

Bischalcogenides and transition metal complexes of cyclodiphosphazane derived diphosphaferrocenophane



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ABSTRACT

Oxidation reactions and transition metal chemistry of diphosphaferrocenophane [$\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2$] (**1**) has been reported. The reactions of **1** with *aq.* H_2O_2 and elemental selenium afforded bis-chalcogenides, [$\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-P(E)N}^t\text{Bu})_2$] ($\text{E} = \text{O}$; **2**, $\text{E} = \text{Se}$; **3**). Treatment of **1** with [$\text{Rh}(\text{COD})\text{Cl}$] $_2$ and [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}$] $_2$ in 1:1 molar ratio afforded binuclear complexes, [$\{\text{RhCl}(\text{COD})\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}$] (**4**) and [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}$] (**5**), respectively. The mixed-ligand binuclear Cu^{I} complex [$\{(2,2'\text{-bpy})\text{Cu}\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}$] (**6**) was synthesized by the reaction of **1** with CuI followed by treatment with 2,2'-bipyridine. The reaction between **1** and [$\text{AuCl}(\text{SMe}_2)$] in 1:2 molar ratio yielded the dinuclear complex [$\{\text{AuCl}\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}$] (**7**) showing intermolecular aurophilic interactions in the crystal lattice. The crystal structures of **2**, **4–7** were established by single-crystal X-ray diffraction studies.

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1. Introduction

Metalloarenoferrocenophanes have attracted tremendous attention during the past few decades due to their highly interesting reactivity patterns and promising applications in transition metal catalyzed ring-opening polymerization [1–3]. [*n*]Ferrocenophanes, in which two cyclopentadienyl rings are connected by *ansa* bridges ($n = 1, 2, 3$ atoms) are an important class of strained metal-containing ring systems. Over the years, phosphorus-bridged [1]ferrocenophanes have been one of the extensively studied strained metalloarenoferrocenophanes, along with Si- and Ge-ferrocenophanes, which are known for promoting ring-opening polymerization in a living fashion [4,5].

In comparison with [1]ferrocenophanes (**I**), the synthesis of phosphorus-bridged [*n*]ferrocenophanes with $n \geq 2$ is highly challenging and are less extensive (Chart 1). The first example of diphospha[2]ferrocenophane (**II**) was isolated in trace amounts during the reaction between dilithiated ferrocene and excess of hexachlorocyclotriphosphazanes ($\text{P}_3\text{N}_3\text{Cl}_6$) [6]. The diphospha[2]ferrocenophane (**III**) having both P(III) and P(V) centers was synthesized by moisture assisted cleavage of 1,1'-bis(phosphenyl)-ferrocene, $\text{Fe}(\text{C}_5\text{H}_4\text{-P=P-R})_2$ [7]. Recently, Mizuta and coworkers

reported the first examples of P^{III} -bridged diphospha[2]ferrocenophanes (**IV**) by the reductive coupling reactions of 1,1'-disubstituted ferrocene [$\text{Fe}(\text{C}_5\text{H}_4\text{P}(\text{Cl})\text{R})_2$] [8].

Cyclodiphosphazanes or diazadiphosphetidines have proved to be versatile soft P^{III} building blocks for the synthesis of interesting metallomacrocycles [9] and coordination polymers [10]. Recently we reported the first example of phosphorus-bridged ferrocenophane (**1**) by the reaction of dilithiated ferrocene with dichlorocyclodiphosphazane and its utility in making the first examples of phosphine based porous sodalite (**sod**) frameworks [11,12]. This paper describes the oxidation reactions and transition metal chemistry of cyclodiphosphazane-derived diphosphaferrocenophane.

2. Results and discussion

2.1. Oxidation reactions, Pd^{II} and Rh^{II} complexes of [$\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2$] (**1**)

The treatment of **1** with excess of *aq.* H_2O_2 in THF at room temperature in dichloromethane resulted in the formation of [$\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-P(O)N}^t\text{Bu})_2$] (**2**). Compound **2** displayed a single resonance in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 17.9 ppm with an upfield shift of 170 ppm, (for [$\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2$], $\delta\text{P} = 188$ ppm). The ^1H NMR spectrum of **2** showed a single resonance at 1.70 ppm due to *tert*-butyl protons and single resonances

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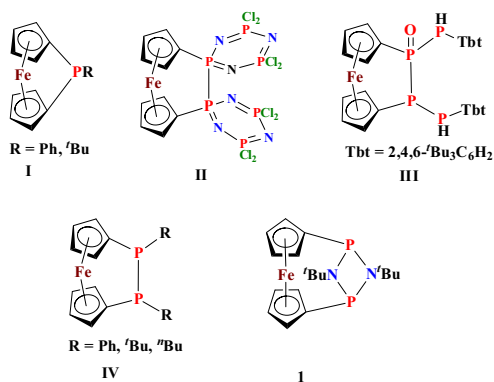
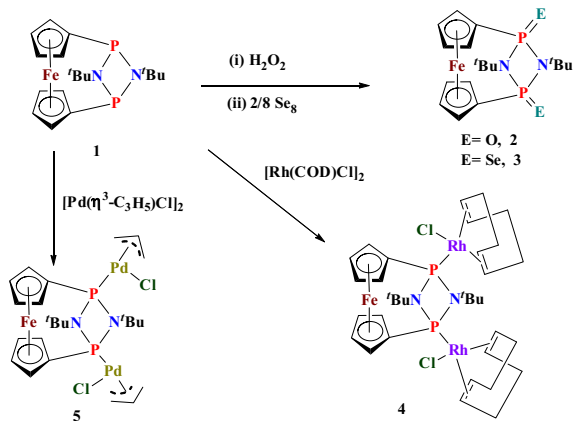


Chart 1. Phosphorus bridged-[*n*]ferrocenophanes, *n* = 1, 2, 3.



Scheme 1. Reactions of diphosphoferrocenophane **1**.

at 4.40 and 4.80 ppm due to the cyclopentadienyl protons, which are slightly deshielded in comparison with those in **1**. The reaction of **1** with two equivalents of elemental selenium in toluene under reflux conditions afforded the diselenide $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-P}(\text{Se})\text{N}^t\text{Bu})_2]$ (**3**) as shown in Scheme 1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** showed a single resonance at 61.8 ppm with a $^1J_{\text{PSe}}$ coupling of 886 Hz. The ^1H NMR spectrum of **3** also showed a singlet at 1.89 ppm for *tert*-butyl protons and two singlets at 4.46 and 4.74 ppm for the ferrocenyl protons.

An equimolar reaction of **1** and $[\text{Rh}(\text{COD})\text{Cl}]_2$ in dichloromethane at room temperature afforded $[\{\text{RhCl}(\text{COD})\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}]$ (**4**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** showed a doublet at 149.3 ppm with a $^1J_{\text{RHP}}$ coupling of 186 Hz. The ^1H NMR spectrum of **4** confirms the presence of cyclooctadiene group. The reaction of **1** with $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ in 1:1 molar ratio in dichloromethane produced $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}]$ (**5**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** shows a single resonance at 162.3 ppm ($\delta\text{P} = 26$ ppm). The ^1H NMR spectrum confirms the presence of the coordinated allyl group. All the five protons of allyl fragment appear distinctly in the ^1H NMR spectrum. In both the complexes the ligand displayed bridged bidentate mode of coordination. The composition of these complexes was confirmed by microanalyses and the structures were confirmed by single crystal X-ray diffraction studies.

2.2. Molecular structures of compounds **2**, **4**–**7**

Crystals of **2** suitable for X-ray diffraction study were obtained by slow evaporation of a solution of **2** prepared from 1:1 mixture of

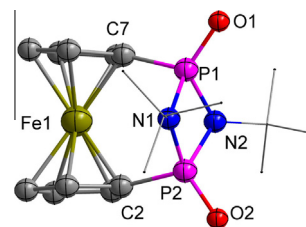


Fig. 1. Molecular structure of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-P}(\text{O})\text{N}^t\text{Bu})_2]$ (**2**). All the hydrogen atoms and lattice solvents have been omitted for clarity, displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond distances and bond angles for **2**.

Bond distances (Å)		Bond angles (°)	
P1–N1	1.6845(6)	P1–N1–P2	92.752(12)
P2–N2	1.6915(6)	P1–N2–P2	92.688(12)
P1–O1	1.4663(3)	N1–P2–C2	104.44(13)
P2–O2	1.4642(4)	N2–P2–C2	104.57(14)
P2–C2	1.7914(6)	N1–P1–C7	105.03(13)
P1–C7	1.7927(6)	N2–P1–C7	103.49(14)

petroleum ether and dichloromethane at room temperature. The structure is shown in Fig. 1, whereas bond distances and bond angles are listed in Table 1. The asymmetric unit consists of four independent molecules of **2**. The P–N bond distances [P1–N1 = 1.684(5), P2–N2 = 1.691(5) Å] are shorter, whereas the P–C bond distances [P1–C7 = 1.792(7), P2–C2 = 1.7914 Å] are longer than those observed in **1** [P–N = 1.741(1) and P–C5 = 1.741(1) Å]. The P–O bond distance is 1.466(3) Å. The C2–P2–N1 and C2–P2–N2 bond angles [104.4(4)° and 104.5(7)°] are longer than those observed in **1** [C–P–N = 98.68(7)° and 85.69(6)°] implying the decrease in the strain of the ring system upon oxidation. The P–N–P [92.68(8)° and 92.75(2)°] and the N–P–N [86.23(8)° and 85.85(2)°] bond angles are comparable with those in **1** [94.07(6) and 85.69°].

Crystals of **4** and **5** suitable for X-ray diffraction studies were obtained by slow evaporation of solution prepared from 1:1 mixture of petroleum ether and dichloromethane at room temperature. The perspective views of molecular structures of **4** and **5** along with the atom labeling schemes are shown in Figs. 2 and 3. The corresponding bond parameters are listed in Table 2. In the

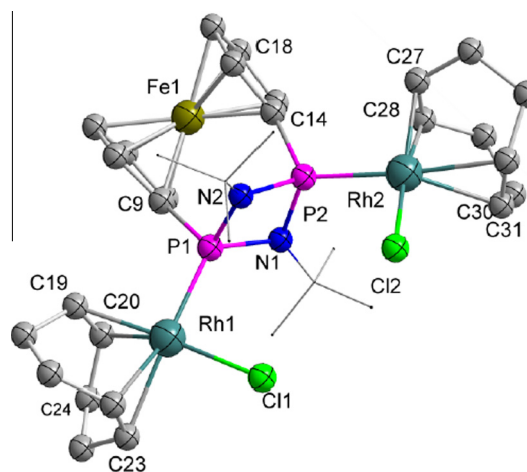


Fig. 2. Molecular structure of $[\{\text{RhCl}(\text{COD})\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\mu\text{-PN}^t\text{Bu})_2\}]$ (**4**). All the hydrogen atoms and lattice solvents have been omitted for clarity, displacement ellipsoids are drawn at the 50% probability level.

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