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Synthesis of 1,1′-Diphospha[4]ferrocenophanes by Molybdenum-Catalyzed Ring-Closing Metathesis

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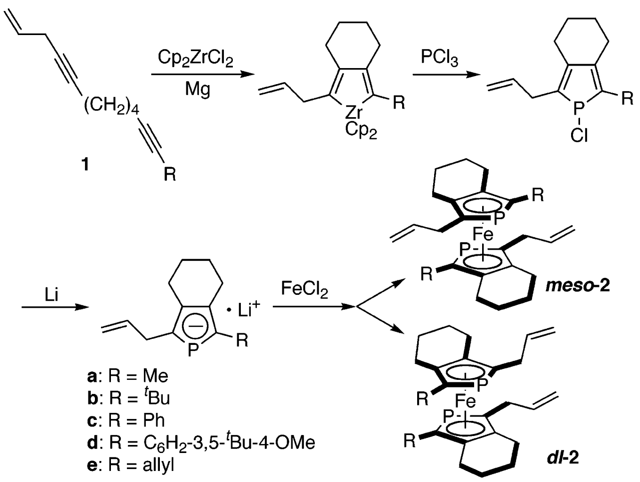
Summary: A variety of 1,1′-diphospha[4]ferrocenophanes were prepared in good to moderate yield with the interannular ring-closing metathesis reaction of diallyl-1,1′-diphosphaferrocenes using the Schrock's molybdenum-carbene catalyst. The Grubbs' ruthenium metathesis catalyst was found inactive for these Lewis basic phosphorus-containing substrates.

Recently, Richards and co-workers reported a novel synthetic method of [4]ferrocenophanes by the ring-closing metathesis (RCM) reaction of 1,1′-diallylferrocenes[1] using Grubbs' ruthenium catalyst RuCl$_2$(=CHPh)(PCy$_3$)$_2$.[2a] Shortly after this report, we independently found analogous reactions and reported that the metathesis route could be applied to preparation of a variety of bridged metallocenes of Fe(II), Ru(II), Zr(IV), and Hf(IV).[3] In the same period, Erker described application of the RCM method for preparing *ansa*-zirconocene species.[4] In certain cases, the metathesis reactions proceed in a diastereoselective fashion[1,3] and either *meso*- or *dl*-bridged metallocenes could be selectively prepared with a proper choice of reaction conditions and the ruthenium-carbene catalysts, RuCl$_2$(=CHPh)(PCy$_3$)$_2$[2a] or RuCl$_2$(=CHPh)(PCy$_3$)(IMes-H$_2$).[2b] In this communication, we wish to report the preparation of 1,1′-diphospha[4]ferrocenophanes[5] using similar metathesis reactions of diallyldiphosphaferrocenes. For the RCM synthesis of the diphospha[4]ferrocenophanes, the Grubbs' ruthenium catalyst was ineffective, but Schrock's molybdenum carbene complex Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(OC(CF$_3$)$_2$Me)$_2$[6] was found to be an active catalyst for the Lewis basic phosphorus-containing substrates.[7]

Scheme 1. Preparation of Diallyl-1,1′-diphosphaferrocenes 2



Synthesis of 2,2′-diallyl-1,1′-diphosphaferrocenes **2** is illustrated in Scheme 1. *P*-Chlorophospholes,[8] which were prepared from 1-substituted-undeca-1,7-diyn-10-enes (**1**) using zirconocene-mediated reaction reported by Fagan and Nugent,[9] were treated with lithium metal to give the corresponding lithium 2-allylphospholides.[8c,d] Subsequent reaction of the lithium phospholides with FeCl$_2$ afforded diallyldiphosphaferrocenes **2**.[8] Because **2a**−**d** possess two unsymmetrically substituted η^5-phospholyl ligands which are planar chiral, two diastereomeric forms, *meso*- and *dl*-isomers, are possible in theory. Among the diphosphaferrocenes used for this study, **2c** was isolated as a mixture of *meso*- and *dl*-isomers after appropriate purification. For **2a** and **2b**, the ^{31}P NMR spectra of crude products showed existence of the corresponding *meso*- and *dl*-isomers. One of the two isomers, however, was selectively crystallized, and thus *meso*-**2a** and *dl*-**2b** were isolated in diastereomerically pure forms. For **2d**, the complexation of the free phospholyl anion to the Fe(II) center proceeded in a

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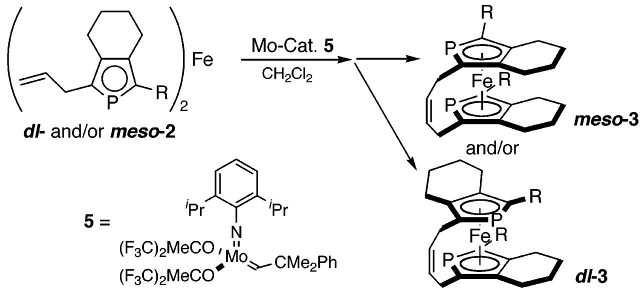
Table 1. Molybdenum-Catalyzed Synthesis of Bridged 1,1′-Diphosphaferrocenes[a]

entry	substrate (δ ^{31}P[b])	[**2**]/mol·L^{-1}[c]	[**5**]/mol %	temp	time/h	yield/%[d]	δ ^{31}P[b]
1	*meso*-**2a** (−51.3)	2.8×10^{-3}	20	reflux	48	77 (*meso*-**3a**)	−87.2
2	*dl*-**2b** (−71.8)	2.8×10^{-3}	20	reflux	36	51[e] (*dl*-**3b**)	−55.5
3	*dl*- and *meso*-**2c**[f] (−51.9 and − 55.7)	1.8×10^{-2}	10	23 °C	15	44[g] (*dl*-**3c**)	−45.4
						39[h] (*meso*-**3c**)	−83.8
4	*meso*-**2d** (−55.1)	3.0×10^{-3}	20	reflux	48	61 (*meso*-**3d**)	−84.2
5	**2e** (−53.0)	2.5×10^{-3}	20	reflux	36	33 (*dl*-**3e**)	−43.9
						31 (**4**)	−91.7

[a] The reaction was carried out in CH_2Cl_2 in the presence of the molybdenum catalyst **5**. [b] Recorded in $CDCl_3$. [c] Initial concentration of the substrate. [d] Yield of the isolated product. [e] The unreacted **2b** was recovered in 39% yield. [f] *dl*-**2c**/*meso*-**2c** = 56/44. [g] 79% of theory. [h] 89% of theory.

Scheme 2. Mo-Catalyzed RCM Route to Diphospha[4]ferrocenophanes 3



diastereoselective manner, and *meso*-**2d** was obtained as a single diastereomer.

The obtained diphosphaferrocene **2a** was examined as a potential substrate for the ring-closing metathesis reaction based on our previous report.[3] That is, **2a** was reacted with 3 mol % of $RuCl_2({=}CHPh)(PCy_3)_2$ in refluxing dichloromethane for 24 h. However, no reaction was observed and the substrate **2a** was recovered in >90% yield. Considering the reported mechanistic study on the Ru-catalyzed metathesis reaction, which claims that a critical process for the Ru-catalyzed metathesis reaction is initial dissociation of one of the PCy_3 ligands from $RuCl_2({=}CHPh)(PCy_3)_2$ giving a 14e$^-$ species,[10] the diphosphaferrocene **2a** probably deactivated the Ru catalyst by coordinating to the ruthenium center. The second-generation Grubbs' catalysts with imidazolylidene or dihydroimidazolylidene were also found inactive for the RCM of **2a**. We then turned our attention to Schrock's molybdenum-carbene complex $Mo({=}CHCMe_2Ph)({=}NC_6H_3\text{-}2,6\text{-}^iPr_2)(OC(CF_3)_2Me)_2$ (**5**).[6] As we expected, transformation of **2a** into the corresponding 1,1′-diphospha[4]ferrocenophane **3a** was efficiently catalyzed by 20 mol % of the molybdenum complex **5** (Scheme 2). Thus, a mixture of **2a** (50 mg, 110 μmol) and **5** (17 mg, 22 μmol) was dissolved in CH_2Cl_2 (40 mL) and the solution was heated to reflux. The substrate **2a** was completely consumed in 48 h, and 35 mg of **3a** (77% yield) was isolated as a bright red crystalline solid by silica gel chromatography under nitrogen (Table 1, entry 1). The results of the Mo-catalyzed RCM reactions of the diallyl-1,1′-diphosphaferrocenes are summarized in Table 1. In most cases, the reactions proceeded smoothly to give the corresponding bridged diphosphaferrocenes in good to moderate yield. The reaction of **2b**, which is with bulky ^{t}Bu substituents, was slow, and 39% of the unreacted **2b** was recovered in 36 h with 51% of the bridged **3b** (entry 2). Dilute conditions are important for high yield of the intramolecular RCM products (except for the reaction of **2c**, vide infra). Under more concentrated conditions, uncharacterized polymeric/oligomeric products were formed to a certain extent and the yield of the diphosphaferrocenophanes became lower. Among the diallyldiphosphaferrocenes examined, **2c** showed exceptionally high reactivity; the RCM reaction of **2c** was completed in a shorter reaction time at the lower temperature with lower catalyst loading (entry 3). In addition, the metathesis reaction of **2c** proceeded in an intramolecular fashion exclusively, and no polymeric/oligomeric byproducts were detected by ^{31}P NMR even in the reaction carried out under the more concentrated conditions.

The diastereomeric mixture of **2c** shows the ^{31}P NMR resonances at δ −51.9 and −55.7 with a 56:44 molar ratio. After the RCM reaction, a pair of newly formed diphospha[4]ferrocenophanes **3c** show distinctive chemical shifts in their ^{31}P NMR spectrum; one is at δ −45.4, which is derived from **2c** of δ −51.9, while the other is in the far upper field region at δ −83.8, which is from the isomer of δ −55.7. It was assumed that this unusual upper field shift of the ^{31}P NMR resonance for the latter would be ascribed to an eclipsed geometry of the two phosphorus nuclei in the diphosphaferrocenophane which would happen in the *meso*-isomer. Indeed, the X-ray crystal structure analysis clarified the isomer of **3c** with the ^{31}P NMR signal at δ −83.8 to be the *meso*-isomer (Figure 1). During the metathesis reaction, no epimerization/racemization at the planar chirality of the η^5-phospholyl ligands was detected. Thus, the stereochemistry of the other diallylphosphaferrocenes **2** and diphospha[4]ferrocenophanes **3** was assigned on the basis of the ^{31}P NMR chemical shifts of the RCM products **3**; **2a**/**3a** and **2d**/**3d** were determined to be *meso*-isomers, while **2b**/**3b** were assigned to be *dl*-isomers.

Two independent molecules of slightly different conformations are present in the asymmetric unit of *meso*-**3c** (see Supporting Information for details). The X-ray crystal structure of one of the two molecules of *meso*-**3c** is shown in Figure 1 with selected bond lengths and angles.[11] The two η^5-phospholyl moieties are nearly eclipsed. Because of the C_4-bridge, the phosphaferrocene

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(11) Crystallographic data for $C_{32}H_{32}P_2Fe$: MW = 534.40; triclinic; space group $P\bar{1}$; a = 14.454(5) Å, b = 14.801(5) Å, c = 12.657(4) Å, α = 109.6992)°, β = 97.07(3)°, γ = 91.86(3)°; V = 2522.2(2) Å^3; Z = 4; d = 1.407 g/cm^3; μ = 7.44 cm^{-1}; $F(000)$ = 1120.00; crystal dimensions 0.30 × 0.20 × 0.20 mm; 15 265 total reflections collected ($I > 3\sigma(I)$), goodness of fit on F 2.36; R = 0.057; R_w = 0.083; maximum/minimum residual density 1.08/−0.90 e/Å^3. Data were collected on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Full details of the crystallographic analysis are described in the Supporting Information.

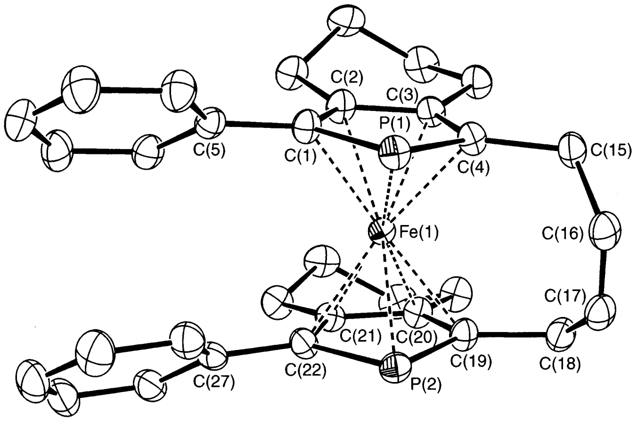
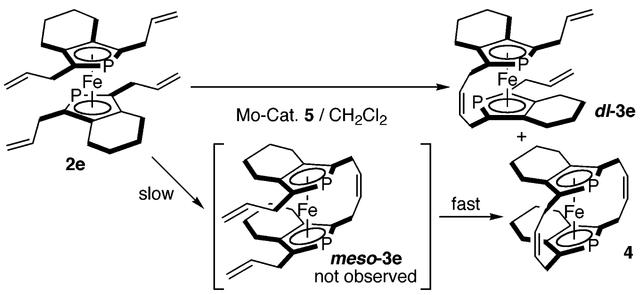


Figure 1. ORTEP drawing of *meso*-**3c** with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): C(4)−C(15) = 1.519(8), C(15)−C(16) = 1.505(9), C(16)−C(17) = 1.28(1), C(17)−C(18) = 1.513(9), Fe(1)−phospholyl$_{P(1)}$ = 1.671(5), Fe(1)−phospholyl$_{P(2)}$ = 1.668(5), C(1)−P(1)−C(4) = 89.4(3), C(19)−P(2)−C(22) = 89.4(3), C(4)−C(15)−C(16) = 114.7(5), C(15)−C(16)−C(17) = 124.4(6), C(16)−C(17)−C(18) = 124.9(6), C(17)−C(18)−C(19) = 112.4(6).

framework is slightly distorted, the dihedral angle of the two phospholyl ligands being 6.4°, which is within the range of those found in the analogous [4]ferrocenophanes.[3] The two phenyl substituents are nearly parallel to each other (7.6° dihedral angle), and $\pi-\pi$ stacking interaction can be seen between them. It is expected that there is similar $\pi-\pi$ attraction between the two phenyl groups in the nonbridged **2c**. The $\pi-\pi$ attraction between the phenyl groups puts the two allyl groups in **2c** in close proximity, assisting the RCM reaction. The high reactivity and the tendency of undergoing intramolecular RCM cyclization of **2c** can be ascribed to the $\pi-\pi$ attraction.

As shown in Scheme 3, the tetraallyldiphosphaferrocene **2e** gave two RCM products with small amounts of uncharacterized polymeric/oligomeric products (Table 1, entry 5). The two RCM products were characterized as single-bridged *dl*-**3e** and double-bridged **4**, respectively. Single-bridged *meso*-**3e** was not detected in the reaction mixture. A corollary of this observation is that the initially formed *meso*-**3e** is more reactive than **2e**. Two remaining allyl substituents in *meso*-**3e** are forced to occupy an eclipsed position because of the restricted rotation of the η^5-phospholyl ligands, and thus a second RCM reaction proceeds rapidly to give **4**. As expected, the double-bridged diphosphaferrocenophane **4**, in which the two phosphorus atoms are eclipsed, shows its ^{31}P NMR resonance in the high-field region at δ −91.7.

Scheme 3. Mo-Catalyzed RCM Reaction of Tetraallyl-1,1′-diphosphaferrocene 2e



In summary, we have established that the RCM route of preparing [4]ferrocenophanes could be applied to preparation of diphosphaferrocene analogues by using Schrock's molybdenum carbene complex as a catalyst. The *dl*- and *meso*-isomers of the diphospha[4]ferrocenophanes are easily distinguished by their ^{31}P NMR spectra, in which the latter show the unusual high-field shift of the resonances.

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Supporting Information Available: Detailed experimental procedures, compound characterization data, and crystallographic data for *meso*-**3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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