Unprecedented Formation of μ-Vinylidene Complexes from Phospharuthenocene and Acyl Chloride via Activation of the C═O Double Bond

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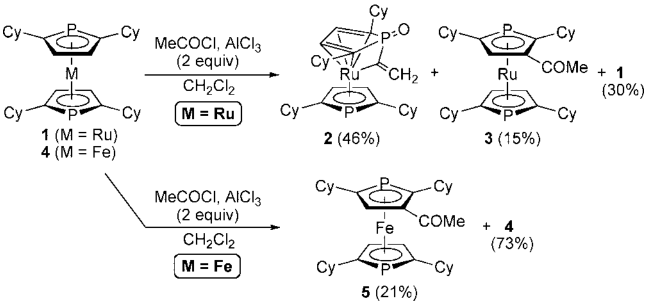
Summary: A novel reaction mode of phosphametallocenes was discovered. The phospharuthenocenes with cyclohexyl substituents at the α*-positions of the η^5-phospholide(s) reacted with acyl electrophiles by an initial electrophilic attack to the ruthenium to produce the μ-alkenylidene species with activation of the acyl C═O double bond and elimination of an* α*-hydrogen.*

Recently, phosphametallocenes have attracted considerable attention in organometallic chemistry.[1] Because a phosphorus atom in an η^5-phospholide possesses a lone pair on it, phosphametallocenes are Lewis basic. Thus, they have been utilized as nucleophilic catalysts[2] or a new class of P-donor ligands with unique electronic/steric properties.[3,4] Although many interesting applications of these compounds have been reported so far, studies on their reactivity are still relatively limited. In general, phosphametallocenes are "aromatic", as seen in (η^5-cyclopentadienyl)metal complexes, and serve as good substrates for electrophilic substitution reactions,[5] such as Friedel–Crafts acylation or Vilsmier formylation. In this report, we would like to describe an unprecedented reaction of phosphametallocene species. During our studies on reactivity of phospharuthenocenes,[4l,6,7] it was found that a reaction between a phospharuthenocene and an acyl electrophile produced a novel μ-vinylidene species, where the vinylidene moiety bridged the Ru center and the phosphorus atom, via activation of the acyl C═O double bond.

Scheme 1. Reactions of Diphosphametallocenes with Acetyl Electrophile



Treatment of the 1,1′-diphospharuthenocene **1** with 2 equiv of an acetyl electrophile, which was generated from CH_3COCl and $AlCl_3$, in refluxing dichloromethane for 24 h gave the pale yellow crystalline product **2** in 46% yield together with recovered **1** (30%) and a small amount of the Friedel–Crafts acetylation product **3** in 15% yield (Scheme 1, top). The products **2** and **3** were air- and moisture-stable and easily purified by silica gel column chromatography. The product **2** showed two signals of equal intensity at δ –26.6 and –21.2 in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum of **2** showed four doublets in the olefinic/phospholyl region [δ 5.40 (d, J_{PH} = 3.9 Hz, 2H), 5.55 (d, J_{PH} = 17.0 Hz, 2H), 6.02 (d, J_{PH} = 64.1 Hz, 1H), 6.83 (d, J_{PH} = 35.5 Hz, 1H)] with a 2:2:1:1 integration ratio. In the phosphorus-decoupled ^{1}H NMR spectrum, these four signals are turned into four singlets. The HRMS

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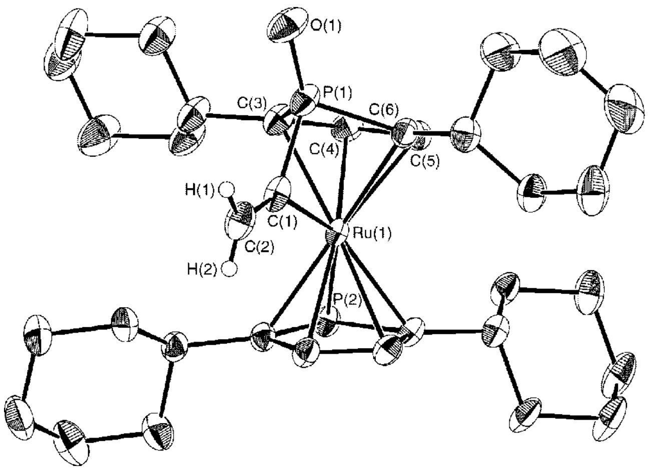
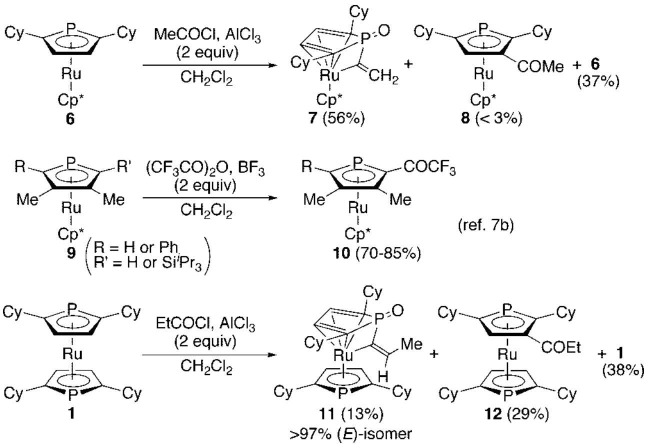
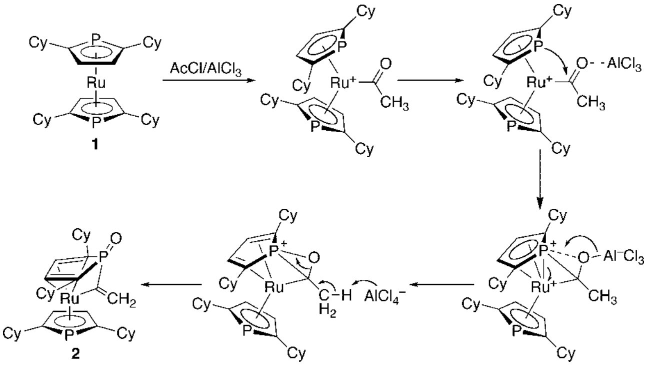


Figure 1. ORTEP drawing of **2** with 30% thermal ellipsoids. All hydrogen atoms except H(1) and H(2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–P(1) (nonbonding) = 2.6360(11), Ru(1)–P(2) = 2.4345(10), Ru(1)–C(1) = 2.152(4), P(1)–C(1) = 1.747(4), P(1)–O(1) = 1.479(3), C(1)–C(2) = 1.315(6); Ru(1)–C(1)–P(1) = 84.42(17), C(3)–P(1)–C(6) = 93.03(19), Ru(1)–C(1)–C(2) = 141.8(3), P(1)–C(1)–C(2) = 133.7(3).

Scheme 2. Scope and Limitation of Preparing *μ*-Alkenylidene Ruthenium Complexes



Scheme 3. Possible Reaction Pathway of Formation of 2 from 1 and AcCl/AlCl₃



analysis suggested a chemical formula of $C_{34}H_{50}OP_2Ru$ for **2**, which was identical to that of the Friedel–Crafts acetylation product **3**.

Recrystallization of **2** from hot ethyl acetate grew prismatic crystals suitable for X-ray structure analysis. The result of the crystallography is shown in Figure 1. One of the two phospholyl ligands in **2** is oxidized at P(1), and the phosphorus shows distorted tetrahedral geometry. There is no bonding interaction between Ru(1) and P(1) with the Ru(1)−P(1) distance of 2.6360(11) Å. The P(1)C(3)C(4)C(5)C(6) core coordinates to Ru(1) at the η^4-diene moiety with the envelope-like bent structure; the dihedral angle between the P(1)C(3)C(6) plane and the C(3)C(4)C(5)C(6) plane is 16.33°, and P(1) lies out of the C(3)C(4)C(5)C(6) plane by 0.360 Å away from Ru(1). The vinylidene moiety C(1)=C(2)H(1)H(2) bridges between Ru(1) and P(1). The C=CH₂ plane is nearly perpendicular to the η^5-phospholyl plane (85.50°), which makes the two hydrogens at the vinylidene terminus inequivalent to each other. The C(1)−C(2) bond length is 1.315(6) Å, that is, within a normal range for typical C=C double bonds. Analogous η^4-coordination of a *P*-oxo-phospholide can be seen in an iron complex reported by Mathey and co-workers.[8]

With free rotation of the η^5-phospholyl ligand around the Ru(1)−phospholyl axis, complex **2** is C_s symmetric in solution, and the ^1H, ^{13}C, and ^{31}P NMR spectra are consistent with the solid-state structure.

The origin of O(1) and the *μ*-vinylidene could be ascribed to acetyl chloride; that is, the phosphorus and the ruthenium atoms in **1** cooperatively activated the C=O double bond in CH_3COCl during the transformation to **2**. The ruthenium center and the cyclohexyl substituents at the α-positions of the phospholides in **1** play important roles for formation of this unique *μ*-vinylidene complex **1**. Treatment of the homologous diphosphaferrocene **4**, which is isostructural to **1**, under the identical conditions afforded the Friedel–Crafts acetylation product **5** in 21% yield (Scheme 1, bottom). Complex **5** was the sole detectable product, and the unreacted **4** was recovered in 73% yield. It was reported that the α-positions of η^5-phospholides in phosphaferrocenes were more reactive than the *β*-positions to electrophilic substitution.[9] The low yield of **5** can be attributed to the cyclohexyl groups, which block the more reactive α-sites in **4**. The unfavorable formation of **3** in the reaction of **1** (Scheme 1, top) could be partly ascribed to the shielding of the α-phospholyl positions in **1** by the four Cy groups in the same way. Indeed, monophospharuthenocenes **9**, which had an α-hydro- or an α-silyl-phospholide, were reported to be active substrates for the Friedel–Crafts acylation with $(CF_3CO)_2O/BF_3 \cdot OEt_2$, and the corresponding α-trifluoroacetylphospharuthenocene species **10** were obtained in good yields (Scheme 2, middle).[7b] On the other hand, the monophospharuthenocene species **6** provided the *μ*-vinylidene species **7** in 56% yield by the reaction with $CH_3COCl/AlCl_3$. The structure of **7** was unambiguously determined by various NMR measurements and X-ray crystallography (see Supporting Information). The formation of the *μ*-vinylidene complex **7** is more selective for **6**: a Friedel–Crafts acetylation product **8** was obtained in less than 3%, and the unreacted **6** was recovered in 37% yield (Scheme 2, top).

The use of propionyl chloride for a reaction with **1** under otherwise identical conditions also afforded the *μ*-alkenylidene species **11** albeit in low yield (13%). Complex **11** was obtained as the *E*-isomer predominantly ($E/Z = >97/<3$ determined by ^1H and ^{31}P NMR; Scheme 2, bottom).

A possible mechanism for the formation of the *μ*-vinylidene complex **2** is shown in Scheme 3. Because all the α-phospholide positions are blocked by the cyclohexyl substituents in **1**, the acetyl electrophile attacks the ruthenium center instead of the

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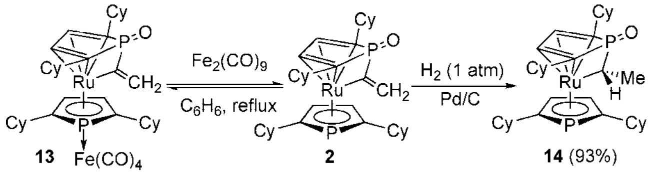
Scheme 4. Reactivity of μ-Vinylidene Complex 2



η^5-phospholide.[10] An intramolecular nucleophilic attack of the phospholide at the acetyl carbonyl carbon, which may be activated by $AlCl_3$, followed by a nucleophilic abstraction of one of the hydrogens in the acetyl moiety by the $AlCl_4^-$ anion affords the μ-vinylidene complex **2**. The final step in Scheme 3 is somewhat similar to the mechanism of the well-known Arbuzov reaction. Apparently, the orientation of the electrophilic (ruthenium) and the nucleophilic (phosphorus) cites in close proximity is an important factor in realizing the reaction.

Complex **2** possesses a lone pair on the phosphorus of the η^5-phospholide. Indeed, treatment of **2** with excess $Fe_2(CO)_9$ in boiling benzene-d_6 showed a partial conversion (ca. 50%) into the $Fe(CO)_4$ adduct **13**.[11] The ^{1}H NMR spectrum of the mixture of **2** and **13** showed broadened resonances due to a slow exchange between the two (Scheme 4). Although **13** was not isolable because of weak coordination of **2** to the iron atom, the downfield shift of one of the two signals in the ^{31}P NMR spectrum clearly indicated the coordination of the $Fe(CO)_4$ fragment in **13**.[12]

The C(1)−C(2) bond length and the H(1)C(2)H(2) angle (114(4)°) suggest olefinic character of the μ-vinylidene moiety in **2**. Indeed, the C=C double bond is smoothly hydrogenated under 1 atm of H_2 in the presence of Pd/C to give the μ-ethylidene complex **14** in 93% isolated yield (Scheme 4). The X-ray crystal structure of **14** is shown in Figure 2. The C(1) atom, which bridges between P(1) and Ru(1), changes its hybridization mode from sp^2 to sp^3 upon hydrogenation of the C(1)=C(2) double bond in **2**. Thus, some distortion can be detected in the local structure around C(1) in **14**. The overall structure of **14** is, however, very similar to that of **2**. Complex **14** is insensitive to both oxygen and moisture and can be handled in air without appreciable decomposition.

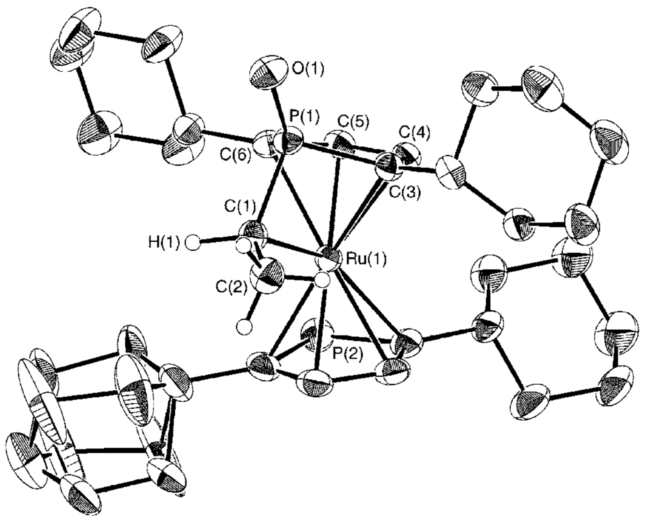


Figure 2. ORTEP drawing of **14** with 30% thermal ellipsoids. All hydrogen atoms except for those on C(1) and C(2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–P(1) (nonbonding) = 2.6103(10), Ru(1)–P(2) = 2.4278(14), Ru(1)–C(1) = 2.229(4), P(1)–C(1) = 1.760(4), P(1)–O(1) = 1.484(3), C(1)–C(2) = 1.510(7); Ru(1)–C(1)–P(1) = 80.83(17), C(3)–P(1)–C(6) = 97.03(19), Ru(1)–C(1)–C(2) = 121.9(3), P(1)–C(1)–C(2) = 119.7(3).

In summary, an unprecedented reaction mode of phosphametallocenes was discovered. The phospharuthenocenes, which have 2,5-dicyclohexylphospholide(s), react with an acetyl or a propionyl electrophile by an initial electrophilic attack at the ruthenium and afford the μ-alkenylidene species with activation of the acyl C=O double bond and elimination of an α-hydrogen.

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Supporting Information Available: Detailed experimental procedures, compound characterization data, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] **2**, ^{31}P NMR (C_6D_6): δ–26.4 and–19.3; **13**, ^{31}P NMR (C_6D_6): δ–16.2 and 38.2.