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Notes

Synthesis and Molecular Structure of 1,3-Di-*tert*-butyl-2,4-bis(cyclodipentadienyl)iron(II) 1,3,2,4-Diazadiphosphetidine, $[Fe(\eta^5\text{-}C_5H_4)_2(PN^tBu)_2]$

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Summary: The reaction of the dichlorocyclodiphosphazane (also called dichlorodiazadiphosphetidine), $[ClP(\mu\text{-}N^tBu)]_2$, with in situ generated ferrocene dilithiate in a 1:1 molar ratio affords the first metallocene derivative of a diazadiphosphetidine, 1,3-di-tert-butyl-2,4-bis(cyclopentadienyl)iron(II) 1,3,2,4-diazadiphosphetidine, $[Fe(\eta^5\text{-}C_5H_4)_2(PN^tBu)_2]$, in good yield.

Introduction

The current interest in cyclodiphosphazanes (also known as diazadiphosphetidines) is largely focused toward the use of the four-membered P_2N_2 rings as building blocks to design interesting macrocycles with or without involving main group or transition metals.[1] The simplest cyclodiphosphazane is the chloro derivative $[ClP(\mu\text{-}N^tBu)]_2$, which is remarkable in its reactivity in generating a host of molecules when treated with difunctional amines or alcohols.[2] Although several alkoxy, aryloxy, and amide derivatives have been prepared, cyclodiphosphazanes containing phosphorus−carbon bonds (both P(V)−C and P(III)−C) are limited to the methyl and phenyl derivatives, which are prepared starting from aryl- or alkylphosphorus dihalides ($RPCl_2$) or by some rearrangement reactions involving organophosphorus (thio)dihalides ($RP(S)Cl_2$) or other organophosphorus derivatives.[3] This may be due to the difficulties involved in reacting $[ClP(\mu\text{-}N^tBu)]_2$ with RLi and RMgX, as these reagents are often known to cleave the P−N bonds. Recently we have reported a series of cyclodiophosphazanes with various donor functionalities and their extensive transition-metal chemistry.[4] As a continuation of our work on phosphorus-based ligands for coordination chemistry and catalytic applications,[5] we describe the synthesis and structural characterization of a novel ferrocene-derived cyclodiphosphazane, $[Fe(\eta^5\text{-}C_5H_4)_2(PN^tBu)_2]$ (**1**).

Results and Discussion

The reaction between chlorocyclodiphosphazane, $[ClP(\mu\text{-}N^tBu)]_2$, and diols, diamines, or amino alcohols can afford simple monomeric bicylic derivatives or dimeric to pentameric macrocycles depending on the stoichiometry of the reagents and the reaction conditions.[6,7] Although the product selection is reported to be kinetically controlled, the reaction temperature and the duration also have a significant influence on product formation.[8] It appears, however, that none of these studies

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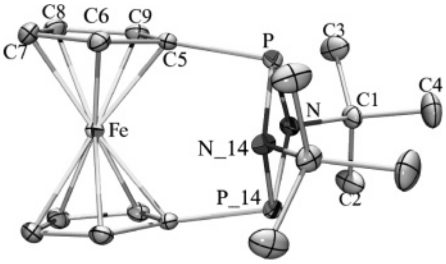
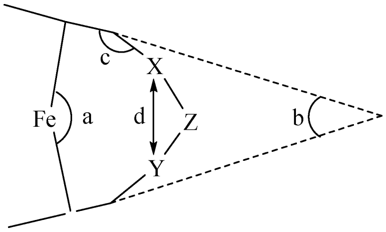


Figure 1. Molecular structure of [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$] in the crystal (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): P−N, 1.741(1); N−C1, 1.481(2); P−C5, 1.822(1); P−N_14, 1.736(1); Fe−C5, 2.109(1); Fe−C6, 2.031(1); Fe−C7, 2.055(1); Fe−C8, 2.056(1); Fe−C9, 2.031(1); Fe−C5−P, 121.02(7); P−N−P_14, 94.07(6); C5−P−N, 98.68(7); C5−P−N_14, 85.69(6).

explored phosphorus−carbon bond formation with [ClP(μ-N^{t}Bu)]$_2$, and moreover, the metallocene derivatives of cyclodiphosphazanes are not known. As a result, we sought to explore the reaction of [ClP(μ-N^{t}Bu)]$_2$ with organolithium derivatives, with an attractive candidate being ferrocene dilithiate. The reaction of ferrocene dilithiate, generated in situ by treating freshly sublimed ferrocene with 2 equiv of ^{n}BuLi in the presence of TMEDA, with the cyclodiphosphazane [ClP(μ-N^{t}Bu)]$_2$ resulted in the formation of [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$] (**1**). The reaction did not afford dimer, trimer, or any other higher oligomers; it, instead, yielded exclusively the monomeric derivative **1** in moderate yield. The ^{31}P NMR spectrum of **1** shows a single resonance at 190.6 ppm, indicating the equivalent nature of both the phosphorus atoms. The ^{1}H and ^{13}C NMR data are consistent with the structure proposed, and this was further confirmed by a single-crystal X-ray study.

Crystals of **1** suitable for X-ray diffraction analysis were grown from a solution prepared from a 1:1 mixture of toluene and *n*-hexane. For the molecular structure of **1** in the crystal, see Figure 1. Compound **1** has crystallographically imposed 2-fold rotation symmetry, with the cyclodipentadienyl rings adopting the eclipsed conformation. The P_2N_2 ring is slightly puckered, with the two NPP planes having a dihedral angle of 172.3(1)°, while the two NNP planes have a dihedral angle of 172.87(9)°. The Cremer−Pople puckering parameter Q_2 is −0.079(1)°. In general, *cis* isomers have puckered P_2N_2 rings, although usually this is somewhat larger than seen here, whereas the rings in the *trans* isomers are planar. The P−N and P−C5 distances are 1.741(1) and 1.822(1) Å, respectively. The Fe−C5 distance of 2.0198(1) Å is slightly longer than the other Fe−C bonds (average Fe−C 2.043(1) Å). This may be due to the size and rigid nature of the P_2N_2 framework, causing a slight elongation of the Fe−C (Fe−C5 and Fe−C5_a) bonds to accommodate the cyclodiphospazane ring. The C5−P−N and C5−P−N_a angles are 98.68(7)° and 85.69(6)°, respectively. The P−N−P angle is 94.07(6)°, while the sum of angles around the nitrogen atom is 342.11(6)°, which indicates the pyramidal nature of the nitrogen atoms. This is also shown by the fact that the N−C5 bond makes an angle of 29.7° with the PNN plane. Although nitrogen prefers a planar geometry in P−N compounds, this deviation is the result of minimizing nonbonded contacts of the *tert*-butyl group with the cyclopentadienyl hydrogens. The interesting features of the structure are that the nitrogen atoms are pyramidal and the P−N bonds are longer than in most examples which have been structurally characterized.[4] This clearly indicates a smaller involvement of nitrogen lone pairs in multiple bonding with phosphorus centers, which gives an opportunity to explore the coordinating ability of nitrogen atoms toward transition metals, which has not been observed in the past.

Table 1: Geometrical Parameters of Selected Ferrocenophanes



X	Y	Z	*a* (deg)	*b* (deg)	*c* (deg)	*d* (Å)	ref
CHMe	CHR^1	CH_2	173.0	9.6	175.7	2.593	9
CH_2	CH_2	CH_2	172.2	10.3	175.9	2.56	10
CH_2	CHPcy$_2$	CH_2	173.9	8.4	174.6	2.575	11
P	P	N(^{t}Bu)$_2$	174.9	7.8	175.2	2.545	this work
SiMe$_2$	SiMe$_2$		176.4	4.2	168.8	2.354	13
CMe$_2$	CMe$_2$		165.4	23.2	170.1	1.548	12
		Sn(^{t}Bu)$_2$	168.6	15.4	143.8		14
		GePh$_2$	166.2	16.6	142.3		15
		SiPh$_2$	167.3	19.1	140.0		16

It is interesting to compare the “bite angle” of nonparallel cyclopentadienyl rings in **1** with those in other related ferrocenophanes, using the angle subtended at the iron atom by the centroids of the two rings (*a*), the angle between the mean planes of the two rings (*b*), the angle between the lines connecting the ring carbon atom to the adjacent bridge atom and to the ring centroid (*c*), and the distance between the ends of the bridging unit (if more than one atom) (*d*) (Table 1), as it gives some information about its utility in ring-opening polymerization and other catalytic applications. From these data, **1** appears to most resemble ferrocenophanes with a three-carbon bridge. Interestingly, the species with the −SiMe$_2$SiMe$_2$− bridge has very similar values for angles *a* and *b* despite the considerably shorter distance *d*. Here the additional strain occasioned by the shorter bridge is manifested primarily in a smaller angle *c*, but in contrast, the complex with the even shorter −CMe$_2$CMe$_2$− bridge actually has a slightly larger value for angle *c*. Instead, the cyclopentadienyl rings are more severely canted. In the case of the single-atom bridges, angle *a* is about the same and the interplanar angle *b* is less than seen for the two-carbon bridge, so greater strain is evident in the much smaller values for the angle *c*. Since the majority of instances of ring-opening polymerization appear to involve the last three entries in Table 1 and their analogues,[17] which have considerably smaller bite angles than does **1**, it is unlikely that **1** will show similar reactivity.

In summary, we report for the first time a metallocene derivative of cyclodiphosphazane, which is interesting as there are not many inorganic rings which have this kind of unique structure. The transition-metal chemistry and catalytic reactions of this novel ligand are under active investigation in our laboratory.

Experimental Section

General Procedures. All experimental manipulations were carried out using standard Schlenk techniques under an argon or

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nitrogen atmosphere. Solvents were dried and deoxygenated before distillation from sodium benzophenone ketyl or Na−K alloy. TMEDA was freshly distilled and ferrocene was freshly sublimed prior to use. The ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR (δ, ppm) spectra were obtained on a Varian VRX 400 spectrometer operating at the appropriate frequencies. The spectra were recorded in $CDCl_3$ (or DMSO-d_6) solutions with $CDCl_3$ (or DMSO-d_6) as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^{1}H and ^{31}P{^{1}H} NMR, respectively. Positive shifts lie downfield of the standard in all of the cases. Microanalyses were carried out on a Carlo Erba (model 1106) elemental analyzer.

Preparation of [Fe(η^5-C_5H_4)$_2$(PN^{t}Bu)$_2$] (1). To a solution of ferrocene dilithiate generated in situ by reacting ferrocene (1 g, 5.37 mmol) with TMEDA (1.29 g, 5.37 mmol) and ^{n}BuLi (4.3 mL, 10.75 mmol, 2.5 M solution in *n*-hexanes) in hexane was added dropwise a solution of [ClP(μ-N^{t}Bu)]$_2$ (1.47 g, 5.37 mmol) in diethyl ether (40 mL) at −40 °C, and the solution was allowed to attain room temperature over 25 min. The orange solution was stirred for 8 h and filtered through Celite, and the filtrate was dried in vacuo. The orange residue was washed several times with *n*-hexane, dissolved in 10 mL of toluene, layered with 2 mL of *n*-pentane, and stored at −10 °C for 24 h, whereupon **2** was obtained as orange crystals in 55% yield (1.14 g, 2.95 mmol). Mp: 52 °C. Anal. Calcd for $C_{18}H_{26}N_2P_2Fe$: C, 55.66; H, 6.75; N, 7.21. Found: C, 55.76; H, 6.74; N, 7.14. ^{1}H NMR ($CDCl_3$): 4.27 (d, 4H, C_5H_4), 4.17 (d, 4H, C_5H_4), 1.20 (s, CMe_3, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$): 74.9 (C_5H_4), 74.8 (C_5H_4), 72.1 (C_5H_4), 72.1 (C_5H_4), 52.1 (CMe_3), 30.8 (CMe_3). ^{31}P{^{1}H} NMR ($CDCl_3$): 190.6 (s).

X-ray Crystallography. An orange crystal of **1** (0.10 × 0.13 × 0.19 mm) crystallized from a mixture of toluene and *n*-pentane at −10 °C was mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of a Bruker Smart APEX CCD diffractometer. A full sphere of data were collected under the control of the SMART[18] software, the raw data reduced to a set of F^2 values with SAINT+,[19] and corrections for absorption applied.[20] The structure was solved by direct methods and was refined by full-matrix least-squares procedures using the SHELXTL program package.[21] Hydrogen atoms were placed in calculated positions and included as riding contributions, with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

Crystal data for **1**: $C_{18}H_{26}FeN_2P_2$, $M_w = 388.20$, orthorhombic, *Fdd*2 (No. 43), $a = 15.543$ (1) Å, $b = 23.253$ (2) Å, $c = 9.9437(7)$ Å, $V = 3593.9(5)$ Å^3, $Z = 8$, $D_c = 1.435$ g cm^{-3}, crystal dimensions 0.10 × 0.13 × 0.19 mm, μ(Mo Kα) = 0.425 mm^{-1}, $F(000) = 696$, $T = 100$ K, $2\theta_{max} = 28.3°$, 15478 reflections measured, 2242 unique reflections ($I > 2.0\sigma(I)$), R1 = 0.027, wR2 = 0.0532.

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Supporting Information Available: CIF files giving crystal data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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