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Homoannular Double Friedel–Crafts Acylation of Phosphametallocenes

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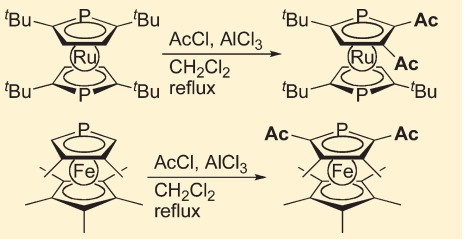
Supporting Information

ABSTRACT: Two reaction modes of homoannular double Friedel–Crafts acylation are realized using polyalkylphosphametallocenes as substrates. The first example is the reaction of tetra(*tert*-butyl)diphospharuthenocene with excess acetyl chloride/aluminum chloride, giving a 2,3-double Friedel–Crafts acylation product with an elimination of one of the *tert*-butyl groups. The other is the 2,5-diacylation of 1′,2′,3,3′,4,4′,5′-Me$_7$-phosphaferrocene using an acyl chloride/aluminum chloride mixture. These reactions provide rare examples of doubly functionalized phosphametallocenes.



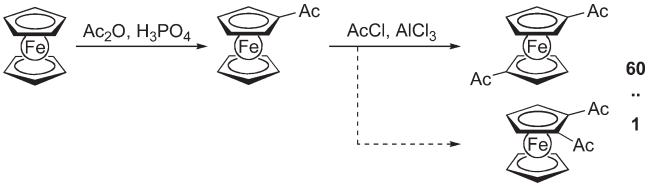
INTRODUCTION

The Friedel–Crafts reaction is an electrophilic aromatic substitution that is a classical protocol for direct functionalization of aromatic compounds. While Friedel–Crafts alkylation tends to afford polyalkyl products, the corresponding acylation typically gives monoacylated products predominantly,[1] because the initial products have an electron-withdrawing acyl substituent that deactivates the aromatic ring toward further electrophilic substitutions. For this reason, double acylation on the same aromatic ring is rather rare and can be achieved only for specific aromatic substrates,[2] while double Friedel–Crafts acylation at two remote reaction sites within a single molecule takes place.

Meanwhile, metallocenes and half-metallocenes exhibit aromaticity, as with benzene derivatives, since the η^5-cyclopentadienyl ligands possess six π-electrons. Indeed, some (η^5-cyclopentadienyl)-metal complexes, such as ferrocenes and cymantrenes, are known to be excellent substrates for Friedel–Crafts acylation reactions.[3] The parent ferrocene (η^5-C_5H_5)$_2$Fe is much more reactive than benzene toward Friedel–Crafts acylations, and double acylation of ferrocene is operational. However, the two acyl substituents are usually distributed between the two η^5-cyclopentadienides, leading to 1,1′-diacylferrocene as a major product. The two η^5-cyclopentadienides in a ferrocene molecule are electronically communicating with each other through the central Fe(II) cation; that is, after the introduction of the first acyl group onto the ferrocene core, the remaining unsubstituted Cp ligand is deactivated by the acyl group in the other cyclopentadienyl moiety. However, the second η^5-Cp is still capable of being acylated under the more rigorous conditions to give a heteroannular double-acylation product in good yield with >98% selectivity (Scheme 1).[3b]

Phosphaferrocenes undergo electrophilic acylation under the standard Friedel–Crafts conditions in a similar manner.[4,5] In the parent monophosphaferrocene, the α-position to the phosphorus atom is preferentially acylated. While the β-acylphospholyl compound is obtained as a minor product, acylation on the η^5-C_5H_5 ring is not detected (Scheme 2).[5a]

Scheme 1. Friedel-Crafts Acetylation of Ferrocene[3b]



Scheme 2. Friedel–Crafts Acetylation of Phosphaferrocene[5a]

On the other hand, we recently demonstrated that certain phosphametallocenes behaved in completely different ways under forcing Friedel–Crafts acylation conditions.[6] Reactions between Cy$_4$-diphospharuthenocene or the corresponding osmocene analogue and an acyl electrophile (AcCl/AlCl$_3$) produce a μ-vinylidene species, where a vinylidene moiety bridges the Ru/Os center and the phosphorus atom. This reaction proceeds via an initial attack of the acetyl electrophile to the metal center followed by activation of the acyl C=O double bond. The homologous Cy$_4$-diphosphaferrocene affords a conventional

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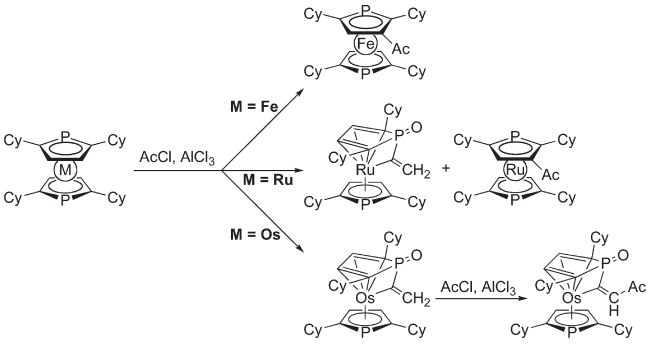
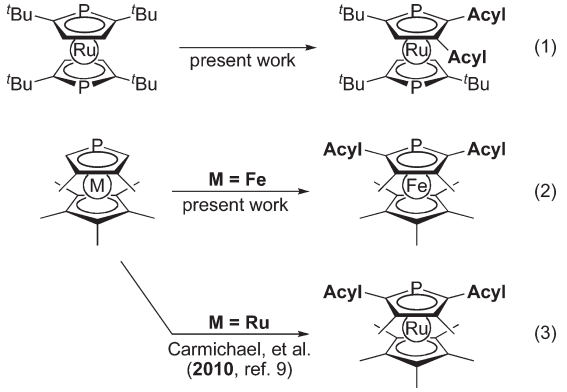
Friedel–Crafts acetylation product under identical conditions (Scheme 3).

Scheme 3. Reactions of Cy_4-Diphosphametallocenes of Group 8 Triad[6]



In this article, we would like to report two examples of homoannular double Friedel–Crafts acylations on phosphametallocene platforms. The first example is the dealkylative 2,3-diacylation of 2,2′,5,5′-^{t}Bu$_4$-diphospharuthenocene (eq 1), and the other one is the 2,5-diacylation of 1′,2′,3,3′,4,4′,5′-Me$_7$-phosphaferrocene (eq 2). These reactions provide rare examples of doubly functionalized phosphametallocenes.[7,8] It should be mentioned that the homoannular double Friedel–Crafts acylation of the Me$_7$-phospharuthenocene, which is closely related to the second reaction in this article, was recently reported by Carmichael, Piechaczyk, and their co-workers independently (eq 3).[9]



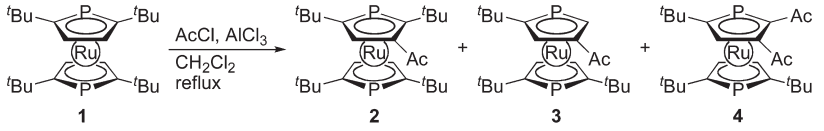
RESULTS AND DISCUSSION

Dealkylative 2,3-Double Acetylation of (η^5-PC$_4$H$_2$-2,5-^{t}Bu$_2$)$_2$Ru. Treatment of 2,2′,5,5′-^{t}Bu$_4$-1,1′-diphospharuthenocene (**1**: prepared from $[RuCl_2(cod)]_n$ and 2,5-^{t}Bu$_2$-1-Ph-phosphole)[10] with an acetyl electrophile (2 equiv to **1**), which was generated from equimolar CH_3COCl and $AlCl_3$, in refluxing dichloromethane for 48 h gave a mixture of three acetylated products, **2**–**4**, in 6%, 21%, and 18% yield, respectively, accompanied by 45% recovery of **1** (Scheme 4). The compounds are separable by conventional silica gel column chromatography. Although **2** and **3** are not crystalline, their structures are unambiguously determined by the combination of the ^{1}H, ^{13}C, and ^{31}P NMR analyses, elemental analyses, and HRMS measurements as 3-acetyl-2,2′,5,5′-^{t}Bu$_4$-diphospharuthenocene (**2**) and 4-acetyl-2,2′,5′-^{t}Bu$_3$-diphospharuthenocene (**3**), respectively. Compound **2** is C_1-symmetric and shows four ^{t}Bu singlets, a CH_3-CO singlet, and three phospholyl resonances in the ^{1}H NMR spectrum. The phospholyl C*H* signals are coupled with the phosphorus nucleus through small coupling constants (J_{PH} < 4.5 Hz), which are typical values for β-CH's in phosphametallocenes. Compound **3** shows three ^{t}Bu singlets, a CH_3-CO singlet, and four phospholyl resonances in the ^{1}H NMR spectrum. While three of the four phospholyl C*H* signals at δ 5.15, 5.33, and 5.78 (in $CDCl_3$) are assigned to β-phospholyl hydrogens with the smaller P–H coupling constants (J_{PH} = 4.6–5.4 Hz), the remaining phospholyl CH resonance at δ 4.78 displays a larger P–H coupling of J_{PH} = 35.0 Hz, which is characteristic of an α-phospholyl hydrogen. A positive NOE correlation between the α-phospholyl CH and the acetyl signals implies the structure shown in Scheme 4 for compound **3**, excluding the isomeric 3-acetyl-2,2′,5′-^{t}Bu$_3$-diphospharuthenocene.

The ^{1}H and ^{13}C NMR spectra of **4** suggest that the compound possesses three ^{t}Bu groups, two acetyl groups, and three β-phospholyl hydrogens; however, the distribution of these substituents in the diphospharuthenocene core could not be identified by the NMR measurements. Prismatic crystals of **4** were grown from EtOAc/EtOH. Their analysis by single-crystal X-ray diffraction confirmed that **4** is the homoannular diacetylation species with an intact diphospharuthenocene core (Figure 1). One of the two η^5-phospholyl ligands remains intact with the two α-^{t}Bu substituents. In the other η^5-phospholyl, the two acetyl groups are located on the adjacent α- and β-carbons, C(5) and C(6), while a ^{t}Bu substituent is placed at the α'-position (C(8)). The two η^5-phospholyls adopt an eclipsed conformation, and the five substituents are located in a way to minimize the steric repulsions between them. The dihedral angle between the two η^5-phospholyl ligands is 4.90°. Overall, the structural characteristics of **4** are similar to those of 2,2′,5,5′-Cy_4-diphospharuthenocene.[10]

A plausible reaction pathway from **1** to **4** is shown in Scheme 5. The first step is the acetylation of **1** at a β-position on the phospholyl rings to give **2**. Since all the α-positions in **1** are blocked by the ^{t}Bu groups, the acetylation is forced to happen at the β-position.[6a] The second step is the de-*tert*-butylation of **2** under Friedel–Crafts conditions. The ^{t}Bu group adjacent to the acetyl substituent is selectively removed from **2** to give **3**, in which a nucleophilic α-phospholyl CH is now available for further electrophilic substitution. Finally, the unprotected α-CH

Scheme 4. Friedel–Crafts Acetylation of Diphospharuthenocene 1



AcCl/AlCl$_3$	**1** (recovery)	**2**	**3**	**4**
2 equiv	45%	6%	21%	18%
4 equiv	40%	8%	16%	23%

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position in **3** is acetylated to furnish the homoannular double acylation product **4**. The scenario that includes initial de-*tert*-butylation of **1** is also considered as an alternative route to **4**. In this case, the primary product **5** possesses a more nucleophilic α-CH. Thus, the subsequent Friedel−Crafts acetylation should produce **6** instead of **3**. The second acetylation of **6** leading to **4** is highly unlikely, because the β-phospholyl CH's are inherently less nucleophilic[5] and the acetylated phospholyl is deactivated from further electrophilic substitution. Indeed, the intermediates **5** and **6** were not detected in the reaction mixture, while **2** and **3** were isolated together with **4** (*vide supra*). An independent experiment also supports the pathway via **2** and **3**: a reaction of the isolated **3** with an equimolar mixture of $AcCl/AlCl_3$ (4 equiv with respect to **3**) in refluxing dichloromethane in 48 h gave **4** in 67% yield.

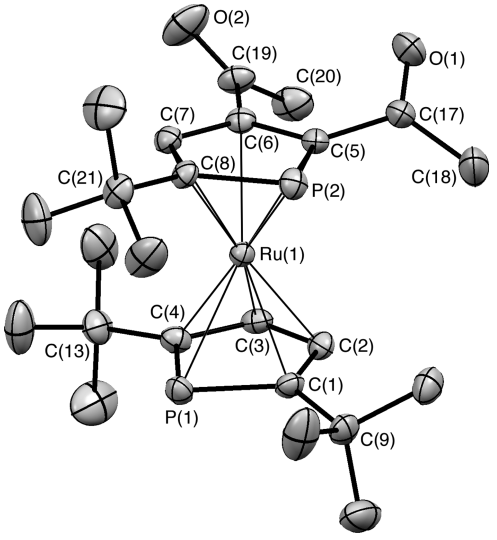


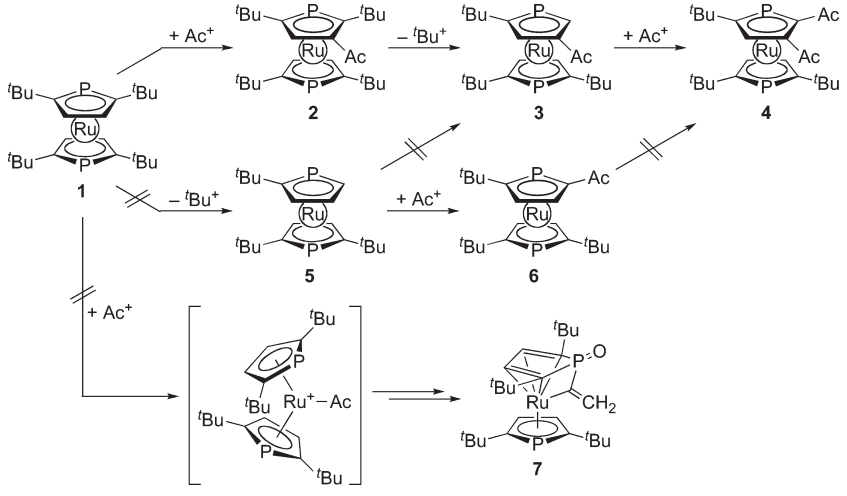
Figure 1. ORTEP drawing of **4** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−P(1) = 2.413(2), Ru(1)−P(2) = 2.404(2), P(1)−C(1) = 1.768(7), P(1)−C(4) = 1.751(6), P(2)−C(5) = 1.793(6), P(2)−C(8) = 1.792(7), Ru(1)−phospholyl$_{P(1)C(1-4)}$ = 1.834, Ru(1)−phospholyl$_{P(2)C(5-8)}$ = 1.823; C(1)−P(1)−C(4) = 90.4(3), C(5)−P(2)−C(8) = 88.3(3).

The yield of **4** could not be greatly improved even with a large excess of acetyl electrophile (4 equiv to **1**; see Scheme 4). After separation of **4** from the reaction mixture by column chromatography, the residual mixture containing **1**, **2**, and **3** was treated with $AcCl/AlCl_3$ (2 equiv) in refluxing dichloromethane to give an additional 20−23% yield of **4**. With these three successive separation/acetylation procedure, the diacetyl compound **4** was obtained in 47−52% combined yields.

In the homoannular double acylation of **1**, the ^{t}Bu substituents function as a protecting group to prevent the more reactive α-phospholyl positions from the initial electrophilic attack.[11] After the introduction of the first acetyl group to **1**, the dealkylation uncovers the "protected" α-CH. Although the unmasked α-CH is deactivated by the adjacent acetyl group, it is still reactive enough for the second acetylation. The key to success in the present dealkylative double acylation is the use of *tert*-alkyl groups on a diphospharuthenocene. In the Friedel−Crafts acetylation of 2,2′,5,5′-Cy_4-diphospharuthenocene, which possesses *sec*-alkyl (cyclohexyl) substituents, an analogous dealkylation did not proceed under the same conditions. Thus, a double acetylation product was not detected, although the Cy_4-Ac-diphospharuthenocene was obtained.[6a] With an α-silyl substituent in a phospharuthenocene core, desilylative acylation takes place to give an α-acylphospharuthenocene.[12]

It should be noted that the reaction of **1** with $AcCl/AlCl_3$ did not afford the μ-vinylidene species **7** (Scheme 5, bottom). This provides a clear contrast to the reaction of the Cy_4-diphospharuthenocene analogue, which gave the μ-vinylidene complex as a major product under identical conditions by way of an initial electrophilic attack of Ac^+ to the ruthenium center (Scheme 3, middle).[6a] The ^{t}Bu groups in **1** are much bulkier than cyclohexyl groups, which might hinder the electrophilic attack to the ruthenium center. Indeed, the local steric impact of the ^{t}Bu groups in **1** is much larger than that of the Cy substituents in $(\eta^5$-2,5-Cy_2-phospholyl$)_2$Ru. The ^{1}H and ^{13}C NMR spectra of $(\eta^5$-2,5-Cy_2-phospholyl$)_2$Ru at 23 °C show only one set of resonances for the Cy and the β-CH groups, indicating rapid rotation of the phospholyl rings about the phospholyl−Ru−phospholyl axis.[10] On the other hand, the NMR spectrum of **1** displays the two ^{t}Bu resonances and the two β-CH signals at 23 °C due to the interlocked C_2-symmetric conformation as shown in Figure 2.[13,14]

Scheme 5. Plausible Reaction Pathways for Reactions of 1 with Acetyl Electrophile



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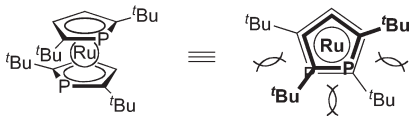
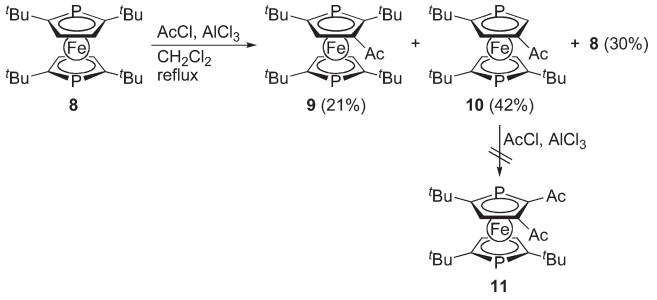


Figure 2. Interlocked conformation of the diphospharuthenocene **1**.

Scheme 6. Friedel–Crafts Acetylation of Diphosphaferrocene 8



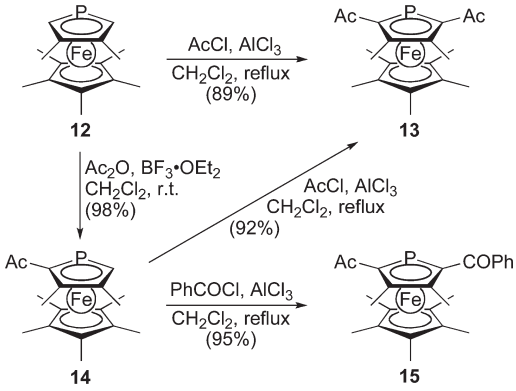
The present dealkylative double acetylation is characteristic to the phospharuthenocene species. Treatment of 2,2′,5,5′-^{t}Bu$_4$-diphosphaferrocene (**8**), which is isostructural to **1**, with AcCl/$AlCl_3$ under conditions identical with Scheme 4 produced a pair of monoacetyl diphosphaferrocenes, **9** (21%) and **10** (42%), but the diacetyl compound **11** was not obtained (Scheme 6). A reaction of the isolated **10** with AcCl/$AlCl_3$ led to partial decomposition of **10**, and **11** could not be obtained.

The diacetyl compound **4** is a rare example of phosphametallocenes having two functional groups in a single η^5-phospholide. Although several homoannular doubly functionalized phosphametallocenes have been reported in recent years,[7−9] all of them possess the functional groups at the 2- and 5-positions of the η^5-phospholide. To the best of our knowledge, compound **4** is the first example of a 2,3-difunctionalized phosphametallocene.

2,5-Double Acylation of (η^5-PC_4H_2-3,4-Me_2)FeCp*. While the homoannular 2,3-double acylation of the diphosphaferrocene **8** was unsuccessful, a different type of homoannular double acylation could be achieved in 1′,2′,3,3′,4,4′,5′-Me_7-phosphaferrocene[15] (**12**). This reaction is analogous to the homoannular double Friedel–Crafts acylation of the isostructural phospharuthenocene, which was reported recently.[9]

Treatment of **12** with an equimolar mixture of AcCl/$AlCl_3$ (3 equiv to **12**) in refluxing dichloromethane for 24 h gave the 2,5-diacetyl-1′,2′,3,3′,4,4′,5′-Me_7-phosphaferrocene (**13**) cleanly. The diacetyl compound was easily purified by silica gel chromatography, and a deep-red crystalline compound was isolated in 89% yield (Scheme 7). Friedel–Crafts acylation of **12** was reported previously.[16] The use of acylation reagents, such as Ac_2O/TfOH or $(CF_3CO)_2O/BF_3\cdot OEt_2$, resulted in the selective monoacylation of **12**, but formation of the corresponding diacylated compounds was not described. We also confirmed that the reaction of **12** with $Ac_2O/BF_3\cdot OEt_2$ afforded the monoacetylphosphaferrocene **14** exclusively in a nearly quantitative yield (98%). It was found that a choice of acylation reagents was important in the second acylation of **14**. A reaction of the isolated **14** with an equimolar mixture of AcCl/$AlCl_3$ (1.5 equiv to **14**) in refluxing dichloromethane in 20 h gave **13** in 92% yield. Similarly, **14** reacted with PhCOCl/$AlCl_3$ (1.5 equiv to **14**) to give **15** in 95% yield. By the stepwise acylation of **12** into **14** and then into **15**, introduction of two different acyl substituents into a single η^5-phospholyl ligand was achieved with complete chemoselectivity.

Scheme 7. Homoannular Double Friedel–Crafts Acylation of Phosphaferrocene 12



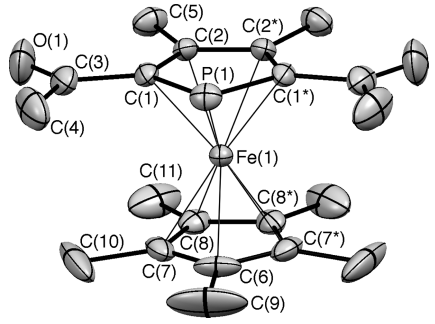


Figure 3. ORTEP drawing of **13** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)–P(1) = 2.269(2), Fe(1)–C(1) = 2.076(4), Fe(1)–C(2) = 2.083(3), Fe(1)–C(6) = 2.052(6), Fe(1)–C(7) = 2.059(5), Fe(1)–C(8) = 2.064(4), P(1)–C(1) = 1.784(4), Fe(1)–phospholyl =1.649, Fe(1)–Cp* = 1.677; C(1)–P(1)–C(1*) = 88.6(2), P(1)–C(1)–C(2) = 113.4(3), C(1)–C(2)–C(2*) = 112.3(3).

Prismatic crystals of **13** were grown from EtOH and analyzed by single-crystal X-ray diffraction (Figure 3). The complex is symmetric with respect to the P(1)–Fe(1)–C(6)–C(9) plane. No intermolecular interaction is detected in **13**. The phospholyl ligand and Cp* are nearly parallel: the dihedral angle between the two is 2.54°. The distance between the least-squares plane of the phospholyl ligand and Fe(1) is 1.649 Å, which is within the range of those in the other phosphaferrocenes. Orientation of the acetyl group displays conjugation with the phosphaferrocene core with the O–C(3)–C(1)–C(2) torsion angle being 1.77°. Overall structural characteristics of **13** are similar to those of the ruthenium homologue.[9]

For the success of the present double acetylation of **12**, the presence of the Cp* ligand seems to be important. Monophosphaferrocene **16**, which possesses η^5-C_5H_5 in place of η^5-Cp* of **12**, reacted with AcCl/$AlCl_3$ rapidly. However, a major product was the monoacetyl compound **17**,[17] and the corresponding double acetylation species were not obtained even with a large excess of AcCl/$AlCl_3$ (up to 5 equiv to **18**). The failure of the double acetylation of **16** can be ascribed to the relatively low electron density of the acetylphospholide in **17**. It is supposed

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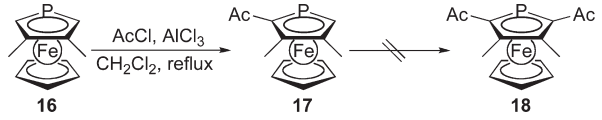
Scheme 8. Friedel−Crafts Acetylation of Phosphaferrocene 16



that the substitution of η^5-Cp by the more electron-donating η^5-Cp* increases the reactivity of the η^5-2-acetyl-3,4-dimethylphospholyl ligand toward electrophilic attack. Analogous activation of an η^5-phospholide by an electron-donating trans ligand was reported in a phosphine-coordinating phosphacymantrene.[18]

CONCLUSIONS

Two examples of homoannular double Friedel−Crafts acylation are realized using the properly polyalkylated phosphametallocene substrates. In the double acetylation of 2,2′,5,5′-^{t}Bu$_4$-diphospharuthenocene, the ^{t}Bu substituents work as a protecting group, preventing the more reactive α-phospholyl positions from the initial electrophilic attack. After the introduction of the first acetyl group at a β-position, the adjacent ^{t}Bu group is removed via Friedel−Crafts retroalkylation. The second acetylation at the unprotected α-position furnishes the homoannular 2,3-double acetylation product. On the other hand, the two α-CH positions in 1′,2′,3,3′,4,4′,5′-Me$_7$-phosphaferrocene are activated by the electron-donating Cp* ligand, and thus 2,5-double acylation can be achieved using acylation reagents derived from acyl chloride/aluminum chloride.

EXPERIMENTAL SECTION

General Procedures. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. $[RuCl_2(\eta^4\text{-}C_8H_{12})]_n$,[19] 1-Ph-2,5-^{t}Bu$_2$-phosphole,[20] and 1′,2′,3,3′,4,4′,5′-Me$_7$-phosphaferrocene (**12**)[15] were prepared as reported. All the other chemicals were obtained from commercial sources and used without additional purification.

2,2′,5,5′-Tetra(*tert*-butyl)-1,1′-diphospharuthenocene (1). Preparation of this compound was achieved according to the synthetic method reported for analogous compounds.[10] A THF (20 mL) solution of 1-Ph-2,5-^{t}Bu$_2$-phosphole (1.50 g, 5.50 mmol) was treated with lithium metal (320 mg, 46.1 mmol), and the mixture was stirred overnight at rt. The mixture was filtered through a plug of glass wool, and to the filtrate was added anhydrous $AlCl_3$ (250 mg, 1.87 mmol) at 0 °C.[21] After stirring for 30 min at room temperature, the resulting mixture was transferred onto a slurry of $[RuCl_2(\eta^4\text{-}C_8H_{12})]_n$ (771 mg, 2.75 mmol/Ru) in THF (3 mL), and the mixture was refluxed for 48 h. After cooling the mixture, all the volatiles were removed under reduced pressure. The residue was extracted with hot hexane. The crude product was purified by silica gel chromatography (elution with hexane) under a nitrogen atmosphere to give the title compound in pure form. Yield: 987 mg (2.01 mmol, 73%). ^{1}H NMR (C_6D_6): δ 1.12 (s, 18H), 1.36 (s, 18H), 4.95 (dd, J_{PH} = 4.4 Hz, J_{HH} = 2.9 Hz, 2H), 4.99 (dd, J_{PH} = 4.5 Hz, J_{HH} = 2.9 Hz, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 33.1 (d, J_{PC} = 6.2 Hz), 33.7 (d, J_{PC} = 13.2 Hz), 33.9 (m), 79.0 (d, J_{PC} = 4.8 Hz), 79.8 (d, J_{PC} = 5.2 Hz), 119.5 (d, J_{PC} = 67.8 Hz), 124.4 (d, J_{PC} = 67.8 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −50.2. Anal. Calcd for $C_{24}H_{40}P_2Ru$: C, 58.64; H, 8.20. Found: C, 58.32; H, 8.19. EI-HRMS calcd for $C_{24}H_{40}P_2Ru$: 492.1649. Found: 492.1640.

Friedel−Crafts Acetylation of Diphospharuthenocene 1. To a suspension of $AlCl_3$ (90 mg, 675 μmol) in dichloromethane (4 mL) was added acetyl chloride (55 mg, 700 μmol) at room temperature. The mixture was stirred at this temperature for 1 h, then added to a dichloromethane (4 mL) solution of **1** (166 mg, 336 μmol). The mixture was refluxed for 48 h. The reaction was quenched by addition of water (0.5 mL), then evaporated to dryness under vacuum. The residue was extracted with dichloromethane, and the extract was further purified by silica gel chromatography. The three acetylation products **2**−**4** were obtained in 6%, 21%, and 18% yield, respectively, together with the recovered **1** (45%). The characterization data for **2**−**4** are given below.

3-Acetyl-2,2′,5,5′-tetra(*tert*-butyl)-1,1′-diphospharuthenocene (2). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H), 1.23 (s, 9H), 1.24 (s, 9H), 1.27 (s, 9H), 2.46 (s, 3H), 5.09 (dd, J_{PH} = 4.5 Hz, J_{HH} = 2.9 Hz, 1H), 5.22 (d, J_{PH} = 4.0 Hz, 1H), 5.38 (br, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −50.1, −34.4. EI-HRMS calcd for $C_{26}H_{42}OP_2Ru$: 534.1754. Found: 534.1753. The ^{13}C NMR spectrum of this compound could not be obtained due to the low yield of the compound.

3-Acetyl-2′,5,5′-tri(*tert*-butyl)-1,1′-diphospharuthenocene (3). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H), 1.13 (s, 9H), 1.19 (s, 9H), 2.46 (s, 3H), 4.78 (dd, J_{PH} = 35.0 Hz, J_{HH} = 0.7 Hz, 1H), 5.15 (dd, J_{PH} = 4.7 Hz, J_{HH} = 3.0 Hz, 1H), 5.33 (dd, J_{PH} = 4.6 Hz, J_{HH} = 3.0 Hz,1H), 5.78 (dd, J_{PH} = 5.4 Hz, J_{HH} = 0.7 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.1 (d, J_{PC} = 3.5 Hz), 32.8−34.1 (m, ^{t}Bu- × 3), 79.6 (d, J_{PC} = 64.7 Hz), 80.6 (d, J_{PC} = 4.3 Hz), 81.3 (d, J_{PC} = 5.7 Hz), 81.7 (d, J_{PC} = 4.4 Hz), 94.8 (d, J_{PC} = 5.7 Hz), 122.4 (d, J_{PC} = 67.3 Hz), 124.3 (d, J_{PC} = 67.0 Hz), 126.7 (d, J_{PC} = 65.6 Hz), 200.8 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −42.9, −32.0. EI-HRMS calcd for $C_{22}H_{34}OP_2Ru$: 478.1128. Found: 478.1126.

2,3-Diacetyl-2′,5,5′-tri(*tert*-butyl)-1,1′-diphospharuthenocene (4). ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 9H), 1.26 (s, 9H), 1.29 (s, 9H), 2.30 (d, J_{PH} = 1.3 Hz, 3H), 2.38 (s, 3H), 5.24 (dd, J_{PH} = 4.6 Hz, J_{HH} = 3.1 Hz, 1H), 5.27 (dd, J_{PH} = 4.6 Hz, J_{HH} = 3.1 Hz, 1H), 5.54 (d, J_{PH} = 5.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.8 (s), 31.5 (d, J_{PC} = 4.4 Hz), 33.2−33.9 (m, ^{t}Bu- × 3), 82.6 (d, J_{PC} = 6.1 Hz), 83.2 (d, J_{PC} = 4.8 Hz), 85.0 (d, J_{PC} = 4.5 Hz), 94.5 (d, J_{PC} = 3.9 Hz), 100.2 (d, J_{PC} = 70.4 Hz), 124.3 (d, J_{PC} = 68.2 Hz), 127.07 (d, J_{PC} = 67.3 Hz), 127.13 (d, J_{PC} = 67.8 Hz), 201.3 (s), 202.2 (d, J_{PC} = 19.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −45.2, −15.8. Anal. Calcd for $C_{24}H_{36}OP_2Ru$: C, 55.48; H, 6.98. Found: C, 55.37; H, 7.01. EI-HRMS calcd for $C_{24}H_{36}OP_2Ru$: 520.1234. Found: 520.1236.

2,2′,5,5′-Tetra(*tert*-butyl)-1,1′-diphosphaferrocene (8). Preparation of this compound was achieved according to the synthetic method reported for an analogous compound.[21] A THF (15 mL) solution of 1-Ph-2,5-^{t}Bu$_2$-phosphole (637 mg, 2.34 mmol) was treated with lithium metal (100 mg, 14.5 mmol), and the mixture was stirred at rt overnight. The mixture was filtered through a glass filter, and to the filtrate was added anhydrous $AlCl_3$ (104 mg, 0.780 mmol) at 0 °C. After stirring for 30 min at room temperature, the THF solution was transferred onto a slurry of anhydrous $FeCl_2$ (148 mg, 1.17 mmol) in THF (10 mL) by means of cannula. After stirring the mixture for 12 h at 60 °C, all the volatiles were removed under reduced pressure. The residue was extracted with hot hexane. The crude product was purified by silica gel chromatography (elution with hexane) under a nitrogen atmosphere to give the title compound in pure form. Yield: 332 mg (0.744 mmol, 64%). ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 18H), 1.32 (s, 18H), 4.88 (dd, J_{PH} = 4.7 Hz, J_{HH} = 2.9 Hz, 2H), 4.94 (dd, J_{PH} = 4.5 Hz, J_{HH} = 2.9 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 33.0 (d, J_{PC} = 6.5 Hz), 33.8 (d, J_{PC} = 14.4 Hz), 33.9 (m), 77.2 (d, J_{PC} = 5.2 Hz), 77.7 (d, J_{PC} = 4.8 Hz), 115.9 (d, J_{PC} = 64.4 Hz), 121.3 (d, J_{PC} = 64.3 Hz). ^{31}P{^{1}H} NMR

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($CDCl_3$): δ −73.7. Anal. Calcd for $C_{24}H_{40}P_2Fe$: C, 64.58; H, 9.03. Found: C, 64.25; H, 8.92. EI-HRMS calcd for $C_{24}H_{40}FeP_2$: 446.1955. Found: 446.1953.

Friedel−Crafts Acetylation of Diphosphaferrocene 8. This reaction was conducted in the same way with the acetylation of **1** as mentioned above. The two acetylation products **9** and **10** were obtained in 21% and 42% yield, respectively, together with the recovered **8** (30%). The characterization data for **9** and **10** are given below.

3-Acetyl-2,2′,5,5′-tetra(*tert*-butyl)-1,1′-diphosphaferrocene (9). ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 9H), 1.28 (s, 9H), 1.32 (s, 9H), 1.37 (s, 9H) 2.43 (s, 3H) 4.88 (d, J_{PH} = 4.2 Hz, 1H), 5.14 (d, J_{PH} = 3.6 Hz, 1H), 5.28 (br, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −73.4, −55.9. EI-HRMS calcd for $C_{22}H_{34}FeOP_2$: 432.1434. Found: 432.1426. The ^{13}C NMR spectrum of this compound could not be obtained due to the low yield of the compound.

3-Acetyl-2′,5,5′-tri(*tert*-butyl)-1,1′-diphosphaferrocene (10). ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 18H), 1.30 (s, 9H), 2.59 (s, 3H), 4.62 (d, J_{PH} = 34.6 Hz, 1H), 4.84 (dd, J_{PH} = 4.4 Hz, J_{HH} = 3.1 Hz, 1H), 5.23 (br, 1H), 5.47 (d, J_{PH} = 4.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.0 (d, J_{PC} = 3.5 Hz), 33.1 (d, J_{PC} = 4.8 Hz), 33.4 (d, J_{PC} = 4.8 Hz), 33.5 (d, J_{PC} = 7.0 Hz), 33.7 (d, J_{PC} = 13.1 Hz), 34.0 (d, J_{PC} = 14.5 Hz), 34.1 (d, J_{PC} = 13.6 Hz), 78.0 (br), 78.5 (d, J_{PC} = 5.7 Hz), 79.4 (br), 80.4 (d, J_{PC} = 62.1 Hz), 91.7 (d, J_{PC} = 4.9 Hz), 120.6 (d, J_{PC} = 64.3 Hz), 121.9 (d, J_{PC} = 64.3 Hz, 2C), 202.9 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −65.5, −47.6. EI-HRMS calcd for $C_{22}H_{34}FeOP_2$: 432.1434. Found: 432.1426.

Friedel−Crafts Acetylation of Phosphaferrocene 12. To a suspension of $AlCl_3$ (110 mg, 825 μmol) in dichloromethane (2 mL) was added acetyl chloride (65 mg, 828 μmol) at room temperature. The mixture was stirred at this temperature for 1 h, then added to a dichloromethane (4 mL) solution of **1** (100 mg, 331 μmol). The mixture was refluxed for 12 h. The reaction was quenched by addition of water (0.5 mL), then evaporated to dryness under vacuum. The residue was extracted with dichloromethane, and the extract was further purified by silica gel chromatography to give **13** in pure form (114 mg, 89%). The monoacetylation of **12** could be realized in the same way using Ac_2O/$BF_3\cdot OEt_2$ in place of AcCl/$AlCl_3$.[16] The acetylation/benzoylation of **14** was conducted in a similar manner. The characterization data for **13**−**15** are given below.

2,5-Diacetyl-1′,2′,3,3′,4,4′,5′-heptamethyl-1-phosphaferrocene (13). ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 15H), 2.27 (s, 6H), 2.32 (d, J_{PH} = 3.3 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.3 (s), 12.3 (s), 32.0 (d, J_{PC} = 11.5 Hz), 84.6 (s), 90.4 (d, J_{PC} = 58.0 Hz), 99.5 (d, J_{PC} = 8.7 Hz), 203.7 (d, J_{PC} = 24.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −25.1. Anal. Calcd for $C_{20}H_{27}FeO_2P$: C, 62.19; H, 7.05. Found: C, 61.98; H, 7.06. EI-HRMS calcd for $C_{20}H_{27}FeO_2P$: 386.1098. Found: 386.1097.

2-Acetyl-1′,2′,3,3′,4,4′,5′-heptamethyl-1-phosphaferrocene (14) (ref 16). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 15H), 2.03 (s, 3H), 2.23 (d, J_{PH} = 2.9 Hz, 6H), 3.65 (d, J_{PH} = 36.4 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.2 (s), 12.5 (s), 14.3 (s), 31.6 (d, J_{PC} = 11.5 Hz), 83.7 (s), 85.0 (d, J_{PC} = 55.6 Hz), 89.3 (d, J_{PC} = 60.4 Hz), 92.9 (d, J_{PC} = 4.8 Hz), 100.2 (d, J_{PC} = 7.7 Hz), 205.2 (d, J_{PC} = 23.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −44.6. Anal. Calcd for $C_{18}H_{25}FeOP$: C, 62.81; H, 7.32. Found: C, 62.79; H, 7.44. EI-HRMS calcd for $C_{18}H_{25}FeOP$: 344.0992. Found: 344.0992.

2-Acetyl-5-benzoyl-1′,2′,3,3′,4,4′,5′-heptamethyl-1-phosphaferrocene (15). ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 15H), 2.03 (s, 3H), 2.31 (br, 6H), 7.40 (t, J = 7.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.6 (s), 12.8 (d, J_{PC} = 12.3 Hz, 2C), 32.0 (d, J_{PC} = 11.8 Hz), 85.1 (s), 90.7 (d, J_{PC} = 60.4 Hz), 92.6 (d, J_{PC} = 59.9 Hz), 97.3 (d, J_{PC} = 5.3 Hz), 101.2 (d, J_{PC} = 4.8 Hz), 127.9 (s), 129.2 (d, J_{PC} = 6.6 Hz), 131.9 (s), 141.8 (s), 200.4 (d, J_{PC} = 21.0 Hz), 204.3 (d, J_{PC} = 24.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −23.4. Anal. Calcd for $C_{25}H_{29}FeO_2P$: C, 66.98; H, 6.52. Found: C, 66.76; H, 6.52. EI-HRMS calcd for $C_{25}H_{29}FeO_2P$: 448.1255. Found: 448.1252.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H, ^{13}C, and ^{31}P NMR spectra for all the new compounds and crystallographic data for **4** and **13** (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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