ORGANOMETALLICS
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Preparation, Structure, and Reactions of Trifluoroacetimidoyl Palladium(II) Complexes

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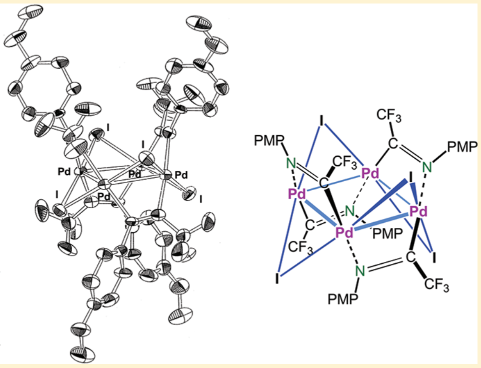
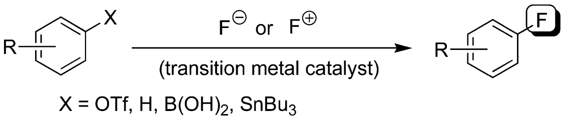
Supporting Information

ABSTRACT: Trifluoroacetimidoyl metal complexes are useful intermediates for the selective synthesis of organofluorine compounds. Herein, we report preparations, structures, and reactions of fluorinated imidoyl palladium complexes. Oxidative addition of trifluoroacetimidoyl halides to $Pd(PPh_3)_4$ afforded quantitatively the imidoyl palladium(II) complexes with phosphine ligands. The reaction of trifluoroacetimidoyl iodides with $Pd_2(dba)_3$ provided the phosphine-free imidoyl palladium complex in high yields. The X-ray crystal structure analysis of the phosphine-free complex $[Pd(\mu\text{-I})\{\mu\text{-C(CF}_3){=}N(PMP)\}]_4$ revealed a cyclic tetranuclear structure containing the imidoyl and iodo bridges. The generation of aminotrifluoromethylcarbene equivalents by protonation or electrophilic alkylation of imidoyl palladium(II) complexes is discussed.



■ INTRODUCTION

The application of transition metals to organic synthesis is one of the most interesting interdisciplinary topics in chemistry. There have been numerous transition-metal-catalyzed reactions that are impossible to be achieved by conventional synthetic methods. In particular, the breadth of organopalladium chemistry has caused revolutionary changes in organic synthesis.[1] Meanwhile, organofluorine compounds have attracted huge interest in various industrial sectors, because incorporation of fluorine atoms or fluoroalkyl groups often furnishes organic molecules with unique properties that cannot be attained using any other element.[2] Thus, enormous numbers of fluorine-containing compounds have been widely used in various fields, including pharmaceuticals, agrochemicals, dyes, liquid crystals, and polymers. Recently, a great deal of attention has been paid to transition-metal-catalyzed reactions to introduce fluorine-containig substituents into organic molecules.[3] For instance, outstanding progress has been made in cross-coupling reactions for installing fluoro and trifluoromethyl groups into aromatic rings (eqs 1 and 2).[4−8] By the use of the Suzuki−Miyaura protocols, trifluoroacetyl and trifluoroacetimidoyl moieties were successfully introduced to aromatic compounds (eqs 3 and 4).[9,10]



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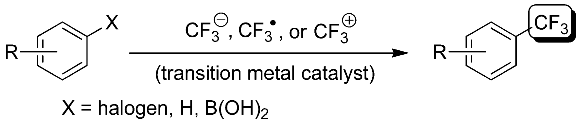

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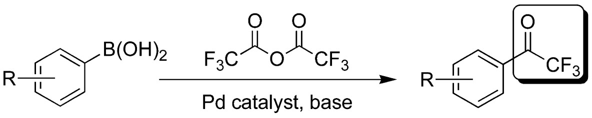

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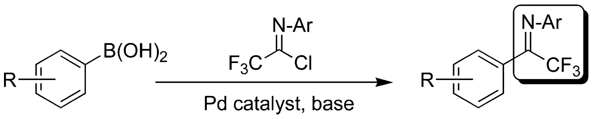


(4)

For synthetic organofluorine chemistry, trifluoroacetimidoyl halides **1** (X = Cl, Br, I) are highly integrated multifunctional building blocks due to their potentially reactive sites, such as halogens, C−N double bonds, CF_3, and *N*-aryl groups.[11] Trifluoroacetimidoyl chlorides are easily prepared in high yield by refluxing a mixture of commercially available trifluoroacetic acid (TFA), amines, PPh_3, and Et_3N in CCl_4 in a one-pot manner.[12] Trifluoroacetimidoyl iodides were obtained by halogen-exchange reaction of the corresponding chlorides with NaI in acetone quantitatively. From the early 1990s, our group started the systematic investigation of palladium-catalyzed transformations by the use of trifluoroacetimidoyl

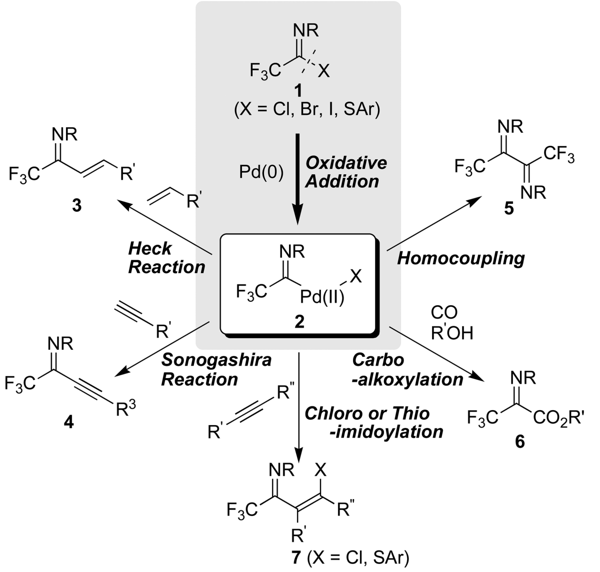
Special Issue: Fluorine in Organometallic Chemistry

Received: October 22, 2011
Published: December 21, 2011

dx.doi.org/10.1021/om201021b | *Organometallics* 2012, 31, 1281−1286

halides **1**. Carbon–carbon bond formations, such as Heck reactions, Sonogashira reactions, and reductive homocoupling of imidoyl halides **1**, were developed (Scheme 1).[13,14]

Scheme 1



Pd-catalyzed carboalkoxylation of imidoyl iodides is a convenient protocol for the synthesis of fluorinated iminoesters **6**,[15] which are useful precursors for asymmetric synthesis of fluorinated amino acids.[16] Besides substitution reactions, trifluoroacetimidoyl halides underwent the addition reactions to unsaturated organic molecules. In 2008, our group demonstrated the first intramolecular chloroimidoylation of carbon–carbon triple bonds.[17] Kuniyasu and Kambe succeeded in the intermolecular thioimidoylation of alkynes to give the adducts **7** in a highly regioselective fashion.[18]

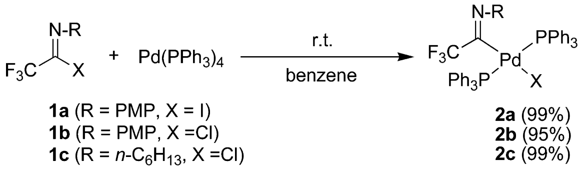
As highlighted so far, the Pd-catalyzed reactions of imidoyl halides **1** are valuable for a wide repertoire of organofluorine compounds. In these transformations, the key intermediates are trifluoroacetimidoyl palladium(II) complexes that are generated by oxidative addition of the C–X bonds of imidoyl halides **1** into Pd(0) species. Toward the evolution of new Pd-catalyzed reactions of imidoyl halides **1**, we were interested in the isolation of trifluoroacetimidoyl palladium complexes **2**. Herein, we report the synthesis and the structural analysis of trifluoroacetimidoyl palladium(II) complexes **2**. Furthermore, we explored the electrophilic transformation of the imidoyl ligands in **2** to give amino(trifluoromethyl)carbene equivalents.

■ RESULTS AND DISCUSSION

Synthesis of Trifluoroacetimidoyl Palladium(II) Phosphine Complexes. To date, there has been considerable interest in the chemistry of metal complexes containing imidoyl ligands because they are equivalents of an acyl metal species. The principal preparative methods for these complexes have involved (1) migratory insertion reaction of isocyanide ligands into carbon–metal σ bonds in alkyl–metal complexes,[19−23] (2) nucleophilic alkylation of isocyanide ligands in metal complexes,[24] (3) isomerization of nitrile-coordinated complexes (π to σ),[25] (4) deprotonation of amino carbene complexes,[26] (5) halogen displacement of imidoyl halides by anion complexes of transition metals,[27] and (6) oxidative addition of C–X bonds of imidoyl halides into metal complexes.[28,29] Among them, oxidative addition of imidoyl halides is the most straightforward method to prepare imidoyl palladium complexes. We commenced synthesis of fluorinated imidoyl palladium complexes **2** using tetrakis(triphenylphosphine)palladium as a Pd(0) source.

Trifluoroacetimidoyl iodide **1a** was treated with $Pd(PPh_3)_4$ in benzene at room temperature for 24 h, and oxidative addition took place to give the trifluoroacetimidoyl palladium(II) complex **2a** quantitatively (Scheme 2). The reactions of the imidoyl chlorides **1b**–**1c** with $Pd(PPh_3)_4$ under the same experimental conditions afforded the corresponding palladium(II) phosphine complexes **2b**–**2c** in high yields.

Scheme 2



The iodide complex **2a** crystallized in the monoclinic space group $P21/n$ (No. 14). The ORTEP drawing of **2a** is shown in Figure 1. The geometry at the Pd is trans square-planar; the sum of the four angles at palladium is 359.97°.

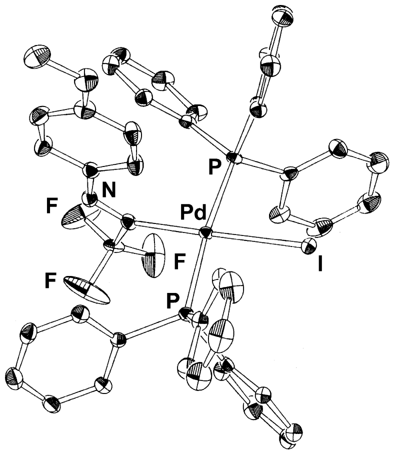
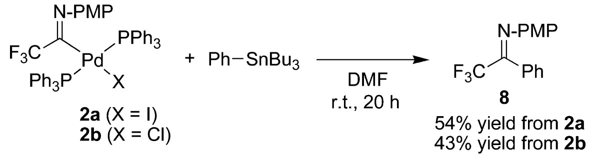


Figure 1. Molecular structure of palladium complex **2a**.

The iminoacyl unit of **2a** has completely trigonal-planar geometry, the sum of the bond angles around the C(1) atom being 359.5°. The C=N bond distance of **2a** (1.28 Å) is similar to those reported for typical C–N double bonds (1.30 Å). The PMP group on the nitrogen of the imine moiety is bound in syn geometry; the lone pair of electrons on the nitrogen atom is anticoplanar to the palladium center. The X-ray structure of **2a** reveals that the imidoyl ligand is bound to the Pd(II) center in an η^1-coordination mode and the plane of the iminoacyl group (involving the p-methoxyphenyl group on nitrogen) is oriented perpendicularly to that of the palladium center in the crystal.

The Migita–Kosugi–Stille coupling is a versatile C–C bond-forming reaction between organostannanes and organic halides with a high level of functional group tolerance under neutral conditions.[30,31] The reactions of the imidoyl palladium(II) complexes **2** with organotin compounds were examined (Scheme 3). A mixture of isolated Pd complex **2a** and Ph-

Scheme 3

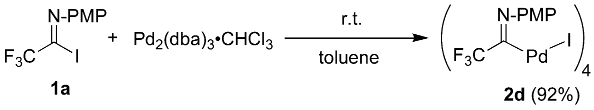


$SnBu_3$ in DMF was heated at 60 °C for 20 h.; the transmetalation and reductive elimination proceeded smoothly to afford trifluoromethylated imine **8** in 54% yield.

Synthesis of Phosphine-Free Trifluoroacetimidoyl Palladium(II) Complex. Phosphines serve as important ligands for transition-metal-catalyzed reactions that coordinate to stabilize the reactive metal centers and that affect the reactivity of the catalysts. In some cases, the coordination of phosphine ligands to metal centers decreases the efficiency of the catalytic reactions, because it is considered that the phosphine ligands occupy the reactive coordination sites in the intermediate metal complexes. For instance, the Pd-catalyzed carboalkoxylation and Heck-type reactions of trifluoroacetimidoyl iodide **1a** proceeded smoothly in the absence of phosphine ligands. Presumably, these reactions involve the intermediate phosphine-free imidoyl palladium(II) complexes. There are several reports of the phosphine-free palladium imidoyl complexes that are stabilized by other ligands, such as tetrahydrothiophene (THT), amines, and isocyanides. To our knowledge, there has been only one report by Usón et al. on the isolation of $[Pd(X)\{C(C_6F_5){=}NMe\}]_n$ (X = Cl, Br, I), which have the imidoyl and halogen ligands without other stabilizing organic ligands.[23q,r] They synthesized these complexes by insertion reaction of methylisocyanide into C−Pd σ bonds in the C_6F_5−palladium complexes; however, they did not provide the structural detail about these oligomeric complexes. From the viewpoint of the structural interest, we have tried isolation and X-ray crystal structure analysis of the phosphine-free complex $[Pd(X)\{C(CF_3){=}NAr\}]_n$ produced by oxidative addition of the imidoyl halides to Pd(0).

The reaction of imidoyl iodide **1a** with $Pd_2(dba)_3{\cdot}CHCl_3$ (2:1 molar ratio) in toluene at room temperature gave a new, stable complex **2d** (Scheme 4). The crude product was purified by silica gel column chromatography to give orange crystals of pure **2d** in 92% yield. Meanwhile, the reaction of imidoyl chloride **1b** with $Pd_2(dba)_3{\cdot}CHCl_3$ did not proceed under the same condition because of the lower reactivity of **1b** compared with that of the corresponding iodide **1a**.

Scheme 4



Elemental analysis of **2d** was in accord with the composition $[Pd(I)\{C(CF_3){=}N(PMP)\}]_4$. Crystals of **2d** (which are monoclinic; a = 18.6641(6) Å, b = 14.0538(5) Å, c = 19.4447(5) Å; β = 108.495(2)°; Z = 16; space group, $C2/c$ (No. 15)) have been confirmed to be cyclic tetranuclear complexes by X-ray crystal structure analysis. The molecular structure of complex **2d** ($[Pd(\mu\text{-}I)\{\mu\text{-}C(CF_3){=}N(PMP)\}]_4$) is shown in Figure 2.

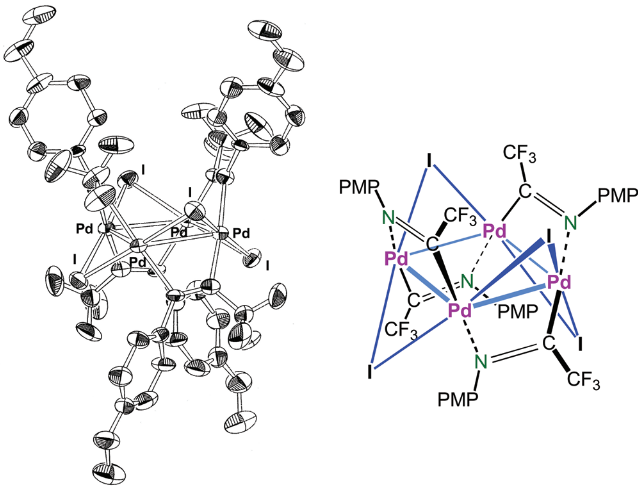
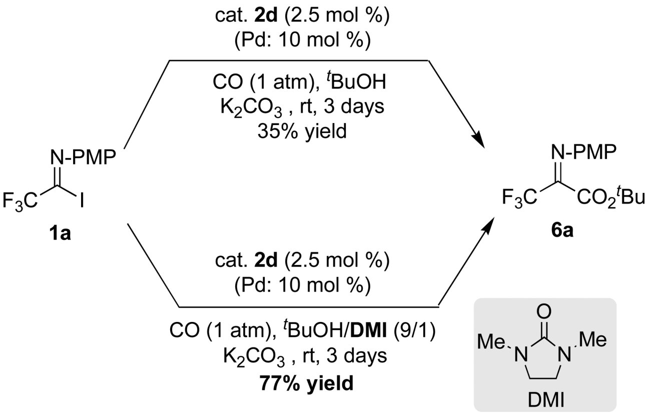


Figure 2. Molecular structure of phosphine-free Pd complex **2d**.

Four pairs of (C- and N-bonded) imidoyl and iodo bridges might contribute a remarkable stability for this structure to achieve a coordination number of 4 (square-planar) at each Pd atom.[32] The distance between Pd(1)···Pd(2) was 3.62 Å. It is much longer than the sum of the covalent radii of Pd(II) (2.56 Å); thus, there is no bond between Pd atoms in the complex **2d**. In comparison with the phosphine complex **2a**, the p-methoxyphenyl group on nitrogen of the imine moiety is bound in anti geometry; the lone pair of electrons on the nitrogen atom is directed toward the neighbor Pd atom. The twist angle around the imidoyl plane and the phenyl ring of PMP group is 37.2°. The C=N bond distances of **2d** (1.27 Å) is similar to those reported for typical C−N double bonds (1.30 Å).

A potential practical use for the complex **2d** is as a catalyst for carboalkoxylation. The *tert*-butyl group is a fascinating protecting group of a carboxylic acid because of easy removal under acidic conditions.[15b] The isolated complex **2d** was treated with *tert*-butyl alcohol (solvent) in the presence of K_2CO_3 at atmospheric pressure of carbon monoxide to give *tert*-butyl iminoester **6a** in 35% yield (Scheme 5). Interestingly, the yield of the *tert*-butyl ester **6a** dramatically increased to 77% when the reaction was conducted in the presence of an additive, such as 1,3-dimethyl-2-imidazolidinone (DMI). The additive DMI might act as a polar solvent to enhance the nucleophilicity of *tert*-butyl alcohol and/or as a weak ligand enough to reduce aggregation of the imidoyl palladium species **2d**, which blocks

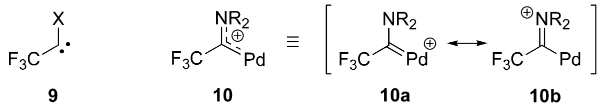
Scheme 5



Pd coordination sites, and to accelerate the coordination of CO to palladium.

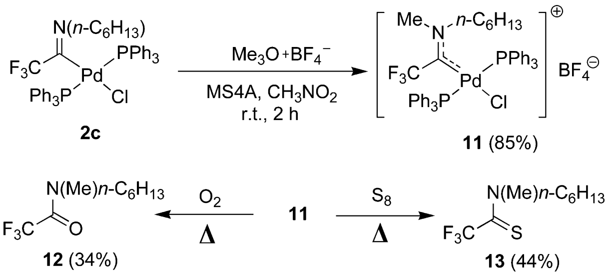
Generation of Trifluoromethyl(amino)carbene Equivalents. The chemistry of carbene intermediates has been of considerable interest to various fields of science.[33,34] These highly reactive species are now widely used in synthesis, and recently, the isolation of stable crystalline carbenes has led to a renaissance in carbene chemistry.[35] Trifluoromethyl carbenes **9** are known to be very unstable because strongly electron-withdrawing trifluoromethyl groups destabilize the carbene centers (Scheme 6).[36,37] Owing to their high reactivities, trifluoromethyl carbenes are used as photoaffinity labels in biochemistry.[38] Heteroatom-substituted trifluoromethyl carbenes are structurally fascinating because they contain both electron-donating and electron-withdrawing substituents on the carbene centers. In 2000, Bertrand succeeded in isolation of stable push−pull carbenes, such as phosphanyl(trifluoromethyl)carbene, which were stabilized by both mesomeric and inductive donating effects of phosphine atoms.[35] To the best of our knowledge, there has been no example of amino(trifluoromethyl)carbenes, the compounds with neutral dicoordinate carbon atoms with trifluoromethyl and amino groups, which are considered to be promising building blocks for synthetic organic chemistry. On the other hand, metal carbenes have been important exhibits in the organometallic showcase.[39] Transition-metal carbene complexes are one of the useful candidates for trifluoromethylated dicoordinate carbon compounds. It is known that the reactions of electrophiles with nitrogen atoms of the iminoacyl ligands in imidoyl metal complexes provide aminocarbene complexes.[40−42] We tried to synthesize amino(trifluoromethyl)carbene−palladium complexes **10** by the use of trifluoroacetimidoyl palladium(II) complexes **2** as starting materials.

Scheme 6



When imidoyl phosphine complex **2c** was treated with trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$, so-called Meerwein's reagent), electrophilic methylation of the nitrogen atom in imidoyl palladium **2c** took place to afford new Pd complex **11** (Scheme 7).

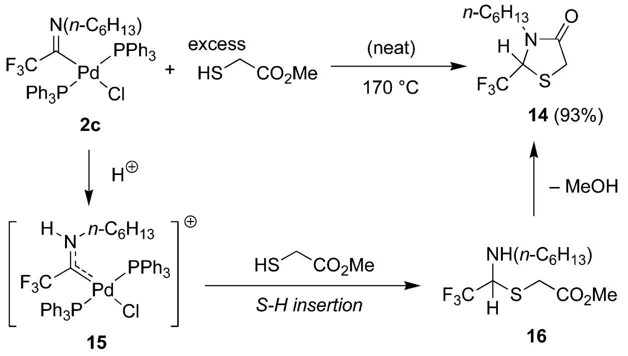
Scheme 7



Elemental analysis of **11** was in accord with the composition of the structure for the amino(trifluoromethyl)carbene−palladium. However, unfortunately, we could not obtain good crystals of the complex **11** for X-ray analysis. To obtain the information for the structure of *N*-methylation product **11**, the following experiments were conducted. When complex **11** was heated under an O_2 atmosphere in a sealed tube at 150−170 °C, *N*-methyl-*N*-hexyl amide **12** was formed in 34% yield. Instead of molecular oxygen, when an excess amount of elemental sulfur (S_8) was utilized, *N*-methyl-*N*-hexyl thioamide **13** was isolated in 44% yield. From these experiments, the existence of an α-(dialkylamino)-α-trifluoromethylcarbene moiety in the palladium complex **11** was proved.

Insertion of carbene ligands into sulfur−hydrogen σ bonds is one of the interesting reactions of metal−carbene complexes. Treatment of the imidoyl palladium(II) complexes **2c** with 2 equiv of methyl thioglycolate at 170 °C under neat conditions afforded 1,3-thiazolin-4-one **14** in 93% yield (Scheme 8). The formation of **14** suggests that thioglycolate serves as a proton source in the reaction and protonation of **2c** at the nitrogen takes place to give the carbene complex **15** in the initial step. The carbene ligand in Pd complex **15** then undergoes insertion into the S−H bond of thioglycolate to provide the *N*,*S*-acetal of fluoral (**16**). Subsequent intramolecular amide formation of the intermediate **16** gives rise to thiazolinone **14**.

Scheme 8



■ CONCLUSIONS

Development of organic transformations based on oxidative addition of fluorinated imidoyl halides to Pd(0) has brought a wide variety of useful organofluorine compounds. We have disclosed preparations, structures, and reactions of trifluoroacetimidoyl palladium(II) complexes. The reactions of trifluoroacetimidoyl halides with $Pd(PPh_3)_4$ afforded the imidoyl palladium(II) phosphine complexes in high yield. By the reaction of the trifluoroacetimidoyl iodide with $Pd_2(dba)_3$, the phosphine-free trifluoroacetimidoyl palladium(II) complex was synthesized and fully characterized. Electrophilic transformations of the trifluoroacetimidoyl palladium(II) complexes gave α-amino-α-trifluoromethylcarbene equivalents. Further studies concerning the catalytic protocols for the generation of trifluoromethylated carbene species are currently under investigation.

■ ASSOCIATED CONTENT

S Supporting Information

Details of experimental procedures and characterization data (^1H, ^{19}F, and ^{31}P NMR; IR; and mass spectrometry) for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

The financial support from the Ministry of Education, Culture, Sports, Science and Technology of Japan is gratefully acknowledged. We thank Prof. Yoshio Nogami (Okayama University), Prof. Toshiyuki Oshiki (Okayama University), and Prof. Soichiro Kyushin (Gunma University) for their kind help of X-ray crystal structure analyses. We are also grateful to Prof. Nobuhiro Takeda (Gunma University) and Ms. Natsuko Uekusa (Gunma University) for their assistance in the ^{31}P NMR study.

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