protein, and that only a single component of the dragline silk was used, the reported results are impressive. It is expected that, by optimizing the process, possibly in combination with a deliberate variation of the primary structure of the protein,[13] fibers that are almost indistinguishable from natural spider silk will be accessible. Nexia Biotechnologies manufactures these fibers under the brand name BioSteel. For the production of larger amounts, they plan to use transgenic goats that express the silk protein in their milk.[14] Applications of spider silk are anticipated in areas where high mechanical strength, in combination with biodegradability, of fibers and films produced thereof are advantageous, for example, in medicine. The presented results show that a production of high-performance polymers on the basis of spider silk is a promising prospect for the very close future.

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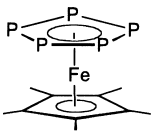
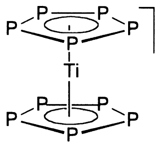
[15] The dimension gpd (grams per denier) used for the modulus of elasticity and tenacity in reference [2] was converted into GPa according to (gpd.δ)/11.33δ, whereby a value of 1.3 g cm^{-3} was assumed for the density (H.-G. Elias, *Makromoleküle*, *Vol. 2*, 5th ed., Hüthig & Wepf, Basel, **1992**, p. 522).

The Decaphosphatitanocene Dianion—A New Chapter in the Chemistry of Naked Polyphosphorus Ligands

Helmut Sitzmann*



1



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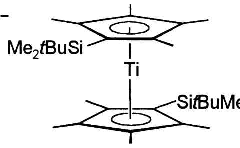

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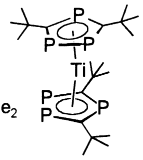

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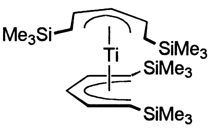

5

Even before those progressive researchers had thought about sandwich complexes, ferrocene had already formed from iron and cyclopentadiene, had been collected,[1] and was awaiting discovery. When [(C$_5$Me$_5$)TiCl$_3$] was distilled from the products of a TiCl$_4$-catalyzed olefin isomerization reaction forty years ago,[2] the affinity of transition metals to this prototype of a pentaalkylcyclopentadienyl ligand became apparent and fueled the boom in cyclopentadienyl complex chemistry.

The interest in transition-metal-promoted self-assembly of five-membered-ring ligands extended to Group 15 at the end of the 1980s, when the dinuclear iron complex [{(C$_5$Me$_5$)Fe(CO)$_2$}$_2$] was allowed to react with white phosphorus.[3] The resulting product, namely pentamethylpentaphosphaferrocene (**1**), stimulated the newly emerging area of P$_n$ complexes and awakened the idea of bis(pentaphosphacyclopentadienyl) metal complexes (often referred to as decaphosphametallocenes).[4]

While steric protection is not available to prevent aggregation of decaphosphametallocenes, electrostatic repulsion is. When Ellis and Urnėžius et al.[5] treated the bis(naphthalene)titanium dianion with 2.5 equivalents of P$_4$ at low temperature, the decaphosphatitanocene dianion [Ti(η^5-P$_5$)$_2$]$^{2-}$ (**2**) was formed in high yield as the 2[Na([18]crown-6)]$^+$ salt.[5]

Whereas the known metallocene dianions that have been generated by electrochemical reduction are highly labile species,[6] **2** is unreactive with carbon monoxide, xylyl isocyanide, or trimethylphosphite, is stable in solution under an atmosphere of pure dioxygen, can be handled in air, and is only slowly attacked by wet pyridine. Crystalline samples of (PPh$_4^+$)$_2$ and (Ph$_3$PNPPh$_3^+$)$_2$ salts of **2** melt at 213–215

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(decomp) and 319–323 °C (decomp), respectively. The nature of the cation has little influence on the ^{31}P NMR singlet resonance of **2**, which is observed between $\delta = 60$ and 63 ppm.

The stability of **2** is attributed in part to steric properties of the *cyclo*-P_5 ligand. The plane of this relatively large ring has to move quite close to the metal to allow typical Ti–P bond lengths of 256 pm. The distance of 360 pm between the two P_5 rings in the fully eclipsed molecule **2** is therefore much shorter than the value of 402 pm observed for centrosymmetric $[Ti(C_5Me_4SiMe_2tBu)_2]$ (**3**)[7] and provides steric shielding of the Ti center.

Even more important for the stability and for the diamagnetic ground state of **2** are the electronic properties of the *cyclo*-P_5 ligand. η^5-P_5 is a weaker donor, but much stronger acceptor than the cyclopentadienyl ligand, according to density functional computations.[5] Diamagnetism has also been found for the hexaphosphatitanocene $[Ti(P_3C_2tBu_2)_2]$ (**4**).[8] The small p,π overlap of the phosphorus atoms results in a closer spacing of the ligand π orbitals and places the empty π orbitals low enough in energy to encourage mixing with the titanium 3d HOMO and formation of a metal–ring δ bond. This electron delocalization facilitates spin pairing to form a diamagnetic ground state.[8] In contrast, the titanocene derivative **3** possesses two unpaired electrons.[7] Similar steric and electronic arguments have been used to explain the stability and the singlet ground state of "open" titanocenes such as $[Ti\{C_5H_5(SiMe_3)_2\}_2]$ (**5**).[9]

Treatment of **2** with potassium pentamethylcyclopentadienide or 1,4,7-triazacyclononane in pyridine leads to the formation of the free P_5^- ion, as indicated by a ^{31}P NMR signal at $\delta = 468$ ppm. If this reactivity of **2** can be developed into a clean process, **2** may not only become a source of the *cyclo*-P_5 ligand, but possibly also of titanium complexes with one P_5 ring. Some of the questions to be answered in future concern the redox behavior of **2** and the possibility of stacking reactions in which **2** is used as a nucleophile analogously to the anionic sandwich complexes with boron heterocycles.[10]

The selective formation of P_5 rings from P_4, and the surprising stability of **2** most likely indicate that the decaphosphatitanocene dianion acts as the energetic sink in a complicated reaction mixture. This feature can be related to the ligand properties of *cyclo*-P_5 and is probably not restricted to the titanium complex. It will therefore be highly interesting to search for decaphosphametallocene mono- and especially dianions of other metals, preferably among Groups 4–7 and possibly including second- and third-row transition metals.

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