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Trapping of Unsaturated Small Molecules through Cyclization with Iron−Iminophosphorane Complexes

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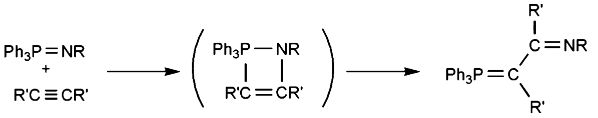
The iron−iminophosphorane−carbonyl complex $Cp^*(CO)_2Fe\{P(NPh)(OMe)_2\}$ (**1**; Cp* stands for η^5-C_5Me_5) reacted with the activated alkyne dimethyl acetylenedicarboxylate (DMAD) to give $Cp^*(CO)Fe\{P(OMe)_2N(Ph)C(CO_2Me)C(CO_2Me)C(O)\}$, in which the alkyne was trapped between the imino nitrogen and one carbonyl carbon to form a six-membered metallacycle. In contrast, **1** reacted with CO_2 to afford aza-Wittig-type metathesis products, PhN═C═NPh and oxophosphorane (phosphonate) complex $Cp^*(CO)_2Fe\{P(O)(OMe)_2\}$, probably via a four-membered aza-phosphacycle as an intermediate. Free acetonitrile did not react with **1**, while the coordinated acetonitrile in $[Cp^*(CO)(NCMe)Fe\{P(NHPh)(OMe)_2\}]PF_6$ was incorporated into a five-membered metallacycle through a base-catalyzed rearrangement to give $[Cp^*(CO)Fe\{P(OMe)_2N(Ph)C(Me)N(H)\}]PF_6$, in which the nitrile carbon was bonded to the imino nitrogen. It was proposed that this intramolecular cyclization reaction is initiated by the formation of the neutral iminophosphorane complex $Cp^*(CO)(NCMe)Fe\{P(NPh)(OMe)_2\}$ as an intermediate, followed by the prompt nucleophilic attack of the resulting imino nitrogen to the carbon atom of the coordinated acetonitrile.

Introduction

Iminophosphoranes ($R_3P{=}NR$), which are variously referred to as phosphinimines, phosphoranimines, or monophosphazenes, have been of special interest not only because of their characteristic structures and versatile reactivities[1,2] but also because of their utilities as practical ligands in coordination chemistry[3] and as precursors of promising materials.[4−6] The P═N bond is described alternatively in an ionic representation as $P^+{-}N^-$ isoelectronic to the P═C bond in phosphorus ylides ($R_3P{=}CR_2 \approx R_3P^+{-}C^-R_2$) well-known as Wittig reagents. In fact, iminophosphoranes readily react with unsaturated molecules, e.g., CO_2, CS_2, RNCO, SO_2, etc., as well as carbonyl compounds to provide aza-Wittig products, and so they have been playing an important role in the syntheses of nitrogen-containing compounds.[1,2,7] The reactions with activated alkynes have also been reported in relation to similar aza-Wittig reactions.[2,7a,8] These reactions are generally accepted to proceed through a four-membered cycloadduct involving a pentacoordinated phosphorus as an intermediate,[1,2,7] which was isolated and fully characterized in some cases (eq 1).[8i,9]



(1)

We recently reported the syntheses of transition-metalated iminophosphoranes, $Cp^*(CO)_2M\{P(NPh)(OMe)_2\}$ (M = Fe (**1**),

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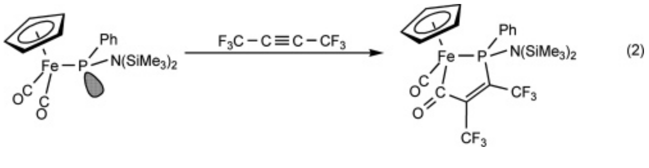
Ru), and demonstrated that the imino nitrogen is fairly basic.[10] In general, transition-metal-functionalized phosphorus compounds display unique reactivities, in part because of the enhanced electron density on the phosphorus by the metal fragment, if covalently bonded to it. One of the simplest examples is a phosphide complex, that is, metallaphosphine, which is highly nucleophilic and susceptible to oxidation. For instance, Paine et al. reported that an iron−phosphide−carbonyl complex, $Cp(CO)_2Fe[PPh\{N(SiMe_3)_2\}]$, traps an activated alkyne, hexafluoro-2-butyne ($F_3CC{\equiv}CCF_3$), to form a condensation product with a five-membered metallacycle (eq 2).[11] The related cyclization reactions with various unsaturated organic small molecules have also been reported for several phosphide complexes.[12]



(2)

The above-mentioned parallel features between organic iminophosphoranes and transition-metalated phosphorus compounds prompted us to investigate the reactions of the transition-metalated iminophosphoranes with various organic and inorganic molecules having multiple bonds. To date, quite limited reports deal with the reactivities of metalated iminophosphoranes. Majoral et al. reported that a zirconium−iminophosphorane, which easily rearranges into an *N*-coordinated zirconium−phosphinoamide at room temperature, affords a variety of products by breaking the zirconium−phosphorus bond in the reactions with several reagents including some unsaturated molecules (vide infra).[13] Because the iron−iminophosphorane **1** is stable even at elevated temperatures,[10] its reactions might proceed with the iron−phosphorus bond retained, to provide unprecedented heterocycles containing phosphorus, nitrogen, and transition-metal atoms, which might exhibit fascinating properties.[14−16]

Results and Discussion

Reaction with Activated Alkyne. The iron−iminophosphorane **1** was treated with DMAD (dimethyl acetylenedicarboxylate) in benzene overnight to give a yellow powder of **2** in moderate yield (28%, eq 3). The IR spectrum shows only one strong absorption band at 1943 cm^{-1}, assignable to a terminal carbonyl, together with absorptions at 1735, 1700 (sh), and 1577 cm^{-1} assignable to acyl carbonyls. The $^{31}P\{^1H\}$ NMR signal of **2** (180.2 ppm) appears fairly downfield from that of the starting complex **1** (122.3 ppm),[10] indicating the lowered valency of the phosphorus in **2**. In the ^1H NMR spectra, **1** shows one doublet at 3.65 ppm (J_{HP} = 11.4 Hz) assignable to the spectroscopically identical POMe groups, while **2** shows two doublets at 3.45 (J_{HP} = 9.9 Hz) and 3.50 ppm (J_{HP} = 10.5 Hz) due to the diastereotopic POMe groups, suggesting the asymmetric geometry around the iron in **2**. In addition to the POMe groups, two inequivalent CO_2Me groups are also observed as two singlets. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows a doublet at 260.8 ppm (J_{CP} = 49.8 Hz), which is in a typical region for the Fe−acyl carbonyls, together with a doublet at 218.2 ppm (J_{CP} = 37.7 Hz) due to the terminal carbonyl.

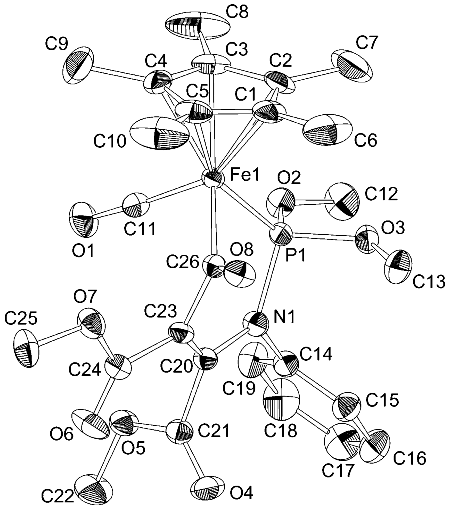
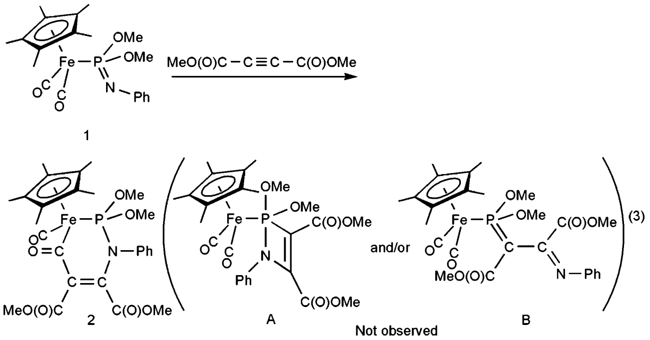


Figure 1. ORTEP drawing of **2** showing the non-hydrogen atoms as 50% probability thermal ellipsoids with a numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)−C(26) = 1.9286(18), Fe(1)−P(1) = 2.1120(5), P(1)−N(1) = 1.7275(16), N(1)−C(20) = 1.398(2), C(20)−C(23) = 1.351(3), C(23)−C(26) = 1.513(2), C(26)−Fe(1)−P(1) = 85.97(6), N(1)−P(1)−Fe(1) = 113.29(6), C(20)−N(1)−P(1) = 122.67(13), C(23)−C(20)−N(1) = 124.68(16), C(20)−C(23)−C(26) = 121.32(16), C(23)−C(26)−Fe(1) = 116.73(12).



1

2

(3)

The structure of **2** was unambiguously determined by a single-crystal X-ray diffraction, and the ORTEP drawing is illustrated in Figure 1 with selected bond distances and angles. Crystal data and a summary of data collection and structure refinement are reported in Table 1. The iron has a distorted piano-stool configuration with one terminal carbonyl ligand. DMAD has been incorporated between the imino nitrogen and one carbonyl carbon to form a six-membered metallacycle, in which the bond length of C(20)−C(23) (1.351(3) Å) is in a normal range for C=C double bonds. The N(1) atom in **2** has a perfectly planar geometry, which is nearly perpendicular to the adjacent phenyl ring plane, suggesting that its lone pair electrons are π-donated rather toward the olefinic carbon and/or the phosphorus atom-

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Table 1. Summary of Crystal Data for 2, 4, and 7

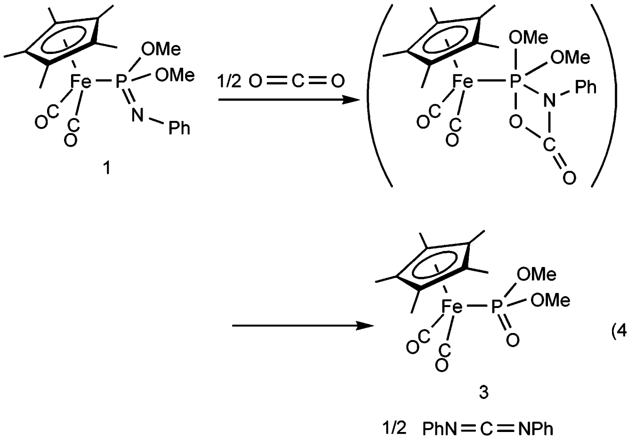
	2	**4**	**7**
empirical formula	$C_{26}H_{32}FeNO_8P$	$C_{21}H_{30}F_6FeN_2O_3P_2$	$C_{21}H_{30}F_6FeN_2O_3P_2$
fw	573.35	590.26	590.26
cryst size (mm)	0.33 × 0.28 × 0.18	0.31 × 0.26 × 0.13	0.55 × 0.48 × 0.38
temperature (K)	200(1)	200(1)	200(1)
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Pbca* (#61)	$P2_12_12_1$ (#19)	*P*2/c (#13)
unit cell dimens			
a (Å)	15.4540(3)	8.5180(2)	11.1990(2)
b (Å)	14.6940(3)	15.7840(4)	17.4430(3)
c (Å)	23.7370(3)	19.4580(4)	14.0260(2)
β (deg)			103.4380(10)
V (Å^3)	5390.22(17)	2616.09(11)	2664.88(8)
Z	8	4	4
D_{calcd} (Mg/m^3)	1.413	1.499	1.471
F(000)	2400	1216	1216
μ (mm^{-1})	0.668	0.767	0.753
θ range for data collection (deg)	2.98 to 27.89	1.66 to 27.93	1.17 to 27.90
index range	$0 \le h \le 20$	$0 \le h \le 11$	$0 \le h \le 14$
	$0 \le k \le 19$	$0 \le k \le 20$	$0 \le k \le 22$
	$-29 \le l \le 0$	$0 \le l \le 25$	$-18 \le l \le 17$
no. of reflns collected	6184	3507	6370
no. of indep reflns	6184	3507	6370
no. of refined params	462	325	473
struct soln	direct methods (SHELX-97)	direct methods (SHELX-97)	direct methods (SHELX-97)
goodness-of-fit on F^2	1.073	1.080	1.029
final R indices [$I > 2\sigma(I)$]	R1 = 0.0441, wR2 = 0.1105	R1 = 0.0580, wR2 = 0.1238	R1 = 0.0414, wR2 = 0.1036
R indices (all data)	R1 = 0.0478, wR2 = 0.1124	R1 = 0.0738, wR2 = 0.1411	R1 = 0.0471, wR2 = 0.1056
largest diff peak and hole (e/Å^3)	0.360 and −0.718	0.440 and −0.751	0.707 and −0.855
absolute struct param		0.06(4)	

(s). The P(1)−N(1) bond in **2** (1.7275(16) Å) is significantly longer than the corresponding P═N bond in **1** (1.574(1) Å),[10] indicative of its reduced bond order in **2**. This observation reveals that the phosphorus in **2** is thus that of coordinated phosphite in nature rather than that of metalated iminophosphorane, consistent with the ^{31}P{^{1}H} NMR spectrum. In other words, the Fe−P bond has correspondingly changed in character formally from covalent to dative through the reaction.

For related cyclization reactions studied for transition-metal−carbonyl-phosphide and -thiolate complexes with alkenes or alkynes, two possible mechanisms have been proposed.[12a,17] One is a concerted mechanism involving a cyclic transition state, and the other is a stepwise mechanism involving an initial nucleophilic attack of the P or S atom to an unsaturated carbon to form a charge-separated intermediate. In either mechanism, the more electron-rich the P or S atom, the more readily the cyclization proceeds. In the corresponding cyclization of **1**, the strong nucleophilicity of the imino nitrogen must be similarly crucial. Furthermore, the electron-withdrawing groups on the alkyne play an essential role; when nonactivated alkynes, such as phenyl- and diphenyl-acetylenes, were treated with **1** in place of DMAD, no reaction occurred.

In the reaction with DMAD, **2** was the only identified product, and there was no evidence for the formation of **A** and/or **B** (eq 3), as expected in eq 1, although they could have immediately decomposed in some way.

Reaction with CO$_2$. In the Wittig-type reaction, the transient formation of the highly strained four-membered phosphacycle would be fully compensated for in energy by the subsequent rearrangement leading to an extremely stable P═O bond. Such energetic benefit might provide aza-Wittig-type products rather than the metallacycle products even in the reaction of **1** with carbonyl molecules. Thus **1** was treated with dry CO$_2$ in benzene for 30 min to give a pale yellow powder of **3** (85% yield, eq 4). Comparison of the spectroscopic data of **3** with those of the authentic sample[18] reveals that **3** is a phosphonate complex with a P═O group. The formation of the other aza-Wittig product PhN═C═NPh was also confirmed by the GC-MS analysis of the reaction mixture, indicating that PhN═C═O afforded by the single aza-Wittig reaction reacted further with **1** to eventually give PhN═C═NPh. This reaction is rationally expected to proceed through a four-membered cycloadduct containing a $\overline{\text{P}{-}\text{N}{-}\text{C}{-}\text{O}}$ linkage (eq 4) like the usual Wittig reaction. Unlike in the reaction with DMAD, the formation of a six-membered metallacycle was not observed. An extensive investigation on aza-Wittig reactions of **1** is now under way with a variety of carbonyl and thiocarbonyl compounds.



(4)

The reactions with DMAD and with CO$_2$ reveal that the nucleophilic iron−iminophosphorane complex serves as an efficient trapping reagent for various organic and inorganic unsaturated molecules. Its reactions involve either of the two different pathways, in both of which the iron−phosphorus bond

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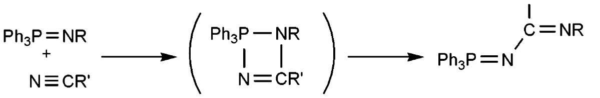
is retained, i.e., the metallacycle formation with the molecule trapped between the imino nitrogen and carbonyl carbon for DMAD, or the formation of a four-membered cycloadduct bearing pentacoordinated phosphorus, which rearranges subsequently to aza-Wittig-type products for CO_2.

Reaction with Acetonitrile. Organic iminophosphoranes react similarly with nitriles via a four-membered cyclic intermediate (eq 5). However, such nucleophilic additions of iminophosphoranes occur only toward the activated nitriles bearing strongly electron-withdrawing groups, such as CN, CF_3, or CCl_3.[2] Because a transition-metal fragment would enhance the nucleophilicity of the phosphorus fragment bonded covalently to it, the metalated, i.e., activated, iminophosphoranes might react even with nonactivated nitriles. Thus **1** was dissolved in neat acetonitrile, but no reaction took place, with no expected cyclization product being obtained (eq 6). This fact indicates that the nitrile carbon as it is would not be electrophilic enough to be attacked by the activated imino nitrogen in **1**, and some activation of the nitrile should be needed.



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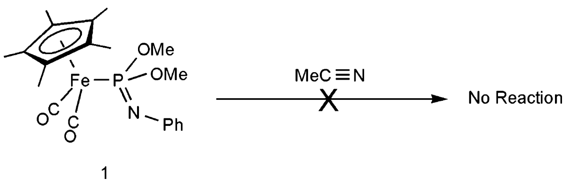
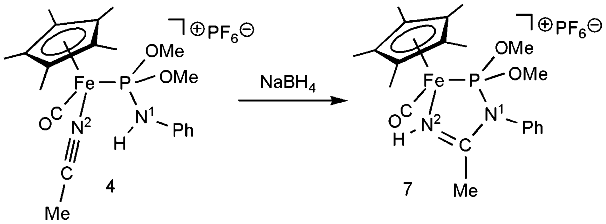


(6)

Because nitriles act as two-electron donor ligands and the metal coordination will reduce the electron density on the nitrile carbon, metal-coordinated nitriles are more susceptible to nucleophilic attack than free nitriles.[19] Thus the cationic acetonitrile complex **4** was allowed to reacted with a base ($NaBH_4$), which might abstract the PN−H proton to provide a neutral iminophosphorane fragment in situ (eq 7). The reaction proceeded quantitatively, and the starting suspension immediately turned into a clear solution. The product **7** was isolated by column chromatography as an air- and moisture-stable yellow powder (76% yield). The ^{1}H NMR spectrum of **7** shows two doublets assignable to the diastereotopic OMe groups on the phosphorus atom, and the difference in chemical shifts of the two groups is 0.38 ppm for **7** and only 0.07 ppm for **4**. The N(1)−H proton in **4** appears at 5.45 ppm as a broad doublet (J_{HP} = 17.15 Hz), whereas the N(2)−H proton in **7** appears at 6.17 ppm as a broad singlet without J_{HP} coupling. In contrast to the ^{1}H NMR, the $^{13}C\{^1H\}$ NMR spectrum shows a singlet at 133.6 ppm due to the N*C*Me carbon for **4**, while a doublet (J_{CP} = 26.1 Hz) at further deshielded 173.5 ppm for **7**. Similarly, the NC*Me* carbon in **7** appears at 21.1 ppm, which is ca. 17 ppm downfield of that in **4**. These observations indicate a significant structural change in the nitrile ligand in **7**. In the $^{31}P\{^1H\}$ NMR spectrum, **7** appears at 196.2 ppm, which is downfield from that of **4** (169.7 ppm). The observation of a septet ^{31}P signal assignable to the PF_6 anion indicates that the complex formed remains positively charged.



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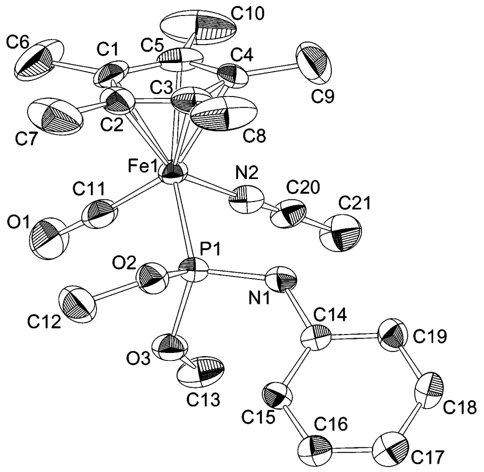

Figure 2. ORTEP drawing of **4** showing the non-hydrogen atoms as 50% probability thermal ellipsoids with a numbering scheme. The PF_6 anion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−N(2) = 1.936(5), Fe(1)−P(1) = 2.1753(16), P(1)−N(1) = 1.657(5), N(2)−C(20) = 1.130(8), N(2)−Fe(1)−P(1) = 92.24(15), N(1)−P(1)−Fe(1) = 113.63(19), C(20)−N(2)−Fe(1) = 177.5(5), N(2)−C(20)−C(21) = 178.4(8).

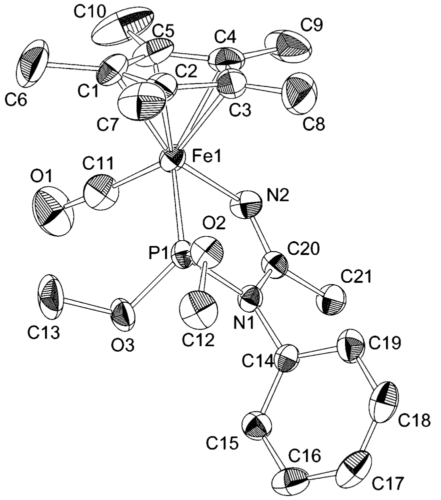

Figure 3. ORTEP drawing of **7** showing the non-hydrogen atoms as 50% probability thermal ellipsoids with a numbering scheme. The PF_6 anion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−N(2) = 1.9642(16), Fe(1)−P(1) = 2.1331(5), P(1)−N(1) = 1.7077(15), N(1)−C(20) = 1.377(2), N(2)−C(20) = 1.285(2), N(2)−Fe(1)−P(1) = 81.90(5), N(1)−P(1)−Fe(1) = 103.26(5), C(20)−N(1)−P(1) = 114.18(12), C(20)−N(2)−Fe(1) = 123.65(13), N(2)−C(20)−N(1) = 116.85(16).

The X-ray structural analyses were performed on both **4** and **7**, and their ORTEP drawings are illustrated in Figures 2 and 3, respectively. **4** and **7** both have distorted piano-stool geometries with one terminal carbonyl ligand on the iron atom. The structural parameters of **4** are basically similar to those of its protonated dicarbonyl analogue, $[\mathbf{1}H]^+PF_6^-$, previously reported.[10] The somewhat shorter Fe(1)−C(11) bond in **4** (1.747(7) Å) than the two Fe−CO bonds in $[\mathbf{1}H]^+PF_6^-$ (1.784(2), 1.780(3) Å) indicates that the back-donation from

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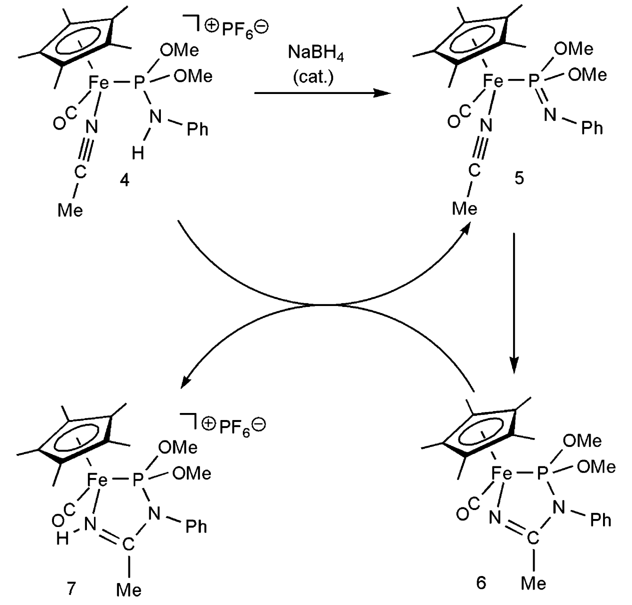
[19] For review articles on the reactions of transition-metal-coordinated nitriles, see: (a) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299. (b) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.

Scheme 1. Plausible Mechanism of the Base-Catalyzed Rearrangement of 4 into 7



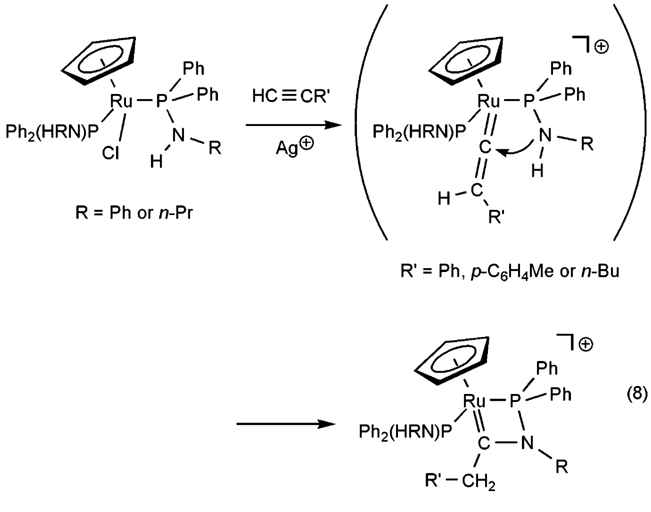
the iron to the carbonyl carbon is more extensive in **4**, suggesting the ample electron donation from the accompanying acetonitrile ligand to the iron. The amino nitrogen N(1) probably has a trigonal-planar geometry (P(1)−N(1)−C(14) angle of 130.0(4)°), like in the usual P−NR$_2$ compounds, and so no interaction is anticipated between the lone-pair electrons on N(1) and the nitrile carbon C(20) at this stage. The lone-pair electrons are donated rather to the σ^*-orbital on P(1), suggesting that the nucleophilicity of the N(1) atom in **4** must be fairly low.

7 has a five-membered metallacycle structure with a new bridging bond formed between the imino nitrogen N(1) and the nitrile carbon C(20), in which the five ring atoms are located practically on the same plane. The location of the N(2)−H proton in **7** was determined experimentally; the N(2) atom, originating from acetonitrile, is no doubt protonated. That is to say, the N(1)−H proton in **4** is once abstracted with NaBH$_4$, but the N(2) is in turn protonated in **7**, meaning that this cyclization proceeds catalytically with a base (vide infra). The N(2)−C(20) bond (1.285(2) Å) is fairly shorter than the N(1)−C(20) bond (1.377(2) Å) in **7**, but it is much longer than the corresponding N(2)−C(20) bond (1.130(8) Å) in **4**. This indicates that the N(2)−C(20) bond has been reduced in bond order in **7** compared with that in **4**, but it still assumes some multiple-bond character. Thus N(2) in **7** is depicted as an imino nitrogen bonded datively to the iron in the formal electronic structure. The P(1)−N(1) bond in **7** (1.7077(15) Å) is comparable to that in **2** (1.7275(16) Å), suggesting that the phosphorus in **7** is regarded also as that of phosphite coordinated to the iron atom.

The plausible mechanism for the present cyclization is as follows (Scheme 1): the starting cationic complex **4** reacts with a base (NaBH$_4$) to give a small amount of neutral metallaiminophosphorane **5** as an intermediate, in which a highly nucleophilic lone pair on sp^2-hybridization has been now generated on the P−N nitrogen upon deprotonation. The subsequent nucleophilic attack of the P−N nitrogen to the coordinated nitrile carbon provides **6** with a five-membered metallacycle structure. The resulting Fe−N nitrogen in **6** then promptly abstracts the PN−H proton in the remaining **4** to give the final product **7** and to reproduce the neutral intermediate **5** as well. The intermediates **5** and **6** could not be detected, and no evidence was obtained for the presence of an equilibrium between **7** and **4**. It is noteworthy that the iron atom in the intermediate **5** plays the following important roles in this rearrangement process: (1) activation of the nucleophilic iminophosphorane fragment by electron donation through the Fe−P covalent bond, (2) activation of the electrophilic nitrile carbon by accepting the lone-pair electrons of the nitrile through the Fe−N dative bond, and (3) promotion of the reaction by keeping the iminophosphorane and nitrile ligands close to each other in its coordination sphere.

Several related intramolecular cyclization reactions of metal-coordinated nitriles have been reported.[19] For instance, the iridium−hydroxymethyl−acetonitrile complex [Ir(CH$_2$OH)(NCMe)(PMe$_3$)$_4$]$^{2+}$ undergoes a base-catalyzed intramolecular cyclization via the nucleophilic attack of the hydroxymethyl oxygen toward the nitrile to form a five-membered metallacycle.[20] This cyclization also takes place without a base, but much more slowly. Similar metallacycle formation was also reported for nitrile-containing complexes in the reactions with hydroxylamine, hydrazines, sulfimides, pyrazoles, etc.[19]

Recently, the metallacycle formation involving aminophosphine ligands was reported for ruthenium−vinylidene or −allenylidene complexes (eq 8),[21] where intramolecular bond formation took place between a weakly nucleophilic amino nitrogen and a highly electrophilic α-carbon of the vinylidene or the allenylidene ligand. In the corresponding cyclization of **4**, the formation of the highly nucleophilic iminophosphorane intermediate **5** is an essential step, since pure **4** itself is stable and is not susceptible to the cyclization. Thus it should be emphasized that the cyclization of **4** contrasts sharply with those of the above ruthenium−aminophosphine complexes, in that the former reaction is due largely to the nucleophilicity of the imino nitrogen, whereas the latter to the electrophilicity of the α-carbon of the vinilidene or the allenylidene.



(8)

Majoral et al. reported that a zirconium−iminophosphorane reacts with nitriles to afford zirconacycles, in which the nitrile is inserted into the zirconium−phosphorus bond and the P=N nitrogen is additionally coordinated to the zirconium center (eq 9).[13] In this reaction, the phosphorus fragment serves formally as if it is iminophosphoranide Me$_2$P$^-$(=NAr) with the zirconium−phosphorus bond broken, and its phosphorus atom, not its imino nitrogen, attacks the nitrile carbon. Such a high reactivity of the zirconium−phosphorus bond would reflect the unfavorable combination of hard zirconium and soft phosphorus under the

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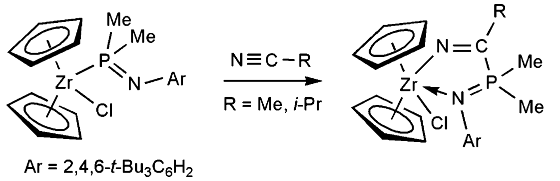
(20) Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, *272*, 283.

(21) Pavlik, S.; Mereiter, K.; Puchberger, M.; Kirchner, K. *Organometallics* **2005**, *24*, 3561.

HSAB concept, in contrast to the favorable soft−soft combination of the iron and phosphorus in **1**. In addition, the resulting zirconium complex is favorably stabilized by the coordination of the hard C═N and P═N nitrogen atoms to form a metallacycle.



(9)

In the metallacycle **7**, the P(OMe)$_2$N(Ph)C(Me)N(H) moiety is serving as a P−N chelate ligand toward the iron center. This type of ligands has been of special interest because of their potentially hemilabile behavior as well as their diversity in the coordination modes, i.e., monodentate, bidentate, and bridging toward homo or hetero metals.[22,23] In this respect, the metal-assisted cyclization of iminophosphoranes with nitriles can be a new direct synthetic route toward the novel transition-metal complexes bearing such fascinating P−N chelate ligands.

Concluding Remarks

In the present paper, it was demonstrated that the highly nucleophilic iron−iminophosphoranes trap various organic and inorganic molecules having multiple bonds in two different ways: one provides condensation products bearing a six- or five-membered metallacycle structure, and the other provides aza-Wittig-type metathesis products probably via a four-membered aza-phosphacycle as an intermediate. The phosphorus−nitrogen systems have been of special interest in the search for wide-range applications to industrial and biomedical uses.[4−6] In this respect, the reactive metallaiminophosphoranes and their cyclic derivatives as well reported here are potential candidates for building blocks for transition-metal-containing materials, which might provide versatile physical and chemical properties.[24]

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk-tube techniques and purified solvents. Column chromatography was done quickly in the air. CH$_2$Cl$_2$ and acetonitrile were purified by distillation from P$_2$O$_5$, while benzene, pentane, ether, hexane, and THF were distilled from sodium metal (with benzophenone ketyl for benzene, ether, and THF), and they were stored under a nitrogen atmosphere. Other solvents, NaBH$_4$ and DMAD, were obtained from common commercial sources and used without further purification. CO$_2$ gas was supplied from a steam of dry ice flakes, which had been passed through a desiccant (Sicapent, Merck) column. Cp*(CO)$_2$Fe{P(NPh)(OMe)$_2$} (**1**),[10] [Cp*(CO)$_2$Fe(NCMe)]PF$_6$,[25] and P{N(SiMe$_3$)Ph}(OMe)$_2$[10] were prepared according to the published procedures.

A JEOL LA-300 spectrometer was used to obtain ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra. ^{1}H NMR and ^{13}C NMR data were referenced to SiMe$_4$ as an internal standard, and ^{31}P NMR data to 85% H$_3$PO$_4$ as an external standard. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer. A Shimadzu QP-2000 was used to obtain GC-MS spectra. A Riko-Kagaku Sangyo UVL-400HA high-pressure mercury lamp was used for UV light irradiation.

Reaction of 1 with DMAD. To a benzene solution (10 mL) of **1** (777 mg, 1.80 mmol) was added DMAD (0.25 mL, 2.03 mmol), and the mixture was stirred overnight at room temperature. After removal of volatile components under reduced pressure, the residual yellow oil was washed with pentane (10 mL) twice and then dissolved in a small amount of benzene. The benzene solution was charged on a silica gel column and eluted with benzene and then with a mixture of benzene/acetone (1:1). A yellow band eluted was collected and dried under vacuum. The resulting yellow residue was washed with pentane until it became a fine yellow powder and then dried under reduced pressure to give **2** (287 mg, 0.50 mmol, 28% yield). Anal. Calcd for C$_{26}$H$_{32}$NFeO$_8$P: C, 54.47; H, 5.63; N, 2.44. Found: C, 54.07; H, 5.48; N, 2.39. IR (ν_{CO}, in CDCl$_3$): 1943, 1735, 1700(sh), 1577 cm^{-1}. ^{1}H NMR (δ, in CDCl$_3$): 1.78 (s, 15H C$_5$Me$_5$), 3.35 (s, 3H,CO$_2$Me), 3.45 (d, J_{HP} = 9.9 Hz, 3H, 3.50 (d, J_{HP} = 10.5 Hz, 3H, POMe), 3.67 (s, 3H, CO$_2$Me), 7.14−7.29 (m, 5H, Ph). ^{13}C{^{1}H} NMR (δ, in CDCl$_3$): 9.4 (s, C$_5$*Me*$_5$), 51.5 (s, CO$_2$*Me*), 51.6 (s, CO$_2$*Me*), 52.9 (d, J_{CP} = 9.1 Hz, POMe), 53.0 (d, J_{CP} = 9.1 Hz, POMe), 96.3 (s, *C*$_5$Me$_5$), 127.4 (s, Ph), 128.5 (s, Ph), 129.0 (s, Ph), 138.4 (d, J_{CP} = 0.9 Hz, N*C*═C), 138.4 (s, NC═*C*), 142.9 (d, J_{CP} = 13.6 Hz, Ph), 164.3 (d, J_{CP} = 8.2 Hz, NC*C*(O)OMe), 164.7 (s, CC*C*(O)OMe), 218.2 (d, J_{CP} = 37.7 Hz, FeCO), 260.8 (d, J_{CP} = 49.8 Hz, Fe*C*(O)C). ^{31}P{^{1}H} NMR (δ, in CDCl$_3$): 180.2(s).

Reaction of 1 with CO$_2$. After passing dry CO$_2$ through a benzene solution (2 mL) of **1** (113 mg, 0.26 mmol) for 30 min, volatile components were removed under vacuum. The residue was then dissolved in a small amount of acetone and charged on a silica gel column. A yellow band eluted with EtOH was collected and dried under reduced pressure to give a pale yellow powder of **3** (79 mg, 0.22 mmol, 85% yield), which was unambiguously characterized by comparison of its spectroscopic data with those of the authentic sample.[18] The formation of PhN═C═NPh was confirmed by the GC-MS analysis of the reaction mixture.

Preparation of 4. An acetonitrile solution (53 mL) of [Cp*(CO)$_2$Fe(NCMe)]PF$_6$ (734 mg, 1.70 mmol) was irradiated with UV light for 1 h at 0 °C, and then volatile components were removed under vacuum. After washing with ether several times, the residue was dissolved in CH$_2$Cl$_2$ (25 mL), to which P{N(SiMe$_3$)Ph}(OMe)$_2$ (0.44 mL, 1.67 mmol) was added. The mixture was refluxed overnight and then evaporated to dryness. The residue was dissolved in THF (53 mL) containing H$_2$O (2 mL) and stirred for 1 h at 45 °C. After removal of volatile components under vacuum, the resulting crude product was dissolved in a small amount of CH$_2$Cl$_2$ and charged on a silica gel column. A reddish-yellow band eluted with a mixture of CH$_2$Cl$_2$/acetone (9:1) was collected and dried under vacuum. The residue was washed with ether several times and dried under reduced pressure to give a yellow powder of **4** (694 mg, 1.18 mmol, 69% yield). Anal. Calcd for C$_{21}$H$_{30}$N$_2$F$_6$FeO$_3$P$_2$: C, 42.73; H, 5.12; N, 4.75. Found: C, 42.77; H, 5.10; N, 4.66. IR (ν_{CO}, in THF): 1970. ^{1}H NMR (δ, in CDCl$_3$): 1.68 (s, 15H, C$_5$Me$_5$), 2.38 (s, 3H, NCMe), 3.68 (d, J_{HP} = 12.0 Hz, 3H, POMe), 3.75 (d, J_{HP} = 11.8 Hz, 3H, POMe), 5.45 (br d, J_{HP} = 17.15 Hz, 1H, NH), 6.97−7.29 (m, 5H, Ph). ^{13}C{^{1}H} NMR (δ, in CDCl$_3$): 4.4 (s, NC*Me*), 9.2 (s, C$_5$*Me*$_5$), 53.0 (d, J_{CP} = 6.2 Hz, POMe), 53.0 (d, J_{CP} = 5.6 Hz, POMe), 94.9 (d, J_{CP} = 1.2 Hz, *C*$_5$Me$_5$), 118.7 (d, J_{CP} = 5.0 Hz, Ph), 122.6 (s, Ph), 129.5 (s, Ph), 133.6 (s, N*C*Me), 139.9 (d, J_{CP} = 3.7 Hz, Ph), 216.3 (d, J_{CP} = 37.9 Hz, CO). ^{31}P{^{1}H} NMR (δ, in CDCl$_3$): 169.7 (s), −143.7 (sep, J_{PF} = 712.4 Hz. PF$_6$).

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(22) For example, see: Wong, W.-Y.; Wong, W.-K.; Sun, C.; Wong, W.-T. *J. Organomet. Chem.* **2000**, *612*, 160, and references therein.

(23) For example, see: Milton, H. L.; Wheatley, M. V.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chim. Acta* **2005**, *358*, 1393, and references therein.

(24) (a) Allcock, H. A.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119. (b) Manners, I. *Science* **2001**, *294*, 1664. (c) Manners, I. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 179.

(25) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

Reaction of 4 with $NaBH_4$. To a THF suspension (14 mL) of **4** (485 mg, 0.82 mmol) was added $NaBH_4$ (31 mg, 0.82 mmol), and the mixture was stirred for 30 min at ambient temperature. The resulting solution was evaporated to dryness, and then the residue was dissolved in a small amount of CH_2Cl_2. The solution was charged on a silica gel column and eluted with a mixture of CH_2Cl_2/acetone (9:1). A reddish-yellow band was collected and dried under vacuum. The residue was washed with ether and then with pentane several times, and dried under reduced pressure to give **7** as a yellow powder (371 mg, 0.62 mmol, 77% yield). Anal. Calcd for $C_{21}H_{30}N_2F_6FeO_3P_2$: C, 42.73; H, 5.12; N, 4.75. Found: C, 42.63; H, 5.20; N, 4.69. IR (ν_{CO}, in THF): 1961. ^{1}H NMR (δ, in $CDCl_3$): 1.72 (s, 15H, C_5Me_5), 1.89 (s, 3H, N(H)C*Me*), 3.33 (d, J_{HP} = 10.6 Hz, 3H, POMe), 3.71 (d, J_{HP} = 13.1 Hz, 3H, POMe), 6.17 (br s, 1H, N(H)C), 7.10−7.39 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 9.4 (s, C_5*Me*$_5$), 21.1 (d, N(H)C*Me*), 53.8 (s, POMe), 55.5 (d, J_{CP} = 13.7 Hz, POMe), 94.6 (d, J_{CP} = 1.9 Hz, *C*$_5$Me$_5$), 129.1 (br s, Ph), 129.5 (s, Ph), 130.0 (s, Ph), 135.8 (d, J_{CP} = 6.2 Hz, Ph), 173.5 (d, J_{CP} = 26.1 Hz, N*C*Me), 215.3 (d, J_{CP} = 31.1 Hz, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 196.2 (s), −143.7 (sep, J_{PF} = 712.5 Hz. PF_6).

X-ray Structure Determination. A single crystal of **2** was obtained through recrystallization from hexane at room temperature, while that of **4** was obtained from CH_2Cl_2 at 0 °C. A single crystal of **7** was obtained by slow diffusion of hexane in a CH_2Cl_2 solution of **7** at room temperature. Each crystal coated with inert oil was mounted on a glass fiber and fixed in the cold nitrogen gas stream. Intensity data were collected on a Mac Science DIP2030 imaging plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at 200 K and then processed using the HKL program package.[26] The structures were determined by direct methods and then were refined by full-matrix least-squares methods on F^2 using the SHELX-97 program package.[27] ORTEP drawings were made using the ORTEP III program.[28] Positions of hydrogen atoms of **4** were calculated by assuming idealized geometries, whereas those of **2** and **7** were determined from subsequent difference Fourier maps. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not refined for **4**, but they were refined isotropically for **2** and **7**. Crystal data, data collection parameters, and results of the analyses are summarized in Table 1. Further details are included in the Supporting Information.

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Supporting Information Available: Crystallographic data for **2**, **4**, and **7** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0510728

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(26) Otwinowski, Z.; Minor, W. In *Methods in Enzymology. Macromolecular Crystallography Part A*; Sweet, R. M., Carter, C. W., Jr., Eds.; Academic Press: New York, 1997; Vol. 276, p 307.

(27) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

(28) Burnett, M. N.; Johnson, C. K. *ORTEP-3*; Report ORNL-6895; Oak Ridge National Laboratory: Oak Ridge, TN, 1996.