.7 ppm),[6a] respectively. The ^1H NMR (C_6D_6, 23 °C) spectrum of **4** shows only one broad resonance at δ = 2.35 ppm ($\delta_{1/2}$ = 0.6 ppm), attributable to the *t*Bu groups of the ligands. However, the resonances in the $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C) spectrum are very weak even after 10 240 scans. The unusual resonances in $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra are likely due to the paramagnetic properties of **4** ($3d^1$).

To help in understanding the structures of **2** and **4**, we carried out B3LYP/LAND2DZ and B3LYP/6-311G* calculations on model compounds in which we replaced the phenyl groups by H atoms. We have also calculated a model of compound **5**[12] closely related to **2m** (Scheme 2).[17]

Scheme 2. Model Compounds

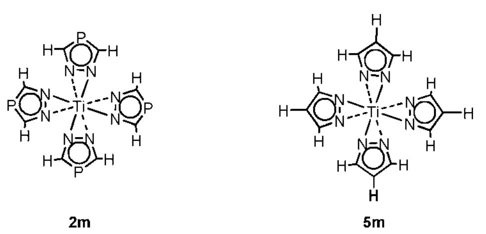

Table 1. Polytopal δ Angles of Four-Coordinated Titanium(IV) Derivatives

	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	sum (deg)	average (deg)
2	136	138	99	98	96	95	665	110
2m[a]	133	133	98	98	98	98	662	110
2m[b]	134	134	98	98	98	98	663	110
5	139	140	97	97	96	96	666	111
5m[a]	133	133	99	99	99	99	662	110
5m[b]	133	133	98	98	98	98	663	110
c	109	109	109	109	109	109	656	109
d	180	180	90	90	90	90	720	120

[a] Full 6-311G*. [b] LANL2DZ. [c] Tetrahedron T_d. [d] Planar D_{4h}.

To discuss the geometry of **2** and **2m**, it is better to consider them tetrahedral than octahedral because of the rigidity imposed to the N−N bond by the heterocycles (dp and pz). Taking the middle point between both N atoms as a dummy **d**, we have calculated at two theoretical levels (B3LYP/LANL2DZ) the eight δ Muetterties' **d**−Ti−**d** angles (Table 1).[18]

The main conclusions from the Table 1 data are as follows: (i) the calculation reproduced very well the experimental geometries (including the Ti−N distances; see the Supporting Information), proving that the phenyl rings can be considered as a perturbation; (ii) the tetrahedral distortion is small (the mean value of the six compounds of 110.7° is much closer to T_d than to D_{4h}; (iii) compounds **2** and **5** are very similar; i.e., diazaphospholes and pyrazoles are geometrically almost identical.

The electron density maps of **2m** (Figure 3) and **5m** calculated at the B3LYP/6-311G* computational level present a bond path between the Ti atom and each of the N atoms of the dp/pz rings.

In conclusion, we present titanium(IV) and titanium(III) 1,2,4-diazaphospholides with η^2(N,N) coordination, in which three or four low-coordination P atoms with electron lone pairs on the periphery of molecule are available. With the bulkiness of two adjacent *tert*-butyl or phenyl groups beside the P atom

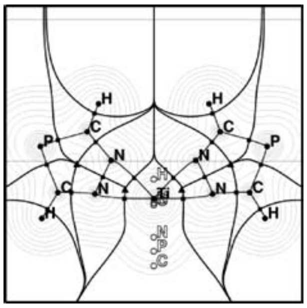

Figure 3. Electron density map of **2m** calculated at the B3LYP/6-311G* level. Circles, squares, and triangles represent the position of the atoms, bond critical points, and ring critical points, respectively.

(ortho to P), the complexes are reminiscent of the phosphaferrocenes with sp^2-hybridized P atoms and the pseudoruthenocene complexes incorporating dp ligands, which have a marked tendency to engage in metal-to-phosphorus π-back-bonding.[2−4,7] The present work demonstrates that the complexes with η^2(*N*,*N*)-1,2,4-diazaphospholide coordination are easily obtained because the hard metal ions are liable to binding to the more negative side (N,N) of the heterocyclic ring, as has been predicted by theoretical calculation.[6f] This allows variation of the metal centers in complexes with η^2(*N*,*N*)-1,2,4-diazaphospholide coordination and renders the possibility of finely tuning the electronic properties of transition metals (soft metal ions) bonded to the P atoms, which might be further advantageous in terms of the catalyst lifetime, sensitivity, selectivity, etc.[19] Despite the similarity of the geometries to titanium pyrazolatos,[12,15] complexes **2** and **4** are expected to be in an extraordinary nature because of the unique structure and redox-active behavior of the 1,2,4-diazaphospholide ligand.[6f] Work is proceeding along these lines.

Computational Details. Geometries were optimized at the B3LYP/6-311G*[20] and B3LYP/LANL2DZ[21] levels using *Gaussian 03*.[22] Frequency calculations were performed at the same level to confirm that they correspond to energy minima.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, analytical and spectroscopic data for **2** and **4**, details of the calculations of the full geometries of **2m** and **5m** (B3LYP/6-311G* and B3LYP/LANL2DZ), and X-ray crystallographic files for **2** and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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