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Transition Metal-Catalyzed Intramolecular Cyclization of 1,5- and 1,6-Dienes via Direct Cleavage and Addition of the Carbon–Hydrogen Bond

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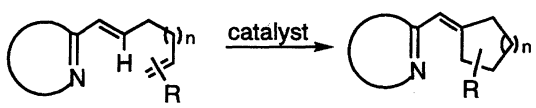
Ruthenium- and rhodium-catalyzed intramolecular C–H/olefin coupling reactions of 1-(2-pyridyl)-, 1-(2-imidazolyl)-, and 1-(2-oxazolyl)-1,5-dienes proceeded in a regiospecific manner to give 5-membered ring products. Their 1,6-diene analogues are also applicable to the cyclization reaction to give the corresponding 5- and 6-membered carbocycles. For the cyclization of the pyridine derivatives, $[RhCl(PPh_3)_3]$ showed the highest catalytic activity with respect to efficiency and selectivity. When the imidazole derivatives were employed to the cyclization reaction, the combination of the rhodium(I) complex and the relatively sterically bulky phosphine (e.g., PCy_3 and PPFOMe) was a quite effective catalyst system. In the case of the oxazoles, the ruthenium complex, $[Ru(H)_2(CO)(PPh_3)_3]$, showed the highest activity among the catalysts examined. These catalytic reactions usually proceed at 120 °C. The $[RhCl(PPh_3)_3]$-catalyzed cyclization reaction of 2-[(1*E*)-4,4-dimethyl-1,5-hexadienyl]pyridine smoothly proceeded even at room temperature to give the corresponding cyclized product in 93% yield after 24 h. A hybrid catalyst system containing the rhodium(I) and both PPh_3 and P(*o*-tolyl)$_3$ had a slightly better catalytic activity compared with that of $[RhCl(PPh_3)_3]$. The intramolecular cyclization can be also applied to the C–H/CO/olefin coupling reactions. These carbonylation reactions gave the 5-membered ring ketones exclusively. The intramolecular C–H/olefin coupling reactions provide a new entry for constructing carbocyclic compounds from 1,*n*-dienes.

A great number of studies of cyclization reactions through a carbon–carbon bond formation (carbocyclization) have appeared in the literature.[1] Metal-catalyzed cyclizations of 1,*n*-dienes are one of the most important strategies for ring constructions, and they have been the subject of a number of studies[2,3] because they provide promising clean chemical processes, without any wasteful by-products. The major methods for olefin dimerization with the aid of transition-metal complexes resulted in no regiospecific C–C bond formation. For example, the sequence of an insertion of an olefin into an M–H bond, followed by an insertion of an olefin into an M–C bond and then by β-hydride elimination, gives a dimerization product having an opposite stereochemistry around the double bond. We have reported transition metal-catalyzed C–H/olefin and C–H/acetylene coupling reactions[4,5] and C–H/CO/olefin coupling reaction,[6] all of which are believed to involve a direct C–H bond cleavage by a transition metal complex. Very recently, other groups have also reported similar C–H/olefin coupling reactions[7—10] and the application of these reactions to synthetic chemistries such as polymerization of acetophenone derivatives.[10] However, there is no previous study on the intramolecular cyclization reactions of 1,*n*-dienes through a direct C–H bond cleavage.[11] Here, we report the transition metal-catalyzed intramolecular C–H/olefin coupling reactions of 1-heteroaryl-1,5- and 1,6-dienes giving 5- or 6-membered carbocycles, which are highly regioselective and stereoselective in most cases. A part of this study has been reported in a preliminary form.[5]

Results

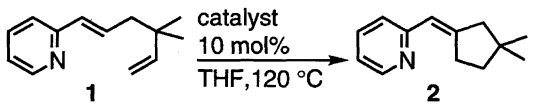
Transition metal-catalyzed intramolecular cyclization of 1,5- and 1,6-dienes having a nitrogen-containing heteroaromatic ring opens a new entry for constructing 5- or 6-membered carbocycles (Eq. 1). The sp^2 nitrogen in pyridine, imidazole, and oxazole rings efficiently worked as a directing atom. Some ruthenium and rhodium complexes are effective for the desired cyclization reactions. The reactions proceeded not only stereospecifically but also regiospecifically in almost all cases. Structures of the heteroaromatic rings and olefin moieties in the 1,*n*-dienes strongly affect the reactivities of the cyclizations. The details of the results are described below.



(1)

Reactions of 1-(2-Pyridyl)-1,5- and 1,6-dienes. Intramolecular cyclization of 2-[(1*E*)-4,4-dimethyl-1,5-hexadienyl]pyridine (**1**) was examined by using various transition-metal complexes as the catalyst (Eq. 2). Some ruthenium complexes, e.g., $[Ru(H)_2(CO)(PPh_3)_3]$, $[Ru(CO)_2(PPh_3)_3]$, and $[Ru(CO)_3(PPh_3)_2]$, were effective for the cyclization reaction with moderate activities. It is important to note that, although the $[Ru(CO)_3(PPh_3)_2]$ complex was an ineffective

catalyst for the reaction of acetophenones with olefins,[4a,4c] this complex catalyzed the cyclization reaction of **1** efficiently. Among the catalyst employed, $[RhCl(PPh_3)_3]$ and $[RhBr(PPh_3)_3]$ showed higher catalytic activities than others. The present cyclization reaction took place cleanly to give the desired 5-membered ring compound **2** as the sole product in high yield.[12] When a rhodium-tricyclohexylphosphine (PCy_3) complex, which was prepared by the reaction of PCy_3 with di-μ-chloro-bis[bis(cyclooctene)rhodium(I)] ($[RhCl(coe)_2]_2$),[7a,7c] was used instead of $[RhCl(PPh_3)_3]$, the yield of **2** reduced to 64% yield. These complexes have been shown by Kim and co-workers to effect intermolecular coupling.[7] Interestingly, the cationic rhodium complex also exhibited catalytic activity, but the efficiency was low compared with those of neutral ones. When $[Ru_3(CO)_{12}]$, which showed a good catalytic activity for the acylation of phenylpyridines,[6b] was used as the catalyst, the reaction gave a complicated mixture. Other complexes such as $[RuCl_2(PPh_3)_3]$, $[Ru(H)(Cl)(CO)(PPh_3)_3]$, [Ru(cod)(cot)], $[RhCl(CO)(PPh_3)_2]$, $[Rh(H)(PPh_3)_4]$, and $[IrCl(CO)(PPh_3)_2]$ were ineffective for the reaction of Eq. 2.

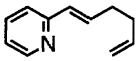
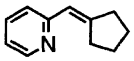
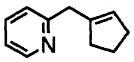
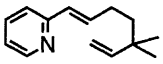
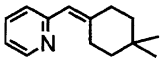
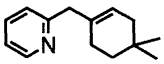
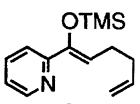
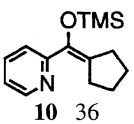
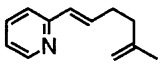
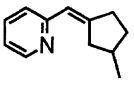
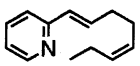
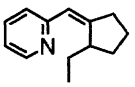


1 **2** (2)

catalyst	time/h	isolated yield/%
$Ru(H)_2(CO)(PPh_3)_3$	15	62
$Ru(CO)_2(PPh_3)_3$	15	86
$Ru(CO)_3(PPh_3)_2$	38	88
$RhCl(PPh_3)_3$	3	89
$RhBr(PPh_3)_3$	2	87
$1/2[RhCl(coe)_2]_2/3PCy_3$	1	64
$[Rh(cod)(PPh_3)_2]PF_6$	19	78

The cyclization reactions can be applied to various pyridyl-1,*n*-dienes (Table 1). The geminal dimethyl groups on **1** are not essential. Cyclization of 1,5-diene **3** took place effectively with the aid of $[RhCl(PPh_3)_3]$ (catalyst **A**) to give **4** in 93% yield (Entry 1). The use of $1/2[RhCl(coe)_2]_2$-$3PCy_3$ (catalyst **B**) in this reaction as the catalyst resulted in the formation of a mixture of double bond isomers **4** and **5** (Entry 2). The cyclization of 1,6-diene **6** using $[RhCl(PPh_3)_3]$ gave the corresponding 6-membered carbocycle **7**,

Table 1. Rhodium-Catalyzed Cyclization of 1-(2-Pyridyl)-1,5- and 1,6-dienes[a]

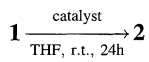
Entry	Catalyst[b]	Substrate	Time/h	Products and Yields/%[c]
1	**A**	 **3**	4	 **4** 93
2	**B**	**3**	3	**4** 52
				 **5** 26
3	**A**	 **6**	70	 **7** 60
4	**B**	**6**	3	**7** 34
				 **8** 52
5	**A**	 **9**	1	 **10** 36
6	**A**	 **11**	1	 **12** 82
7	**A**	 **13**	3	 **14** 84

a) Reaction conditions: 10 mol% of a catalyst in THF, a substrate (0.2 M), 120 °C (oil bath temp).
b) Catalyst **A**: $[RhCl(PPh_3)_3]$; catalyst **B**: $1/2[RhCl(coe)_2]_2$-$3PCy_3$.

though a prolonged reaction period was required (Entry 3). While the catalyst **B** showed the higher activity compared with that of [RhCl(PPh$_3$)$_3$], a double bond isomerization of the product also took place to considerable extent (Entry 4). Addition of the olefinic C–H bond in the enol silyl ether **9** to the double bond also occurred effectively to give the product **10** in 36% isolated yield (Entry 5). This low yield seems to stem from the instability of **10**. The reaction of 2-[(1*E*)-5-methyl-1,5-hexadienyl]pyridine (**11**) was faster than **3** (Entry 6). Interestingly, the addition of the C–H bond to the internal double bond also took place smoothly to afford the corresponding cyclization product (Entry 7). This is in contrast to the results of aromatic ketone/olefin coupling, where internal olefins except for cyclopentene and norbornene were not effective for the ruthenium-catalyzed intermolecular C–H/olefin coupling reactions.[4c] It is also noted that the solvent of choice for the present reaction by rhodium catalysts is THF and not toluene, since conversion of [RhCl(PPh$_3$)$_3$] to insoluble rhodium dimer [RhCl(PPh$_3$)$_2$]$_2$ in an aromatic solvent is a well-known phenomenon.[13]

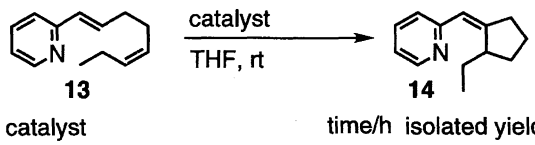
The cyclization of diene **1** proceeded with the aid of [RhCl(PPh$_3$)$_3$] under very mild reaction conditions. The rate of the catalytic reaction decreased with lowering the reaction temperature. Surprisingly, the catalyst was still active for the cyclization reaction even at room temperature.[14] The cyclization reaction of **1** afforded **2** in 93% yield after 24 h. These results are almost satisfactory, but deactivation occurred before complete conversion of **1**. We conjectured that this deactivation might come from the formation of an inactive rhodium dimer, e.g., [RhCl(PPh$_3$)$_2$]$_2$. Actually, after 24 h, the reaction mixture changed from a red solution to an orange suspension which seemed to be the dimer.[13] To improve the catalytic activity, we screened ligands for the reaction of **1** at room temperature (Table 2). The catalytic system consisting of tri(*o*-tolyl)phosphine, (P(*o*-tolyl)$_3$), and [RhCl(coe)$_2$]$_2$ was fairly effective. Although the initial reaction rate of this system was high compared with [RhCl(PPh$_3$)$_3$], a serious deactivation of the catalyst happened at an early stage of the reaction. The use of four equivalents of PPh$_3$ relative to the rhodium atom was also fairly effective. The co-presence of both phenyl- and *o*-tolyl groups on the same phosphorus atom resulted in an intermediate reactivity between PPh$_3$ and P(*o*-tolyl)$_3$. We were pleased to find a notable improvement in the catalytic activity. When a hybrid system using PPh$_3$ and P(*o*-tolyl)$_3$ (20 mol% each) was employed to the reaction, the starting diene **1** was completely converted to **2** within 23 h. Combinations of several other ligands with [RhCl(coe)$_2$]$_2$ gave poorer results compared to that of the hybride system. The use of triphenylarsine was not good for attaining high catalytic activities. Though the combination of PCy$_3$ ligand and [RhCl(coe)$_2$]$_2$ in the cyclization of **1** at 120 °C showed good activity, as described in Eq. 2, this phosphine ligand seriously retarded the catalytic activity at room temperature. Some other phosphine ligands, e.g., PMe$_3$, PPh$_2$Me, and P(2,4,6-Me$_3$C$_6$H$_2$)$_3$, were not effective at all. These results indicate that the efficiency is not consistent with neither steric bulkiness of the phosphine ligand (i.e., cone angle) or the coordination ability (pK_a) of the ligands. When bidentate phosphines, such as 1,3-bis(diphenylphosphino)propane, DPPF,[15] and BINAP[16] were used as the additive, the reaction did not proceed at all even at 120 °C. For the room temperature reaction, [RhBr(PPh$_3$)$_3$] was less effective than [RhCl(PPh$_3$)$_3$]. While the combination of PPh$_3$ and P(*o*-tolyl)$_3$ is still puzzling, this catalyst system can be also applied to the cyclization of **13** (Eq. 3). In this case, the efficiency of the present hybrid phosphine system was much higher than that of [RhCl(PPh$_3$)$_3$]. Detailed understanding of the high activity of the hybrid catalyst system must await further studies.

Table 2. Rhodium-Catalyzed Cyclization of **1** at Room Temperature[a]



Catalyst[b]	Ligands	Yield/%[c]
A	None	93
C	P(*o*-tolyl)$_3$ 30 mol%	29
C	PPh$_3$ 40 mol%	27
C	PPh$_2$(*o*-tolyl) 40 mol%	49
C	PPh$_3$,P(*o*-tolyl)$_3$ (20 mol% each)	Quant (81)[d]
C	AsPh$_3$ 30 mol%	11
C	PCy$_3$ 30 mol%	Trace
D	None	36

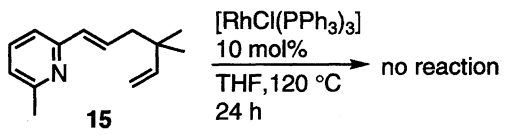
a) Reaction conditions: **1** (0.2 M), Rh-catalyst (5—10 mol%), room temperature (26—29 °C). b) Catalyst **A**: [RhCl(PPh$_3$)$_3$] (10 mol%); catalyst **C**: [RhCl(coe)$_2$]$_2$ (5 mol%); catalyst **D**: [RhBr(PPh$_3$)$_3$] (10 mol%). c) GC yields. d) Isolated yield.



catalyst	time/h	isolated yield/%
[RhCl(PPh$_3$)$_3$]: 10 mol%	74	39
[RhCl(coe)$_2$]$_2$/PPh$_3$/P(*o*-tolyl)$_3$: 5 mol%/20 mol%/20 mol%	20	75

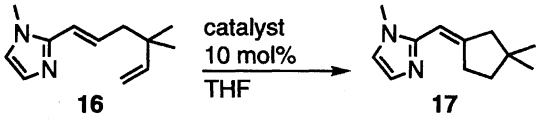
(3)

In all entries, the C–H bonds at the γ-position facing the nitrogen are the bonds which add to the double bonds. These results imply that the coordination of the nitrogen to the rhodium is important to attain these intramolecular cyclization reactions.[17] To confirm the importance of the coordination, a reaction of **15**, in which the coordination of the nitrogen atom to the rhodium center seems to be more difficult than that in **1** due to the steric congestion, was carried out under the same reaction conditions as described in Table 1. Even after 24 h, no conversion of the **15** was observed (Eq. 4). This result indicates that the initial step of the present intramolecular cyclization involves a chelation-assisted C–H bond cleavage.



(4)

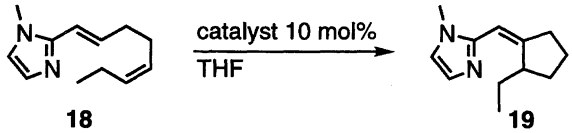
Reactions of (*E*)-1-(2-Imidazolyl)-1,5-dienes. In the reaction of 1-methyl-2-[(1*E*)-4,4-dimethyl-1,5-hexadienyl]-imidazole **16**, $[Ru(H)_2(CO)(PPh_3)_3]$ showed high catalytic activity. Even at lower reaction temperature (70 °C), the desired cyclization reaction also proceeded to give **17** in 78% yield. When $[Ru(CO)_3(PPh_3)_2]$ was used as the catalyst, forcing reaction conditions (vigorously refluxing THF) were required to complete the reaction. The higher reaction temperature seems to be slightly better for attaining high yield, even though the actual parameter of the reaction temperature is not clear at the present time. While the $[RhCl(PPh_3)_3]$ complex showed a low catalytic activity, the catalyst system $[RhCl(coe)_2]_2$-PCy_3 showed the highest catalyst activity among the catalysts examined (Eq. 5).



catalyst	temp/°C	time/h	isolated yield/%
$[Ru(H)_2(CO)(PPh_3)_3]$	120	2	87
$[Ru(H)_2(CO)(PPh_3)_3]$	70	2	78
$[Ru(CO)_3(PPh_3)_2]$	120	40	quant
$[Ru_3(CO)_{12}]$	120	26	83
$[RhCl(PPh_3)_3]$	120	24	83
1/2 $[RhCl(coe)_2]_2$/ 3 PCy_3	120	5	quant

(5)

In contrast to the results as shown in Eq. 5, $[Ru(H)_2(CO)(PPh_3)_3]$ was completely inactive for the cyclization of internal olefin **18** (Eq. 6). Unfortunately, both PPh_3 and PCy_3 rhodium complexes have only low catalytic activity. After screening some other phosphine ligands to find a more effective catalyst system, we finally found that PPFOMe[18] had good activity for the reaction of Eq. 6.[5b] The starting diene **18** was completely converted to the desired cyclization product **19**. This cyclization reaction proceeded even at 50 °C to give **19** in 85% yield after 20 h (Eq. 6).

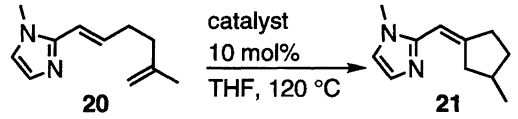


catalyst	temp/°C	time/h	GC yield/%
$[Ru(H)_2(CO)(PPh_3)_3]$	120	60	0
$[RhCl(PPh_3)_3]$	120	24	38
1/2$[RhCl(coe)_2]_2$/3PCy_3	120	16	30
1/2$[RhCl(coe)_2]_2$/3PPFOMe	120	1	quant
1/2$[RhCl(coe)_2]_2$/3PPFOMe	50	20	85

(6)

The Rh-PPFOMe catalyst system was also effective for the cyclization of geminal disubstituted 1,5-diene **20** (Eq. 7). In this case, the use of PPFOMe also improved the catalytic activity of the rhodium complex. Unfortunately, however, this catalyst was completely ineffective for the reaction of 1,6-dienes, as shown in Chart 1.

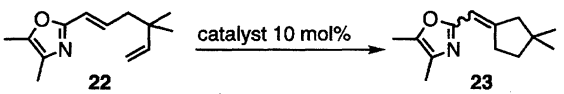
Chart 1. Unreactive 1,6-dienes.



catalyst	time/h	isolated yield/%
$[RhCl(PPh_3)_3]$	24	23
1/2$[RhCl(coe)_2]_2$/3PPFOMe	1	85

(7)

Reaction of (*E*)-1-(2-Oxazolyl)-1,5-dienes. The present intramolecular C–H/olefin coupling reaction can be also applied to oxazole derivatives. The cyclization of 2-[(1*E*)-4,4-dimethyl-1,5-hexadienyl]-4,5-dimethyl-1,3-oxazole **22** proceeded in the presence of $[Ru(H)_2(CO)(PPh_3)_3]$ as the catalyst to give the corresponding product **23** in quantitative yield (Eq. 8). However, in this case, the reaction gave a mixture of *E*- and *Z*-isomers in a ratio of 1 : 1. By switching the reaction parameters, i.e., solvent and reaction temperature, the efficiency dramatically increased (quantitative yield after 1 h), but the stereoselectivity was still low. When the reaction temperature was lowered to 90 °C, the stereoselectivity was slightly improved (*E* : *Z*=7 : 1) albeit in a low yield (20% yield after 24 h). This result suggests that the *E*-isomer should be the kinetic product, not the thermodynamic one. In the reaction of Eq. 8, the use of the rhodium-phosphine complexes as the catalyst resulted in a formation of only *E*-isomer in good to excellent yields while the prolonged reaction period was required. This complete retention of the stereochemistry around the double bond also strongly suggests that the direct cleavage of the C–H bond is the predominant pathway for the present cyclization reaction (vide infra).

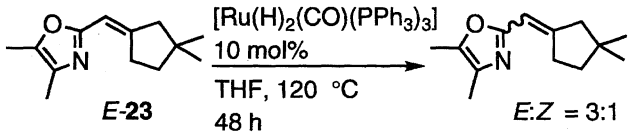


catalyst	solvent	temp/°C	time/h	GC yield/%	*E*:*Z* ratio
$[Ru(H)_2(CO)(PPh_3)_3]$	THF	120	20	quant	1:1
$[Ru(H)_2(CO)(PPh_3)_3]$	octane	140	1	quant	1:1
$[Ru(H)_2(CO)(PPh_3)_3]$	toluene	120	1	quant	1:1
$[Ru(H)_2(CO)(PPh_3)_3]$	toluene	90	24	20	7:1
$[RhCl(PPh_3)_3]$	THF	120	96	21	*E* only
1/2$[RhCl(coe)_2]_2$/ 3PCy_3	THF	120	48	71	*E* only

(8)

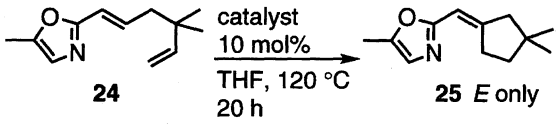
To obtain more information with respect to the stereochemical isomerization from *E* to *Z*, we carried out the reaction of *E*-**23** under the reaction conditions shown in Eq. 9.

This reaction gave a mixture of the *E*- and *Z*-isomers in a ratio of 3 : 1. This stereochemical isomerization of the *E*-isomer indicates that the primary product in the catalytic reaction of Eq. 8 is the *E*-isomer.



(9)

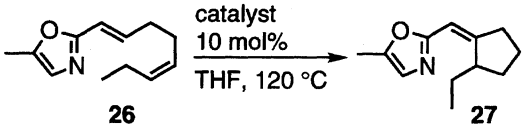
We supposed that this isomerization with inversion of the stereochemistry might be decreased with decreasing the steric crowdness around the sp^2 nitrogen atom, making the *E*-isomer less unstable. Actually, when the reaction of the oxazole **24** which has a methyl group only at the 5 position, the cyclization reaction proceeded with no isomerization around the double bond (Eq. 10)



catalyst	yield/%
$[Ru(H)_2(CO)(PPh_3)_3]$	71 (isolated)
$1/2[RhCl(coe)_2]_2/3PCy_3$	20 (GC)

(10)

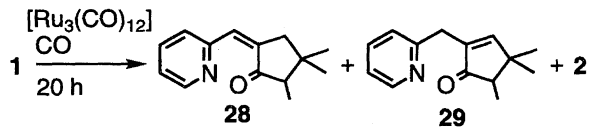
The ferrocenylphosphine PPFOMe also showed a high catalytic activity for the oxazolyl internal olefin **26** (Eq. 11) as observed in the reaction of the imidazolyl olefin **18** (Eq. 6). In this case, the use of tricyclohexylphosphine as the additive resulted in the formation of trace amounts of the cyclization product.



catalyst	time/h	yield/%
$[Ru(H)_2(CO)(PPh_3)_3]$	48	complicated
$1/2[RhCl(coe)_2]_2/3PPFOMe$	24	54 (GC)
$1/2[RhCl(coe)_2]_2/3PCy_3$	48	trace

(11)

Intramolecular C–H/CO/Olefin Coupling Reactions. Chelation-assisted intermolecular C–H/CO/olefin coupling reactions by using transition-metal complexes as the catalyst have been demonstrated by us[6] and others.[19] We extend these carbonylation reactions to intramolecular variants. When the $[Ru_3(CO)_{12}]$-catalyzed coupling reaction of **1** with CO (20 kg cm^{-2}) was carried out in toluene at 160 °C, 5-membered ring ketone **29** was obtained in 47% GC yield, along with C–H/olefin coupling product **2** in 15% GC yield (Scheme 1). Under the milder reaction conditions, the 5-membered ketones **28** and **29** were isolated in 38 and 9% yields, respectively. In this case, the simple cyclization products, which were the mixture of *E*- and *Z*-isomers (*E*/*Z*=89/11) of **2** and the two double-bond isomerization products, were also obtained in 24% total yield. In both cases, only the 5-membered ring ketones were obtained. The present intramolecular C–H/CO/olefin coupling reaction proceeded through an *exo* cyclization predominantly, even though both *exo* and *endo* cyclizations were able to take place.



catalyst	CO	solvent	temp/°C	yield/%		
				28	29	2
10 mol%	20 kg cm^{-2}	toluene	160	0	47	15
3.3 mol%	3 kg cm^{-2}	THF	140	38	9	24

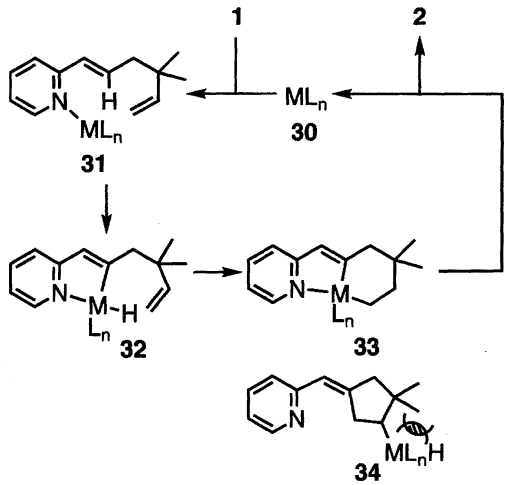
Scheme 1. Carbonylative Intramolecular coupling of 1,5-diene **1**.

Discussion

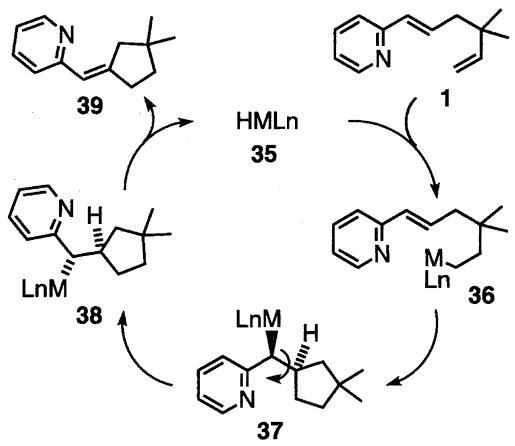
It is premature to speculate on the reaction mechanism at the present time. However, some observations allow us to establish several important features with respect to the intramolecular cyclizations through a C–H bond cleavage. A proposed catalytic cycle is outlined in Scheme 2.

As we previously mentioned in the studies of ruthenium-catalyzed intermolecular C–H/olefin coupling reactions, the present intramolecular C–H/olefin coupling reaction also began with the coordination of the sp^2-nitrogen atom to the metal center.[15] Therefore, the coordination of the nitrogen atom to the metal center brings the metal closer to the C–H bond at the γ-position. After the C–H bond cleavage resulting in **32**, the addition of M–H bond to the olefin moiety (i.e., hydrometallation) occurred to give a 6-membered matallacycle **33**. The addition of M–C bond to the olefin moiety (i.e., carbometallation) giving 5-membered ring intermediate **34** seemed less likely because of the steric congestion. A reductive elimination from **33** (or also **34**) results in a formation of the cyclized product and regenerates the active catalyst **30**.

An alternative mechanism can be drawn for the present carbocyclization reaction and is shown in Scheme 3. The catalytic reaction starts with the addition of the M–H bond to the terminal double bond giving the alkyl-metal intermediate



Scheme 2. A plausible pathway via C–H bond cleavage.

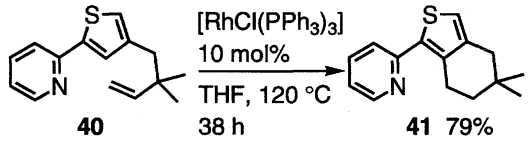


Scheme 3. An alternative mechanism for the cyclization reaction.

36. An intramolecular addition of the M–C bond to the double bond leads to the intermediate **37**. Rotation of the C1–C2 bond forms **38**, in which the MLn fragment is located *syn* to the adjacent hydrogen atom, and following β-hydride elimination this provides the cyclization product **39** and the catalytic active species **35**.

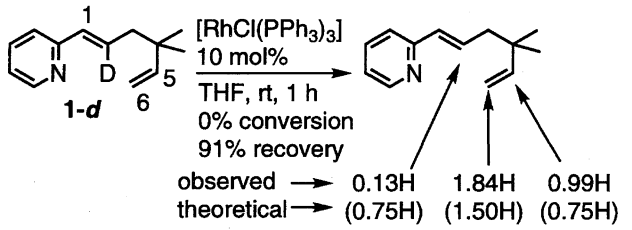
The most important difference between these two mechanisms is the stereochemistry around the double bond. In the former case, the stereochemistry of the double bond should be retained completely in the primary product. On the contrary, in the latter mechanism, the stereochemistry should be completely inverted to the opposite one. In all cases, the very high stereoselectivity of this reaction strongly suggests that the present catalytic reaction proceeds through the direct C–H bond cleavage step (Scheme 2).

The C–H bond in the thiophene ring **40**, in which the C–H bond is not an olefinic one, also added to the olefin under similar reaction conditions. This reaction gave the desired carbocycle **41** as a single regioisomer in 79% yield (Eq. 12). This result also strongly suggests that the present intramolecular C–H/olefin coupling reaction proceeds through the direct C–H bond cleavage reaction by the transition metal complex, not through the hydrometallation pathway shown in Scheme 3.

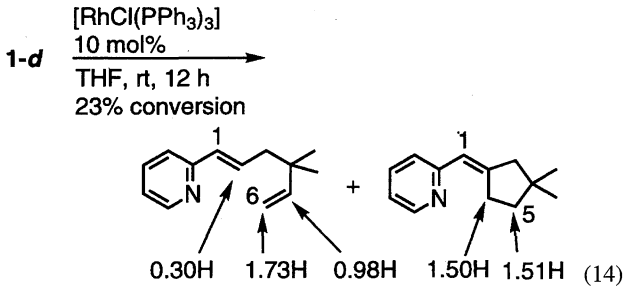


(12)

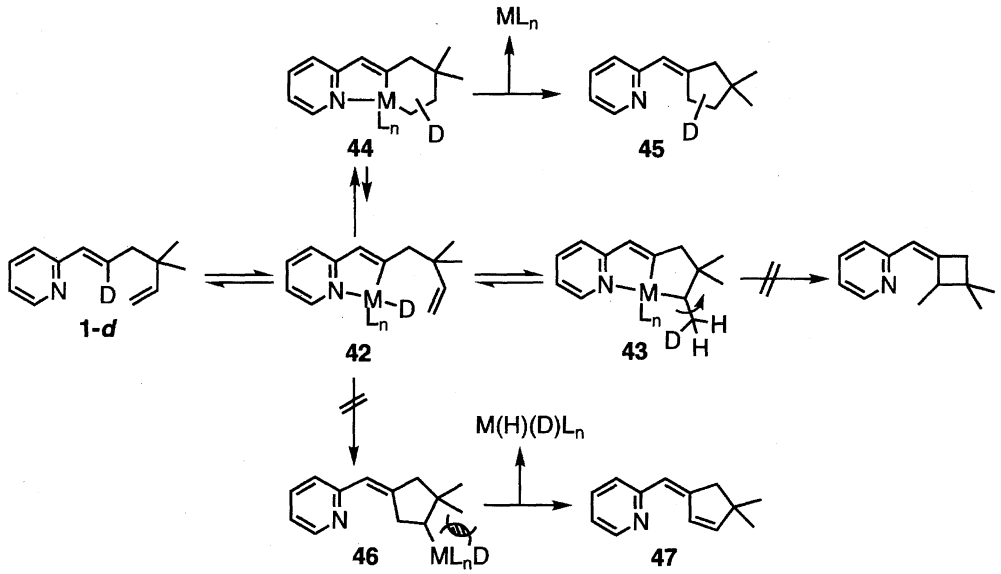
Deuterium labeling experiments are a good probe for uncovering detailed reaction mechanisms. The reactions of monodeuterated compound **1-*d*** were carried out in the presence of $[RhCl(PPh_3)_3]$ as the catalyst (Eqs. 13, 14, and 15). In the reaction of Eq. 13, the reaction was performed at room temperature (26—29 °C) for 1 h, not giving a cyclization product. However, carefull analysis of the recovered starting material by ^{1}H NMR spectroscopy revealed that a partial H/D scrambling took place among four vinylic positions, i.e., one at C2, one at C5 and two at C6 positions, (Eq. 13). If the H/D scrambling occurred completely over these olefinic C–H bond, the integration values at the each hydrogen should be 0.75H (3H/4). Therefore, the vinylic hydrogens at C2 and C5 positions should be observed with 0.75H intensity in each and vinylic hydrogens at C6 position should be observed with 1.50H (0.75H×2) intensity in the ^{1}H NMR spectrum. Even though the observed integration value of each vinylic hydrogen was far from the theoretical value for the complete H/D scrambling, the observed partial H/D scrambling implied that the C–D bond cleavage followed by deuteriometallation of the olefin occurred even at room temperature. The second derterium labeling experiment led to more informative results. The room temperature reaction was stopped after 12 h. The starting material was recovered in 77% yield. The ^{1}H NMR spectrum of this material indicated that the hydrogen intensities of the vinylic positions C2, C5, and C6 were observed with 0.30H, 0.98H, and 1.73H intensities, respectively. This result suggests that the hydrometallation (or deuteriometallation) mainly occurred with *exo* fashion to form a 5-membered metallacycle **43** (vide infra). The cyclization product was isolated in 8% yield. In the ^{1}H NMR spectrum of the cyclization product, the hydrogen intensities of the methylene hydrogens at C5 and C6 were observed with 1.51H and 1.50H, respectively. Another H/D scrambling experiment was examined under the reaction conditions shown in Eq. 15. The starting **1-*d*** was completely converted to the cyclized product and the product was isolated in 91% yield. In the ^{1}H NMR spectrum of the product, the hydrogen intensities of the methylene hydrogens at C5 and C6 were observed with 1.67H and 1.35H, respectively. When the hydrogen intensity at C6 position of the cyclization products of reaction 15 was compared with that of reaction 14, the hydrogen intensity was decreased to 1.33H. This decrease in the intensity showed that the H/D scrambling between at C2 and at C6 positions occurred to a higher extent. Therefore, the equilibrium between **42** and **43** (Scheme 4) seemed to become rapid at a higher temperature than that at room temperature.



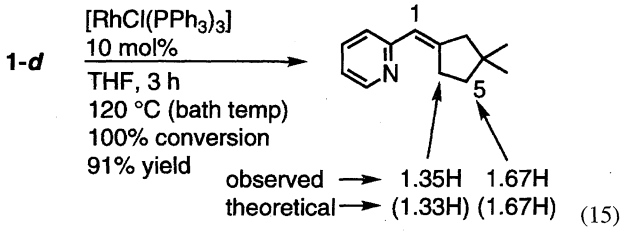
(13)



(14)



Scheme 4. Proposed mechanism for the cyclization reaction.



(15)

The more detailed mechanism involving an equilibrium which is apparently present in the catalytic process is shown in Scheme 4. The direct cleavage of the C–D bond (i.e., C–H bond in Scheme 2) followed by deuterium migration to the terminal carbon atom of the olefinic bond afforded the intermediate **43**. Since no 4-membered carbocycles were observed as the product, the intermediate **43** did not undergo a reductive elimination. The β-hydride (or β-deuterio) elimination from **43** regenerates **42**. By this reaction, one exchange reaction of deuterium and hydrogen was performed. If the equilibrium between **42** and **43** is not present in the catalytic reaction, the hydrogen intensity at C5 in **45** should be observed with 1H intensity. On the other hand, if the equilibrium between **42** and **43** is much faster than the *endo*-hydrometallation step (**42**→**44**), the hydrogen intensities at C5 and C6 in **45** should be observed theoretically with 1.67H and 1.33H, respectively. Actually, when the reaction was carried out at the higher temperature (at 120 °C, Eq. 15), the hydrogen intensities at the C5 and C6 in the cyclization product were observed with 1.67H and 1.35H intensities, respectively, which are almost the same as those of the theoretical values. Therefore, at the higher reaction temperature (at 120 °C), the H/D scrambling is much faster than that of the *endo*-hydrometallation step (**42**→**44**). These findings are close to those of our previous results in the ruthenium-catalyzed intermolecular C–H/olefin coupling reaction.[4c] That a sequence of the carbon–hydrogen cleavage step followed by the olefin insertion step into the metal-hydride bond is easy to attain is the important key feature for accomplishing catalytic C–H/olefin coupling reactions.

There are two possible pathways with respect to the olefin insertion step, as shown in Scheme 4. One is the hydrometallation mechanism (i.e., **42**→**44** in Scheme 4) and the other one is the carbometallation mechanism (i.e., **42**→**46** in Scheme 4). The deuterium labeling study alone does not allow us to distinguish which mechanism is more suitable for the present cyclization reaction. However, we prefer the former mechanism (hydrometallation mechanism) rather than the latter one on the basis of the following reasons: 1) If the reaction takes place through the carbometallation pathway, the cyclization of **11** (Entry 6 in Table 1) should involve a sterically and also electronically less favorable tertiary alkylrhodium intermediate. 2) The formation of the intermediate **46** in the rapid equilibrating system as mentioned above is unlikely since the intermediate **46**, if formed, should give the corresponding by-product **47** by a β-hydride elimination. However, such a by-product **47** was not observed in the reaction mixture. 3) If the reaction of **1** proceeds through the carbometallation mechanism, the rate of the formation of product should become low because of the large vicinal steric repulsion between the MLn fragment and the dimethyl groups on **34** (Eq. 2 and Entry 1 in Table 1), The [RhCl(PPh$_3$)$_3$]-catalyzed reaction of **1** proceeded with the same reaction rate as that of **3** (which has no methyl group) (Entry 2 in Table 1), so that the hydrometallation mechanism leading to the intermediate **33** in Scheme 2, which corresponds to the intermediate **44** in Scheme 4, seems to be more reasonable than the carbometallation mechanism.

The exclusive formations of the 5-membered ketones in the C–H/CO/olefin coupling reaction as described in Scheme 1 may suggest that the reductive elimination from the 6-membered acylmetallacycle species is faster than that from the 7-membered acylmetal species. Thus, insertion of CO into the M–C bond in 5-membered metallacycle such as **43** seem to be faster than that in 6-membered metallacycle such as **44**, which gives the 7-membered metallacycle.

Conclusion

Intramolecular cyclization of 1-(2-pyridyl)-, 1-(2-imidazolyl)-, and 1-(2-oxazolyl)-1,5-dienes and their 1,6-diene analogues took place in the presence of a ruthenium or a rhodium complex as the catalyst to give the corresponding 5- or 6-membered carbocycles. These reactions took place through a C–H bond cleavage, in which the coordination of the sp^2 nitrogen atom to the transition metal center is important for bringing the metal closer to the C–H bond, as we have previously demonstrated in the ruthenium-catalyzed intermolecular C–H/olefin coupling reaction.[4] In the reaction of 1-(2-pyridyl)-1,5- and 1,6-dienes with the aid of $[RhCl(PPh_3)_3]$ as the catalyst, both terminal and internal olefins cyclized to the corresponding carbocycles without any double bond isomerization in high yields. The correct combination of the catalysts and the substrates is essential to attain high catalytic activities. The control experiment with respect to the loss of the stereochemistry in the cyclization of **22** leading to **23** indicated that the isomerized product (*Z*-isomer) seemed to be formed from the primary cyclization product (*E*-isomer). The rhodium-catalyzed cyclization of 1-(2-pyridyl)-1,5-dienes took place even at room temperature. This room-temperature reaction required the co-presence of PPh_3 and P(*o*-tolyl)$_3$ ligands for attaining the high catalytic activity. The deuterium labeling study for the present reaction revealed that the sequence of the C–H bond cleavage followed by the hydrometallation of olefin moiety is easy to accomplish.

Experimental

General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. Chemical shifts of the ^{1}H NMR and ^{13}C NMR signals are quoted relative to tetramethylsilane. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s= singlet, d=doublet, t=triplet, m=multiplet, br=broad), coupling constant (Hz), relative intensity, and assignment. Chemical shifts of ^{13}C NMR spectra are reported in ppm (δ). IR spectra were recorded on a Hitachi 270-50 infrared spectrometer. GCMS analysis was performed on a Shimadzu GCMS-QP 5000 gas chromatography mass spectrometer.

GC Analysis. The conditions of the GC analysis used are as follows: Shimadzu GC-14A (equipped with capillary column Shimadzu CBP-20 25 m×0.2 mm); temperature program 120 °C (0 min)→8 °C/min→230°C (30 min); injection temperature, 270 °C; detector temperature, 270 °C.

Solvents, Materials, and Catalysts. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Toluene was distilled under nitrogen from CaH_2. Diphenyl(2-methylphenyl)phosphine(PPh_2-(*o*-tolyl)) was prepared by the reaction of 2-methylphenyllithium and chlorodiphenylphosphine. Other ligands were purchased from Aldrich Chemical Co. Catalysts, $[Ru(H)_2(CO)(PPh_3)_3]$,[4c,20] $[Ru(CO)_2(PPh_3)_3]$,[21] $[Ru(CO)_3(PPh_3)_2]$,[22] $[Ru(H)(Cl)(PPh_3)_2]$,[20] [Ru(cod)(cot)],[23] $[RhBr(PPh_3)_3]$,[14a] $[RhCl(coe)_2]_2$,[24] Rh[(cod)-$(PPh_3)_2$]PF_4,[25] and $[Rh(H)(PPh_3)_4]$[26] were prepared according to the published methods. Other catalysts, $[RuCl_2(PPh_3)_3]$, $[Ru_3(CO)_{12}]$, $[RhCl(PPh_3)_3]$, $[RhCl(CO)(PPh_3)_2]$, and $[IrCl(CO)$-$(PPh_3)_2]$ were purchased from Aldrich Chemical Co.

2-[(1*E*)-4,4-Dimethyl-1,5-hexadienyl]pyridine (1). To a tetrahydrofuran (70 cm^3) solution of 2-methylpyridine (9.31 g, 100 mmol), butyllithium (1.6 M in hexane, 65 cm^3, 104 mmol, 1 M=1 mol dm^{-3}) was added dropwise below −40 °C under nitrogen. After 10 min, methyl 3,3-dimethyl-4-pentenoate (**48**, 18.5 g, 130 mmol, purchased from Tokyo Kasei Inc.) was added in one quick portion. The reaction mixture was stirred for 10 min, and then worked up in the usual manner. The crude product was purified by silica-gel column chromatography (47 mm i.d.×150 mm length; eluent, hexane/AcOEt=9/1 then 4/1) to give 4,4-dimethyl-1-(2-pyridyl)-5-hexen-2-one (**49**) in 33% yield (6.75 g) as a yellow oil. The NMR spectrum of **49** showed the presence of an equilibrium mixture of keto and enol forms. ^{1}H NMR ($CDCl_3$) δ=1.11, 1.12, 1.13, 1.14 (s, 6H), 2.22 (d, *J*=3.0 Hz, 0.7H), 2.55 (d, *J*=3.2 Hz, 1.3H), 3.87 (d, *J*=3.5 Hz, 1.3H), 4.90—4.99 (m, 2H), 5.26 (d, *J*=3.0 Hz, 0.4H), 5.86—6.03 (m, 1H), 6.86—6.88 (m, 0.7H), 7.12—7.28 (m, 1H), 7.5—7.7 (m, 1H), 8.2 (m, 0.3H), 8.5 (m, 0.7H), 14.8 (br s, 0.3H); ^{13}C NMR ($CDCl_3$) δ=26.92, 36.35, 37.00, 48.97, 53.78, 54.04, 97.70, 109.79, 110.84, 118.02, 120.34, 121.82, 124.15, 136.41, 136.78, 144.40, 146.99, 148.34, 149.43, 154.73, 158.56, 167.94, 206.05; IR (neat) 2956 s, 1716 s, 1642 s, 1600 s, 1554 s, 1474 s, 1390 m, 1236 m, 1166 m, 1046 m, 996 m, 906 s, 800 m, 742 s cm^{-1}. To a methanol (50 cm^3) solution of ketone **49** (5.75 g, 28.4 mmol), sodium borohydride (1.42 g, 37.5 mmol) was added with cooling by an ice bath; the mixture was stirred for 30 min at the same temperature. After the usual workup, 4,4-dimethyl-1-(2-pyridyl)-5-hexen-2-ol (**50**) was obtained as a colorless oil. The crude **50** was dissolved in acetic anhydride (13.4 cm^3, 142 mmol) with a catalytic amount of 4-dimethylaminopyridine, and the mixture was heated at 120 °C for 2.5 h. The mixture was allowed to cool to room temperature and worked up in the usual manner. The crude product was purified by silica-gel column chromatography (30 mm i.d.×140 mm length; eluent, hexane/AcOEt=20/1 then 10/1) to give **1** in 97% yield (5.14 g) from **49** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.06 (s, 6H, CH_3), 2.25 (d, *J*=7.6 Hz, 2H, CH_2), 4.95 (d, *J*=11.8 Hz, 1H, CH=C*H*H), 4.96 (d, 1H, *J*=16.5 Hz, CH=CH*H*), 5.88 (dd, *J*=10.5, 17.8 Hz, 1H, C*H*=CH_2), 6.47 (d, *J*=15.4 Hz, 1H, pyridyl C*H*=CH), 6.88 (dt, *J*=15.7, 7.6 Hz 1H, pyridyl CH=C*H*), 7.09 (dd, *J*=4.7, 7.3 Hz, 1H), 7.25 (d, *J*=7.3 Hz, 1H), 7.59 (t, *J*=7.6 Hz, 1H), 8.53 (d, *J*=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=26.72 (CH_3), 37.20, 46.02, 110.73, 120.95, 121.60, 132.29, 132.43, 136.33, 147.94, 149.43, 156.01; IR (neat) 3076 m, 2960 s, 1642 m, 1586 s, 1470 s, 1432 s, 1380 w, 1298 w, 1186 w, 972 s, 760 s, 742 m cm^{-1}. MS *m/z* (% rel intensity) 187 (M^+; 19), 119 (84), 118 (100). HRMS Found: *m/z* 187.1357. Calcd for $C_{13}H_{17}N$: M, 187.1361.

2-[(1*E*)-4,4-Dimethyl-2-deuterio-1,5-hexadienyl]pyridine (1-*d*) was synthesized as a colorless oil by a similar procedure as described for the preparation of **1** using sodium borodeuteride instead of sodium borohydride for the reduction of **49**.

2-[(1*E*)-1,5-Hexadienyl]pyridine (3). To a mixture of 3-buten-1-ol (2.88 g, 40 mmol), triethylamine (8.3 cm^3, 60 mmol), and dichloromethane (15 cm^3), methanesulfonyl chloride (3.4 cm^3, 44 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 10 min at the same temperature, then worked up in the usual manner to give 3-butenyl methanesulfonate (**51**) as a colorless oil. A mixture of crude **51**, powdered sodium cyanide (2.94 g, 60 mmol), a catalytic amount of sodium iodide, and dimethyl sulfoxide (30 cm^3) heated at 50—60 °C overnight. To the reaction mixture, water (50 cm^3) was added and extracted with three 30 cm^3 portions of diethyl ether. The organic layer was combined and washed with water and then brine, dried over anhydrous magnesium sulfate, and

distilled directly under normal pressure to give 1-cyano-3-butene (**52**) as a colorless liquid. To a tetrahydrofuran (40 cm^3) solution of 2-methylpyridine (6.0 cm^3, 61 mmol), butyllithium (1.6 M in hexane, 39 cm^3, 62 mmol) was added dropwise below −40 °C under nitrogen. After 10 min, **52** was added dropwise to the resulting mixture. The reaction mixture was warmed to room temperature and stirred overnight, and then worked up in the usual manner. The crude product was purified by silica-gel column chromatography (30 mm i.d. ×150 mm length; eluent, hexane/AcOEt=4/1 then 2/1) to give 1-(2-pyridyl)-5-hexen-2-one (**53**, 1.80 g, 26% yield from 3-butene-1-ol) as a yellow oil. **3** was prepared from **53** in 70% yield as a colorless oil by a procedure similar to that described in the preparation of **1** from **49**. ^{1}H NMR ($CDCl_3$) δ=2.22—2.48 (m, 4H, CH_2), 5.01 (d, 1H, J=10.3 Hz, CH=CH*H*), 5.07 (dd, 1H, J=1.6, 17.0 Hz, CH=C*H*H), 5.80—5.95 (m, 1H, C*H*=CH_2), 6.50 (d, J=15.9 Hz, 1H, pyridyl C*H*=CH), 6.74 (dt, J=15.7, 6.2 Hz, 1H, pyridyl CH=C*H*), 7.09 (dd, J=5.9, 7.6 Hz, 1H), 7.24 (d, J=8.1 Hz, 1H), 7.59 (dt, J=1.6, 7.6 Hz, 1H), 8.53 (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=32.22, 33.10, 115.02, 121.02, 121.62, 130.31, 134.91, 136.39, 137.95, 149.43, 155.99; IR (neat) 3072 m, 2916 s, 2844 m, 1736 w, 1646 m, 1586 s, 1472 s, 1298 w, 972 s, 908 s, 750 s cm^{-1}. MS *m/z* (% rel intensity) 159 (M^+; 31), 118 (100), 117 (63). HRMS Found: *m/z* 159.1027. Calcd for $C_{11}H_{13}N$: M, 159.1048.

2-[(1*E*)-5,5-Dimethyl-1,6-heptadienyl]pyridine (6). To a mixture of lithium aluminum hydride (1.5 g, 40 mmol) and dry tetrahydrofuran (15 cm^3), **48** (5.0 g, 35 mmol) was added dropwise at 0 °C. After stirring at room temperature for 10 min, the reaction mixture was worked up in the usual manner given in the literature (see: M. Fieser and L. S. Fieser, "Reagents for Organic Synthesis," Vol. 1, p. 581, John Wiley & Sons, New York (1967)) to give 3, 3-dimethyl-4-penten-1-ol (**53**) as a colorless oil in quantitative yield. Diene **6** was synthesized from **53** by a procedure similar to that described in the preparation of **3** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.03 (s, 6H, CH_3), 1.45—1.52 (m, 2H, CH_2), 2.18 (dd, J=6.8, 15.3 Hz, 2H, CH_2), 4.90—4.97 (m, 2H, CH=C*H*$_2$), 5.73—5.84 (m, 1H, C*H*=H_2), 6.47 (d, J=15.7 Hz, 1H, pyridyl C*H*=CH), 6.72 (dt, J=15.4, 7.0 Hz, 1H, pyridyl CH=C*H*), 7.07 (dd, J=5.4, 1.4 Hz, 1H), 7.22 (d, J=8.1 Hz, 1H), 7.58 (dt, J=1.6, 7.6 Hz, 1H), 8.51 (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=26.70, 28.14, 36.55, 41.72, 110.73, 120.86, 121.47, 129.50, 136.35, 147.96, 149.32, 156.13; IR (neat) 2960 s, 1652 m, 1586 s, 1470 s, 1204 m, 966 m, 908 s, 742 s cm^{-1}. MS *m/z* (% rel intensity) 201 (M^+; 31), 186 (95), 132 (73), 130 (100), 118 (88), 117 (96), 93 (86). HRMS Found: *m/z* 201.1530. Calcd for $C_{14}H_{19}N$: M, 201.1517.

Trimethylsilyl (1*Z*)-1-(2-Pyridyl)-1,5-hexadienyl Ether (9). To a mixture of 5-hexenoic acid (1.98 g, 17 mmol), triethylamine (7.2 cm^3, 52 mmol), and dichloromethane (34 cm^3), ethyl chloroformate 2.2 cm^3, 22 mmol) was added dropwise below −20 °C. After the reaction mixture was stirred for 20 min at the same temperature, diethylamine (2.7 cm^3, 26 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h, and worked up in the usual manner. The crude product was filtered through a pad of silica-gel and eluted (hexane/AcOEt=4/1) to give *N,N*-diethyl-5-hexenamide **54** (impure, 3.5 g) as a colorless oil. To a tetrahydrofuran (10 cm^3) solution of 2-bromopyridine (2.52 g, 16 mmol), butyllithium (1.56 M in hexane, 10.7 cm^3, 16.7 mmol) was added dropwisely below −50 °C under nitrogen. After 1 h, **54** (1.35 g) was added to the resulting mixture. The reaction mixture was stirred at 0 °C for 1 h, and then worked up in the usual manner. The crude product was purified by silica-gel column chromatography (30 mm i.d. ×140 mm length; eluent, hexane/AcOEt=20/1) to give 2-(5-hexenoyl)pyridine (**55**, 845 mg, 63% from 5-hexenoic acid) as a yellow oil. Enol silyl ether **9** was obtained from **55** by the usual method of enol silyl ether formation by using trimethylsilyl trifluoromethanesulfonate and diethylisopropylamine. ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 9H, $(CH_3)_3SiO$), 2.22 (dd, 2H, J=6.5, 13.5 Hz, CH_2), 2.35 (dd, 2H, J=6.2, 14.3 Hz, CH_2), 4.99 (d, 1H, J=10.0 Hz, CH=CH*H*), 5.07 (d, 1H, J=17.0 Hz, CH=C*H*H), 5.80—5.95 (m, 1H, C*H*=CH_2), 6.03 (t, J=7.0 Hz, 1H, pyridyl C=C*H*), 7.13 (dd, J=4.6, 7.6 Hz, 1H), 7.46 (d, J=7.8 Hz, 1H), 7.64 (dt, J=1.9, 7.8 Hz, 1H), 8.52 (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.63, 25.68, 33.43, 113.21, 114.66, 119.05, 121.94, 136.23, 138.33, 148.01, 148.82, 155.72.

2-[(1*E*)-5-Methyl-1,5-hexadienyl]pyridine (11). A mixture of 2-methyl-2-propen-1-ol (5 cm^3), trimethyl orthoacetate (15 cm^3), and a catalytic amount of pivalic acid was heated at 140 °C overnight. After a distillation of the reaction mixture, 4-methyl-4-pentenoic acid methyl ester (**56**, 4.0 g, bp 150—152 °C) was obtained as a colorless liquid. Diene **11** was obtained from **56** by a procedure similar to that described for the preparation of **1** from **48** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.77 (s, 3H, CH_3), 2.22 (t, J=8.4 Hz, 2H, CH_2), 2.40 (dd, J=7.3, 14.9 Hz, 2H, CH_2), 4.75 (s, 2H, C=C*H*$_2$), 6.51 (d, J=15.9 Hz, 1H, pyridyl C*H*=CH), 6.74 (dt, J=15.9, 6.5 Hz, 1H, pyridyl CH=C*H*), 7.09 (dd, J=7.6, 12.2 Hz, 1H), 7.25 (d, J=8.9 Hz, 1H), 7.60 (dt, J=1.6, 7.6 Hz, 1H), 8.53 (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=22.50, 30.96, 37.05, 110.35, 120.95, 121.56, 130.13, 135.18, 136.33, 144.99, 149.40, 156.04; IR (neat) 2916 s, 1652 m, 1588 s, 1472 s, 1146 m, 966 s, 886 s, 744 s cm^{-1}. MS *m/z* (% rel intensity) 173 (M^+; 28), 118 (100), 117 (75). HRMS Found: *m/z* 173.1185. Calcd for $C_{12}H_{15}N$: M, 173.1204.

2-[(1*E*,5*Z*)-1,5-Octadienyl]pyridine (13) was obtained from (*Z*)-3-hexen-1-ol as a colorless oil by a procedure similar to that described for the preparation of **3**. ^{1}H NMR ($CDCl_3$) δ=0.96 (t, J=7.3 Hz, 3H, CH_3), 2.06 (dt, J=13.2, 7.3 Hz, 2H, CH_2), 2.18—2.39 (m, 4H, CH_2), 5.40 (ddt, J=8.9, 10.5, 5.9 Hz, 2H, CH_2CH=C*H*CH_2), 6.50 (d, J=15.9 Hz, 1H, pyridyl C*H*=CH), 6.74 (dt, J=15.9, 6.8 Hz, 1H, pyridyl CH=C*H*), 7.05—7.10 (m, 1H), 7.24 (d, J=7.8 Hz, 1H), 7.59 (dt, J=2.2, 8.1 Hz, 1H), 8.52 (d, J=4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.30, 20.59, 26.65, 33.01, 120.91, 121.56, 128.03, 130.24, 132.41, 135.25, 136.33, 149.41, 156.10; IR (neat) 2964 s, 1654 m, 1586 s, 1470 s, 968 s, 746 s cm^{-1}. MS *m/z* (% rel intensity) 187 (M^+; 5), 119 (67), 118 (100). HRMS Found: *m/z* 187.1340. Calcd for $C_{13}H_{17}N$: M, 187.1361.

2-[(1*E*)-4,4-Dimethyl-1,5-hexadienyl]-6-methylpyridine (15) was obtained from 2,6-dimethylpyridine and **48** as a colorless oil by a procedure similar to that described for the preparation of **1**. ^{1}H NMR ($CDCl_3$) δ=1.05 (s, 6H, CH_3), 2.24 (d, J=7.3 Hz, 2H, CH_2), 2.53 (s, 3H, CH_3), 4.95 (d, J=11.9 Hz, 1H, CH=C*H*H), 4.96 (d, 1H, J=16.2 Hz, CH=CH*H*), 5.87 (dd, J=10.0, 17.8 Hz, 1H, C*H*=CH_2), 6.46 (d, J=15.9 Hz, 1H, pyridyl C*H*=CH), 6.60 (dt, J=15.7, 7.6 Hz, 1H, pyridyl C*H*=C*H*), 6.95 (d, J=7.6 Hz, 1H), 7.12 (d, J=7.8 Hz, 1H), 7.48 (t, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=24.6, 26.72 (CH_3×2), 37.20, 46.04, 110.65, 117.52, 121.13, 131.96, 132.81, 136.44, 148.01, 155.60, 157.91; IR (neat) 2964 s, 1642 m, 1576 s, 1454 s, 1376 m, 974 s, 776 s cm^{-1}. MS *m/z* (% rel intensity) 201 (M^+; 24), 133 (68), 132 (100). HRMS Found: *m/z* 201.1509. Calcd for $C_{14}H_{19}N$: M, 201.1517.

1-Methyl-2-[(1*E*)-4,4-dimethyl-1,5-hexadienyl]imidazole (16) was obtained from 1,2-dimethylimidazole and **48** as a colorless oil by a procedure similar to that described for the preparation of **1**. ^{1}H NMR ($CDCl_3$) δ=1.05 (s, 6H, CH_3), 2.23 (dd, J=7.6, 1.3 Hz, 2H, CH_2), 3.61 (s, 3H, NCH_3), 4.93 (d, J=11.0 Hz, 1H, CH=C*H*H), 4.94 (d, J=16.8 Hz, 1H, CH=CH*H*), 5.84 (dd, J=11.0, 16.8 Hz, 1H, C*H*=CH_2), 6.23 (dt, J=15.4, 1.3 Hz, 1H, imidazolyl C*H*=CH),

6.63 (dt, J=15.4, 7.6 Hz, 1H, imidazolyl CH=C*H*), 6.79 (s, 1H), 6.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=26.58 (CH_3), 32.58 (NCH_3), 37.02 ($C(CH_3)_2$), 46.29 (CH_2), 110.73 (CH=*C*H$_2$), 117.77 (imidazolyl *C*H=), 120.68, 128.10, 132.60 (imidazolyl CH=*C*H), 145.55, 147.67 (*C*H=CH$_2$); IR (neat) 2962 s, 1655 m, 1515 m, 1485 s, 1413 s, 1378 m, 1281 s, 1184 m, 1152 m, 1074 m, 968 s, 909 s, 800 m, 722 s cm^{-1}. MS *m/z* (% rel intensity) 190 (M^+; 15), 121 (100). HRMS Found: *m/z* 190.1453. Calcd for $C_{12}H_{18}N_2$: M, 190.1470.

1-Methyl-2-[(1*E*, 5*Z*)-1,5-octadienyl]imidazole (18). (*Z*)-1-Cyano-3-hexene **57** was prepared from (*Z*)-3-hexen-1-ol by a procedure similar to that described for the preparation of **52** as a colorless oil. A mixture of **57** (5.5 g, 50 mmol), sodium hydroxide (11 g), and ethylene glycol (100 cm^3) was heated at 130 °C overnight, and then acidified (3 M hydrochloric acid). After the usual work-up, (*Z*)-4-heptenoic acid **58** (5.8 g, 90%) was obtained. *N,N*-Diethyl-(*Z*)-4-hexenamide **59** was obtained from **58** by a procedure similar to that described for the preparation of **54** as a colorless oil. To a tetrahydrofuran (5 cm^3) solution of 1,2-dimethylimidazole (576 mg, 6 mmol), butyllithium (1.6 M in hexane, 4.8 cm^3, 7.2 mmol) was added dropwise below −50 °C under nitrogen. After 1 h, **59** (915 mg, 5 mmol) was added to the resulting mixture. The reaction mixture was warmed to room temperature and stirred for 1 h, and then worked up in the usual manner. The crude product was purified by silica-gel column chromatography (25 mm i.d. ×200 mm length; eluent, dichloromethane/methanol/28%NM_3 aq=300/5/0.5) to give (*Z*)-1-(1-methyl-1*H*-imidazole-2-yl)-5-octen-2-one (**60**, 196 mg, 20%) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ=0.94 (t, J=7.6 Hz, 3H, CH_3), 2.03 (quintet, J=7.6 Hz, 2H, CH_2), 2.29 (quartet, J=7.4 Hz, 2H, CH_2), 2.57 (t, J=7.4 Hz, 2H, CH_2), 3.56 (s, 3H, CH_3), 3.84 (s, 2H, CH_2), 5.17—5.42 (m, 2H, CH=CH), 6.84 (s, 1H), 6.95 (s, 1H). **18** was prepared from **60** in 32% yield as a oil by a procedure similar to that described for the preparation of **1** from **49**. ^{1}H NMR ($CDCl_3$) δ=0.96 (t, J=7.6 Hz, 3H, CH_3), 2.05 (quintet, J=7.6 Hz, 2H, CH_2), 2.20—2.32 (m, 4H, CH_2CH_2), 3.62 (s, 3H, CH_3), 5.39 (ddt, J=5.1, 10.3, 6.2 Hz, 2H, (*Z*)CH=CH), 6.26 (d, J=15.4 Hz, 1H, imidazolyl C*H*=CH), 6.70 (dt, J=15.4, 6.6 Hz, 1H, imidazolyl CH=C*H*), 6.79 (s, 1H), 6.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=14.22, 20.52, 26.54, 32.58, 33.28, 115.87, 120.68, 127.85, 128.03, 132.38, 135.54, 145.62; IR (neat) 3006 s, 2964 s, 1657 m, 1515 m, 1486 s, 1411 m, 1281 s, 962 s, 725 s cm^{-1}. MS *m/z* (% rel intensity) 190 (M^+; 5), 121 (100). HRMS Found: *m/z* 190.1456. Calcd for $C_{12}H_{18}N_2$: M, 190.1470.

1-Methyl-2-([(1*E*)-5-methyl-1,5-hexadienyl]imidazole (20) was obtained from 1,2-dimethylimidazole and **56** by a procedure similar to that described for the preparation of **1** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.75 (s, 3H, CH_3), 2.20 (t, J=8.1 Hz, 2H, CH_2), 2.40 (dd, J=8.4, 15.4 Hz, 2H, CH_2), 3.62 (s, 3H, CH_3), 4.73 (br s, 2H, C=C*H*$_2$), 6.27 (d, J=15.9 Hz, 1H, imidazolyl C*H*=CH), 6.67 (dt, J=15.9, 6.8 Hz, 1H, imidazolyl CH=C*H*), 6.79 (s, 1H), 6.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=22.45, 31.22, 32.60 37.04, 110.41, 115.85, 120.72, 128.16, 135.44, 144.87, 145.68; IR (neat) 2932 s, 1650 m, 1516 s, 1484 s, 1130 m, 960 s, 884 s, 732 s cm^{-1}. MS *m/z* (% rel intensity) 176 (M^+; 29), 121 (100). HRMS Found: *m/z* 176.1319. Calcd for $C_{11}H_{16}N_2$: M, 176.1313.

2-[(1*E*)-4,4-Dimethyl-1,5-hexadienyl]-4,5-dimethyl-1,3-oxazole (22) was obtained from 2,4,5-trimethyloxazole and **48** as a colorless oil by a procedure similar to that described for the preparation of **1**. ^{1}H NMR ($CDCl_3$) δ=1.04 (s, 6H, CH_3), 2.07 (s, 3H, oxazolyl CH_3), 2.20 (dd, J=7.9, 1.7 Hz, 2H, CH_2), 2.22 (s, 3H, oxazolyl CH_3), 4.95 (dd, J=17.8, 1.3 Hz, 1H, CH=CH*H*), 4.95 (dd, J=10.2, 1.3 Hz, 1H, CH=CH*H*), 5.83 (dd, J=10.2, 17.8 Hz, 1H, C*H*=CH$_2$), 6.15 (dt, J=15.8, 1.3 Hz, 1H, oxazolyl CH=C*H*), 6.53 (dt, J=15.8, 7.9 Hz, 1H, oxazolyl CH); ^{13}C NMR ($CDCl_3$) δ=9.92 (oxazolyl CH_3), 11.11 (oxazolyl CH_3), 26.63 (CH_3), 37.10 ($C(CH_3)_2$), 45.90 (CH_2), 110.93 (CH=*C*H$_2$), 118.85 (oxazolyl *C*H), 131.21, 134.72 (oxazolyl CH=*C*H), 142.39, 147.49 (*C*H=CH$_2$), 158.63; IR (neat) 2962 s, 1642 m, 1453 w, 1383 w, 1337 w, 1258 w, 1190 w, 1001 w, 971 m, 800 w, 680 w cm^{-1}. MS *m/z* (% rel intensity) 205 (M^+; 9), 136 (100). HRMS Found: *m/z* 205.1465. Calcd for $C_{13}H_{19}NO$: M, 205.1467.

2-[(1*E*)-4,4-Dimethyl-1,5-hexadienyl]-5-methyl-1,3-oxazole (24) was obtained from 2,5-dimethyloxazole[27] and **48** as a colorless oil by a procedure similar to that described for the preparation of **1**. ^{1}H NMR ($CDCl_3$) δ=1.04 (s, 6H, CH_3), 2.21 (dd, J=7.9, 1.3 Hz, 2H, CH_2), 2.30 (d, J=1.0 Hz, 3H, $ArCH_3$), 4.96 (dd, J=10.6, 1.3 Hz, 1H, CH=C*H*H), 4.96 (dd, J=17.8, 1.3 Hz, 1H, CH=CH*H*), 5.83 (dd, J=10.6, 17.8 Hz, 1H, C*H*=CH$_2$), 6.20 (dt, J=15.8, 1.3 Hz, 1H, ArCH), 6.56 (dt, J=15.8, 7.9 Hz, 1H, ArCH=C*H*), 6.68 (d, J=1.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ=10.87 (oxazolyl CH_3), 26.63 (CH_3), 37.07 ($C(CH_3)_2$), 45.82 (CH_2), 110.98 (CH=*C*H$_2$), 118.83 (oxazolyl CH), 123.61, 135.20 (oxazolyl CH=*C*H), 147.44 (*C*H=CH$_2$), 147.89, 160.18; IR (neat) 2966 s, 1662 w, 1606 m, 1532 m, 1461 w, 1381 w, 1259 w, 1194 w, 1012 m, 973 m, 822 w, 732 w cm^{-1}. MS *m/z* (% rel intensity) 191 (M^+; 9), 123 (100), 122 (54), 69 (84). HRMS: Found: *m/z* 191.1296. Calcd for $C_{12}H_{17}NO$: M, 191.1310.

2-[(1*E*)-1,5-Octadienyl]-5-methyl-1,3-oxazole (26) was obtained from 2,5-dimethyloxazole[27] as a colorless oil by a procedure similar to that described in the preparation of **18**. ^{1}H NMR ($CDCl_3$) δ=0.96 (t, J=7.4 Hz, 3H, CH_3), 2.05 (quintet, J=7.4 Hz, 2H, CH_2), 2.20—2.30 (m, 4H, CH_2CH_2), 2.30 (d, J=0.9 Hz, 3H, CH_3), 5.38 (ddt, J=5.1, 10.3, 6.2 Hz, 2H, (*Z*)CH=CH), 6.24 (d, J=15.9 Hz, 1H, oxazolyl C*H*=CH), 6.62 (dt, J=15.9, 6.5 Hz, 1H, oxazolyl CH=C*H*), 6.69 (d, J=0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=10.82 (oxazolyl CH_3), 14.14 (CH_3), 20.51 (CH_2CH_3), 26.18 (CH_2), 32.72 (CH_2), 117.02, (oxazolyl *C*H), 123.58, 127.44 ((*Z*)CH=CH), 132.61 ((*Z*)CH=CH), 137.81 (oxazolyl CH=*C*H), 147.82, 160.23; IR (neat) 2966 s, 1663 m, 1532 m, 1454 m, 1347 m, 1239 w, 1106 m, 1012 m, 970 s, 823 m cm^{-1}. MS *m/z* (% rel intensity) 191 (M^+; 10), 122 (100). HRMS Found: *m/z* 191.1294. Calcd for $C_{12}H_{17}NO$: M, 191.1310.

2-[4-(2,2-Dimethyl-3-butenyl)-2-thienyl]pyridine (40). To a mixture of 3-thiophenecarbaldehyde (5.60 g, 50 mmol), *N,N*-dimethylformamide (15 cm^3), and zinc powder (4.9 g, 75 mmol) was added a solution of 1-bromo-3-methyl-2-butene (10.0 g, 67 mmol) in *N,N*-dimethylformamide (20 cm^3) at 90 °C over a period of 4 h. After being heated overnight at 90 °C, the reaction mixture was allowed to cool to room temperature, poured into ice-cooled 3 M hydrochloric acid (100 cm^3), and worked up by the usual method. The crude product was purified by silica-gel column chromatography (30 mm i.d. ×70 mm length; eluent, hexane/AcOEt=20/1) to give 1-(3-thienyl)-2,2-dimethyl-3-buten-1-ol (**61**) in 49% yield (4.46 g) as a pale yellow oil. ^{1}H NMR ($CDCl_3$) 0.99 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 2.10 (d, J=3.0 Hz, 1H, OH), 4.53 (d, J=3.0 Hz, C*H*OH), 5.08 (d, J=17.6 Hz, 1H, CH=CH*H*), 5.13 (d, J=10.8 Hz, 1H, CH=C*H*H), 5.92 (dd, J=17.6, 10.8 Hz, 1H, C*H*=CH$_2$), 7.02 (dd, J=1.4, 4.9 Hz, 1H, thienyl), 7.13 (t, J=1.9 Hz, 1H, thienyl), 7.23 (dd, J=3.0, 4.6 Hz, 1H, thienyl). To a mixture of **61** (4.46 g, 24.5 mmol) and triethylsilane (5.9 cm^3, 36.7 mmol) was added trifluoroacetic acid (3.8 cm^3, 49 mmol). The reaction mixture was kept at room temperature for 10 min, and then worked up in the usual manner. The crude product was purified by silica-gel column chromatography (30 mm i.d. ×150 mm length; eluent, hexane) to give 3-(2,2-dimethyl-3-butenyl)thiophene (**62**) in 34% yield (1.39

g) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.00 (s, 6H, CH_3), 2.60 (s, J=3.0 Hz, CH_2), 4.88 (d, J=17.3 Hz, 1H, CH=CH*H*), 4.92 (d, J=9.4 Hz, 1H, CH=C*H*H), 5.85 (dd, J=17.0, 10.5 Hz, 1H, C*H*=CH_2), 6.86—6.90 (m, 2H, thienyl), 7.18 (dd, J=4.6, 3.2 Hz, 1H, thienyl). To a solution of **62** (310 mg, 1.86 mmol) in tetrahydrofuran (2 cm^3) was added butyllithium (1.57 M in hexane, 1.7 cm^3, 2.7 mmol) dropwise below −40 °C. The solution was warmed to 0 °C and stirred for 10 min, and then cooled below −40 °C again. To the reaction mixture, a solution of anhydrous zinc bromide (840 mg, 3.7 mmol) in tetrahydrofuran (1.0 cm^3) was added, then warmed to 0 °C. To the reaction mixture, 2-bromopyridine (442 mg, 2.8 mmol) and tetrakis(triphenylphosphine)palladium (108 mg, 0.093 mmol) were added. The reaction mixture was stirred at 50 °C for 1 h, and then worked up in the usual manner. The crude product was purified by silica-gel column chromatography (21 mm i.d. ×80 mm length; eluent, hexane/AcOEt=50/1 then 30/1) to give **40** (167 mg) in 37% yield as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.03 (s, 6H, CH_3), 2.59 (s, 2H, CH_2), 4.90 (d, J=17.6 Hz, 1H, CH=CH*H*), 4.94 (d, J=10.5 Hz, 1H, CH=C*H*H), 5.88 (dd, J=10.5, 17.6 Hz, 1H, C*H*=CH_2), 6.97 (s, 1H, thienyl), 7.05—7.15 (m, 1H), 7.37 (s, 1H, thienyl), 7.56—7.64 (m, 2H), 8.54 (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=26.40, 37.20, 43.47, 110.71, 118.49, 121.49, 124.75, 127.51, 136.37, 140.14, 143.16, 147.72, 149.33, 152.54; IR (neat) 2956 s, 1640 m, 1588 s, 1476 s, 1380 m, 1290 m, 1150 m, 996 m, 908 s, 846 m, 778 s, 696 m cm^{-1}. MS m/z (% rel intensity) 243 (M^+; 28), 174 (100). HRMS Found: m/z 243.1087. Calcd for $C_{15}H_{17}NS$: M, 243.1082.

A Typical Procedure for the Reaction of 1-Heteroaryl-1,5- and 1,6-Dienes. A 10 cm^3, two-neck round-bottomed flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen, and then the apparatus was flame-dried under a flow of dry nitrogen. In the flask was placed catalyst (0.040 mmol), hexadecane (50 mg), and solvent (0.5 ml) under a flow of nitrogen. After the mixture was stirred for 5 min, a solvent (1.5 ml) solution of substrate (0.4 mmol) was charged. The mixture was stirred at the appropriate temperature. Progress of the reaction was monitored by TLC and GC. After being stirred for an appropriate period, the mixture was allowed to cool to room temperature and tetrahydrofuran was removed by rotary evaporation (35 °C/5 mmHg, 1 mmHg=133.322 Pa). The residue was purified by column chromatography.

((*E*)-3,3-Dimethylcyclopentyliden)(2-pyridyl)methane (2). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.03 (s, 6H, CH_3), 1.62 (t, J=7.6 Hz, 2H, CH_2), 2.35 (s, 2H, CH_2), 2.82 (t, J=7.6 Hz, 2H, CH_2), 6.45 (d, J=1.9 Hz, 1H, CH=), 7.00 (t, J=5.4 Hz, 1H), 7.22 (d, J=7.8 Hz, 1H), 7.57 (dt, J=1.6, 7.6 Hz, 1H), 8.55 (d, J=4.1 Hz, 1H). Irradiation of the vinyl proton at δ=6.45 gave a 3% NOE of the singlet methylene proton at δ=2.35 (at the 2-position). ^{13}C NMR ($CDCl_3$) δ=27.44 (CH_3), 30.77 (CH_2), 37.70 ($C(CH_3)_2$), 40.72 (CH_2), 51.12 (CH_2), 120.02 (pyridyl), 121.78 (C=*C*H), 122.55 (pyridyl), 135.74 (pyridyl), 140.09 (pyridyl), 152.69, 157.39 (pyridyl or *C*=CH); IR (neat) 2940 s, 1656 s, 1586 s, 1466 s, 738 m, 528 m cm^{-1}. MS m/z (% rel intensity) 188 (M+1$^+$; 15), 187 (M^+; 100), 172 (94), 130 (65). HRMS Found: m/z 187.1360. Calcd for $C_{13}H_{17}N$: M, 187.1361.

(Cyclopentyliden)(2-pyridyl)methane (4). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.67 (quintet, J=6.8 Hz, 2H, CH_2), 1.78 (quintet, J=6.8 Hz, 2H, CH_2), 2.55 (br t, 2H, CH_2), 2.71 (br t, 2H, CH_2), 6.48 (s, 1H, CH=), 7.01 (t, J=5.1 Hz, 1H), 7.21 (d, J=7.8 Hz, 1H), 7.58 (t, J=7.6 Hz, 1H), 8.55 (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=25.61 (CH_2), 27.13 (CH_2), 31.93 (CH_2), 36.19 (CH_2), 120.11 (pyridyl), 121.11 (C=*C*H), 122.60 (pyridyl), 135.78 (pyridyl), 149.14 (pyridyl), 152.72, 157.55 (pyridyl or *C*=CH); IR (neat) 2948 s, 1654 s, 1586 s, 1468 s, 736 s cm^{-1}. MS m/z (% rel intensity) 159 (M^+, 69), 158 (100). HRMS Found: m/z 159.1037. Calcd for $C_{11}H_{13}N$: M, 159.1048.

(1-Cyclopentenyl)(2-pyridyl)methane (5). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.87 (quintet, J=7.8 Hz, 2H, CH_2), 2.20—2.40 (br m, 4H, CH_2), 2.71 (br t, 2H, CH_2), 3.59 (s, 2H, pyridyl CH_2), 5.37 (s, 1H, C=CH), 7.08—7.21 (m, 2H), 7.60 (t, J=7.6 Hz, 1H), 8.54 (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=23.36, 32.41, 34.85, 40.53, 120.99, 122.94, 126.19, 136.21, 142.18, 149.21, 160.08; IR (neat) 2948 s, 2846 s, 1593 s, 1571 m, 1477 s, 1436 s, 1293 w, 1144 w, 1034 m, 917 w, 774 s, 729 s cm^{-1}. MS m/z (% rel intensity) 159 (M^+; 66), 158 (74), 131 (100), 130 (70). HRMS Found: m/z 159.1053. Calcd for $C_{11}H_{13}N$: M, 159.1048.

(4,4-Dimethylcyclohexyliden)(2-pyridyl)methane (7). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.98 (s, 6H, CH_3), 1.38 (t, J=6.8 Hz, 2H, CH_2), 1.47 (t, J=6.5 Hz, 2H, CH_2), 2.32 (t, J=6.2 Hz, 2H, CH_2), 2.68 (t, J=6.8 Hz, 2H, CH_2), 6.29 (s, 1H, CH=), 7.05 (t, J=7.6 Hz, 1H), 7.15 (d, J=7.8 Hz, 1H), 7.59 (dt, J=1.4, 7.6 Hz, 1H), 8.55 (d, J=4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=25.39 (CH_2), 28.16 (CH_3), 30.37 ($C(CH_3)_2$), 33.83 (CH_2), 40.14 (CH_2), 40.81 (CH_2), 120.52 (pyridyl), 122.06 (C=*C*H), 123.90 (pyridyl), 135.79 (pyridyl), 149.87 (pyridyl or *C*=CH), 149.14 (pyridyl), 157.36 (pyridyl or *C*=CH); IR (neat) 2950 s, 1649 m, 1585 s, 1468 s, 752 m cm^{-1}. MS m/z (% rel intensity) 201 (M^+; 61), 145 (81), 144 (100). HRMS Found: m/z 201.1523. Calcd for $C_{14}H_{19}N$: M, 201.1517.

(4,4-Dimethyl-1-cyclohexenyl)(2-pyridyl)methane (8). A colorless oil. ^{1}H NMR ($CDCl_3$) 0.88 (s, 6H, CH_3), 1.34 (t, J=6.8 Hz, 2H, CH_2), 1.75—2.05 (br m, 4H, CH_2), 3.46 (s, 2H, pyridyl CH_2), 5.44 (br, 1H, C=CH), 7.05—7.22 (m, 2H), 7.59 (dt, J=1.9, 5.7 Hz, 1H), 8.53 (d, J=4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=26.06, 28.21 (CH_3), 28.45 ($C(CH_3)_2$), 35.63, 39.39, 46.86, 121.02, 122.87, 122.94, 134.57, 136.21, 149.20, 160.70; IR (neat) 2948 s, 1589 s, 1474 s, 746 s, 602 m cm^{-1}. MS m/z (% rel intensity) 201 (M^+; 100), 200 (84), 186 (64), 158 (92), 144 (98), 131 (59). HRMS Found: m/z 201.1513. Calcd for $C_{14}H_{19}N$: M, 201.1517.

Trimethylsilyl Cyclopentyliden(2-pyridyl)methyl Ether (10). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.11 (s, 9H, $(CH_3)_3SiO$), 1.67 (m, 4H, CH_2), 2.41—2.52 (br t, 2H, CH_2), 2.58—2.65 (br t, 2H, CH_2), 7.08 (dd, J=5.7, 6.5 Hz, 1H), 7.43 (d, J=8.1 Hz, 1H), 7.62 (dt, J=1.6, 7.8 Hz, 1H), 8.56 (d, J=4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ= 0.67, 25.70, 27.64, 31.13, 31.29, 121.00, 121.51, 130.76, 135.53, 139.96, 148.34, 157.45.

((*Z*)-3-Methylcyclopentyliden)(2-pyridyl)methane (12). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.08 (d, J=6.2 Hz, 3H, CH_3), 1.19—1.34 (m, 1H, 4-position CH*H*), 1.80—1.92 (m, 1H, 4-position C*H*H), 2.01—2.28 (m, 2H, 2-position CH*H* and 3-position CH), 2.44—2.70 (m, 2H, 5-position CH_2), 2.92—3.08 (dd, J=6.5, 17.0 Hz, 1H, 2-position C*H*H), 6.44 (t, J=2.4 Hz, 1H, CH=), 7.02 (dd, J=5.1, 7.6 Hz, 1H), 7.22 (d, J=8.1 Hz, 1H), 7.59 (dt, J=2.2, 7.6 Hz, 1H), 8.56 (d, J=3.8 Hz, 1H). Irradiation of the vinyl proton at δ=6.44 gave a 3% NOE of the methylene proton at δ=2.44—2.70 (at the 5-position). ^{13}C NMR ($CDCl_3$) 20.09, 33.71, 35.47, 35.56, 40.63, 120.11, 121.31, 122.64, 135.78, 149.14, 152.63, 157.55; IR (neat) 2940 s, 1654 m, 1586 s, 1468 s, 1140 m, 862 m, 738 m cm^{-1}. MS m/z (% rel intensity) 173 (M^+; 31), 158 (100). HRMS Found: m/z 173.1214. Calcd for $C_{12}H_{15}N$: M, 173.1204.

((*Z*)-2-Ethylcyclopentyliden)(2-pyridyl)methane (14). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=7.0 Hz, 3H, CH_3), 1.12—1.28 (m, 1H, C*H*H), 1.49—1.74 (m, 4H, CH_2), 1.77—1.89

(m, 1H, CH*H*), 2.16—2.59 (m, 2H, CH_2), 3.24—3.36 (br m, 1H, CH), 6.40 (d, J=1.9 Hz, 1H, CH=), 7.00 (dd, J=6.5, 4.9 Hz, 1H), 7.17 (d, J=8.1 Hz, 1H), 7.56 (dt, J=1.9, 7.8 Hz, 1H), 8.54 (d, J=4.0 Hz, 1H). Irradiation of the vinyl proton at δ=6.40 gave a 4% NOE of the methylene proton at δ=2.16—2.59 (at the 5-position); ^{13}C NMR ($CDCl_3$) δ=12.42 (CH_3), 23.09 (CH_2), 26.47 (CH_2), 31.45 (CH_2), 35.85 (CH_2), 42.93 (CH), 120.12 (pyridyl), 120.75 (C=*C*H), 122.77 (pyridyl), 135.72 (pyridyl), 149.14 (pyridyl), 157.16, 157.28 (pyridyl or *C*=CH); IR (neat) 2936 s, 1650 s, 1586 m, 1468 s, 1374 m, 860 s, 738 s cm^{-1}. MS *m/z* (% rel intensity) 188 (M+1$^+$; 11), 187 (M$^+$; 67), 172 (100). FAB-HRMS Found: *m/z* 187.1357. Calcd for $C_{13}H_{17}N$: M, 187.1361.

((*E*)-3,3-Dimethylcyclopentyliden)(1-methyl-1*H*-imidazol-2-yl)methane (17). A colorless solid. Mp (under air) 91 °C. ^{1}H NMR ($CDCl_3$) δ=1.03 (s, 6H, CH_3), 1.60 (t, J=7.6 Hz, 2H, CH_2), 2.30 (d, J=1.3 Hz, 2H, CH_2), 2.90 (td, J=7.6, 1.0 Hz, 2H, CH_2), 3.59 (s, 3H, NCH_3), 6.14 (tt, J=1.3, 1.0 Hz, 1H, CH=), 6.77 (s, 1H), 7.07 (s, 1H). Irradiation of the vinyl proton at δ=6.14 gave a 2% NOE of the methylene proton at δ=2.30 (at the 2-position). ^{13}C NMR ($CDCl_3$) δ=27.41 (CH_3), 31.07 (CH_2), 32.53 (NCH_3), 38.17 (*C*(CH_3)$_2$), 40.31 (CH_2), 50.44 (CH_2), 106.34 (CH), 119.59, 127.94, 146.15, 152.90 (CH=*C*); IR (KBr) 2952 s, 1660 m, 1505 s, 1464 s, 1383 m, 1278 s, 1190 w, 1072 w, 968 w, 838 m, 727 m cm^{-1}. MS *m/z* (% rel intensity) 190 (M$^+$; 100), 175 (58). Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.72%. Found: C, 75.74; H, 9.52; N, 14.66%.

((*Z*)-2-Ethylcyclopentyliden)(1-methyl-1*H*-imidazol-2-yl)methane (19). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.87 (t, J=7.3 Hz, 3H, CH_3), 1.10—1.29 (m, 1H), 1.60—1.90 (m, 5H), 2.35—2.60 (m, 2H), 3.39 (br m, 1H), 3.57 (s, 3H, NCH_3), 6.09 (d, J=1.9 Hz, 1H, CH=), 6.75 (s, 1H), 7.03 (s, 1H). Irradiation of the vinyl proton at δ=6.09 gave a 3% NOE of the methylene proton at δ=2.35—2.60 (at the 5-position). ^{13}C NMR ($CDCl_3$) δ=11.95, 23.56, 26.17, 31.00 32.62, 35.33, 42.82, 106.38, 119.43, 127.98, 145.66, 157.54; IR (neat) 2956 s, 1657 w, 1513 m, 1485 m, 1461 m, 1278 s, 1114 m, 841 m, 728 m cm^{-1}. MS *m/z* (% rel intensity) 190 (M$^+$; 29), 175 (100), 96 (80). Anal. Found: C, 75.81; H, 9.53; N, 14.52%. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.72%.

((*Z*)-3-Methylcyclopentyliden)(1-methyl-1*H*-imidazol-2-yl)methane (21). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.07 (d, J=6.5 Hz, 3H, CH_3), 1.19—1.34 (m, 1H, 4-position CH*H*), 1.80—1.92 (m, 1H, 4-position C*H*H), 2.01—2.20 (m, 1H, 3-position CH), 2.22—2.36 (m, 1H, 2-position CH*H*), 2.40—2.62 (m, 2H, 5-position CH_2), 3.14 (dd, J=6.5, 18.1 Hz, 1H, 2-position C*H*H), 3.59 (s, 3H), 6.13 (t, J=1.9 Hz, 1H, CH=), 6.77 (d, J=1.4 Hz, 1H), 7.09 (d, J=1.4 Hz, 1H). Irradiation of the vinyl proton at δ=6.13 gave a 2% NOE of the methylene proton at δ=2.40—2.62 (at the 5-position); ^{13}C NMR ($CDCl_3$) δ=20.03, 32.67, 34.12, 34.99, 35.18, 40.80, 106.02, 119.73, 128.01, 146.31, 153.06; IR (neat) 2948 s, 1678 m, 1514 s, 1458 s, 1278 s, 908 s, 726 s cm^{-1}. MS *m/z* (% rel intensity) 176 (M$^+$; 31), 161 (100). HRMS Found: *m/z* 176.1314. Calcd for $C_{11}H_{16}N_2$: M, 176.1313.

((*E*)-3,3-Dimethylcyclopentyliden)(4,5-dimethyl-1,3-oxazol-2-yl)methane (*E*-23). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.01 (s, 6H, CH_3), 1.59 (t, J=7.6 Hz, 2H, CH_2), 2.06 (s, 3H, oxazolyl CH_3), 2.21 (s, 3H, oxazolyl CH_3), 2.27 (d, J=1.3 Hz, 2H, CH_2), 2.79 (td, J=7.6, 1.0 Hz, 2H, CH_2), 6.13 (tt, J=1.3, 1.0 Hz, 1H, vinyl). Irradiation of the vinyl proton at δ=6.13 gave a 2% NOE of the methylene proton at δ=2.27 (at the 2-position); ^{13}C NMR ($CDCl_3$) δ=9.98 (oxazolyl CH_3), 11.18 (oxazolyl CH_3), 27.33 (C(*C*H_3)$_2$), 31.00 (CH_2), 38.40 (*C*(CH_3)$_2$), 40.29 (CH_2), 50.30 (CH_2), 108.21 (CH), 130.94, 141.76, 155.31 (CH=*C*), 159.62; IR (neat) 2954 s, 1662 m, 1544 w, 1465 w, 1385 w, 1263 w, 1170 w, 1072 w, 989 w cm^{-1}. MS *m/z* (% rel intensity) 206 (M$^+$; 10), 205 (71), 190 (100). Anal. Found: C, 75.89; H, 9.41; N, 6.84%. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33 N, 6.82%.

((*Z*)-3,3-Dimethylcyclopentyliden)(4,5-dimethyl-1,3-oxazol-2-yl)methane (Z-23). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.02 (s, 6H, CH_3), 1.52 (t, J=7.6 Hz, 2H, CH_2), 2.08 (s, 3H, oxazolyl CH_3), 2.23 (s, 3H, oxazolyl CH_3), 2.55 (d, J=1.3 Hz, 2H, CH_2), 2.59 (td, J=7.6, 1.0 Hz, 2H, CH_2), 6.13 (tt, J=1.3, 1.0 Hz, 1H, vinyl); ^{13}C NMR ($CDCl_3$) δ=9.99 (oxazolyl CH_3), 11.22 (oxazolyl CH_3), 28.05 (C(*C*H_3)$_2$), 33.48 (CH_2), 39.46 (*C*(CH_3)$_2$ and CH_2), 47.10 (CH_2), 108.43 (CH), 130.98, 141.73, 155.00 (CH=*C*), 159.60. MS *m/z* (% rel intensity) 205 (M$^+$; 13), 190 (100).

((*E*)-3,3-Dimethylcyclopentyliden)(5-methyl-1,3-oxazol-2-yl)methane (25). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.01 (s, 6H, CH_3), 1.60 (t, J=7.6 Hz, 2H, C*H*$_2$CH$_2$), 2.29 (s, 5H, CH_2 and oxazolyl CH_3), 2.81 (t, J=6.5 Hz, 2H, CH$_2$C*H*$_2$), 6.17 (t, J=1.9 Hz, 1H, vinyl), 6.71 (d, J=1.1 Hz, 1H). Irradiation of the vinyl proton at δ=6.17 gave a 3% NOE of the methylene proton at δ=2.29 (at the 2-position); ^{13}C NMR ($CDCl_3$) δ=10.44 (oxazolyl CH_3), 26.85 (C(*C*H_3)$_2$), 30.62 (CH_2), 37.97, 39.77, 49.83, 107.66, 123.02, 146.63, 155.44 (CH=*C*), 160.63; IR (neat) 2956 s, 1663 m, 1606 s, 1543 m, 1467 m, 1387 w, 1264 w, 1096 m, 1013 m, 973 m cm^{-1}. MS *m/z* (% rel intensity) 191 (M$^+$; 48), 176 (100), 148 (51), 53 (50). HRMS Found: *m/z* 191.1308. Calcd for $C_{12}H_{17}NO$: M, 191.1310.

((*Z*)-2-Ethylcyclopentyliden)(5-methyl-1,3-oxazol-2-yl)methane (27). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.95 (t, J=7.3 Hz, 3H, CH_3), 1.18—1.35 (m, 1H), 1.53—1.85 (m, 5H), 2.30 (d, J=1.0 Hz, 3H, CH_3), 2.33—2.60 (m, 2H, CH_2), 3.16 (br m, 1H), 6.16 (d, J=2.0 Hz, 1H, vinyl), 6.70 (d, J=1.0 Hz, 1H). Irradiation of the vinyl proton at δ=6.16 gave a 5% NOE of the methylene proton at δ=2.33—2.60 (at the 5-position); ^{13}C NMR ($CDCl_3$) δ=10.91 (oxazolyl CH_3), 12.51 (CH_3), 23.25 (CH_2), 27.01 (CH_2CH_3), 31.13 (CH_2), 34.92 (CH_2), 43.97 (CH), 107.64 (ArC*H*=C), 123.47, 147.17, 160.05 (ArCH=*C*), 160.70; IR (neat) 2964 s, 1662 m, 1542 m, 1460 m, 1378 w, 1224 w, 1104 m, 976 m, 860 m cm^{-1}. MS *m/z* (% rel intensity) 191 (M$^+$; 64), 176 (100). HRMS Found: *m/z* 191.1288. Calcd for $C_{12}H_{17}NO$: M, 191.1310.

Intramolecular C–H/CO/Olefin Coupling Reactions. An oven-dried 50 cm^3 stainless-steel autoclave, with a magnetic stirring bar, was flushed with dry nitrogen. In the apparatus were placed $Ru_3(CO)_{12}$(10.6 mg, 0.017 mmol), **1** (94.0 mg, 0.50 mmol), hexadecane (42.9 mg), and THF (2.5 cm^3). The system was flushed with 10 kg cm^{-2} of carbon monoxide three times, and was finally pressurized to 3 kg cm^{-2}. The reaction mixture was heated at 140 °C (oil bath temp) for 20 h and was allowed to cool to room temperature. After unreacted carbon monoxide was carefully bled off, the contents were transferred to a 30 cm^3 round-bottomed flask and the autoclave was rinsed with three 3 cm^3 portions of THF. The combined solution was evaporated on a rotary evaporator. The residue was purified twice by silica-gel column chromatography (20 mm i.d. ×80 mm length; eluent, hexane/AcOEt=20/1 then 5/1) and a bulb-to-bulb distillation to give **28** (35 mg) and **29** (10 mg).

2, 3, 3- Trimethyl- 5- [(*Z*)- 1- (2- pyridyl)methylene]- 1- cyclopentanone (28). A colorless oil. ^{1}H NMR ($CDCl_3$) δ=0.79 (s, 3H, CH_3), 1.07 (d, J=6.8 Hz, 3H, CH_3), 1.23 (s, 3H, CH_3), 2.16 (q, J=6.8 Hz, 1H, CH), 2.75 (dd, J=17.8, 3.2 Hz, 1H, CH_2), 3.25 (dd, J=17.8, 2.1 Hz, 1H, CH_2), 7.20 (dd, J=7.8 Hz, 5.1 Hz), 7.37 (dd, J=3.2 Hz, 2.1 Hz, 1H, pyridyl C*H*=C), 7.43 (d, J=7.8 Hz, 1H), 7.69 (dt, J=7.8, 1.6 Hz, 1H), 8.69 (d, J=1.6, 5.1 Hz, 1H). Irradiation of the vinyl proton at δ=7.37 gave a 5% NOE of the methylene proton δ=3.25 (at the 2-position); ^{13}C NMR ($CDCl_3$) δ=8.16

(CH_3), 22.84 ($C(CH_3)_2$), 27.74 ($C(CH_3)_2$), 37.27 ($C(CH_3)_2$), 44.15 (CH_2), 54.68 (CH), 122.70, 126.63, 129.92 (pyridyl *C*H=C), 136.21, 139.86 (pyridyl CH=*C*), 149.88, 155.13, 209.36 (C=O). IR (neat) 2964 m, 1724 s, 1644 m, 1588 m, 1470 m, 1392 w, 1238 m, 1162 m, 984 m, 782 m cm^{-1}. MS 215 (M^+; 17), 200 (100). HRMS Found: *m/z* 215.1309. Calcd for $C_{14}H_{17}NO$: M, 215.1310.

4,4,5-Trimethyl-2-(2-pyridylmethyl)-2-cyclopenten-1-one (29). A colorless oil. ^1H NMR ($CDCl_3$) δ=0.98 (s, 3H, CH_3), 1.08 (d, *J*=7.6 Hz, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.16 (quintet, 1H, *J*=7.6 Hz), 3.66 (s, 2H, CH_2), 7.02 (s, 2H, vinyl), 7.14 (dd, *J*=4.9, 7.6 Hz, 1H), 7.20 (d, *J*=7.8 Hz, 1H), 7.61 (dt, *J*=1.6, 7.6 Hz, 1H), 8.53 (d, *J*=3.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=10.44, 24.71, 28.03, 34.25, 42.54, 52.51, 121.77, 123.76, 136.95, 140.29 (vinyl), 149.75, 159.21, 167.46 (vinyl *C*H), 211.09 (C=O); IR (neat) 2966 m, 1705 s, 1594 m, 1475 m, 964 m, 754 m cm^{-1}. MS *m/z* (% rel intensity) 215 (M^+; 30), 200 (94), 187 (59), 172 (57), 145 (63), 117 (100). HRMS Found: *m/z* 215.1298. Calcd for $C_{14}H_{17}NO$: M, 215.1310.

2-(5,5-Dimethyl-4,5,6,7-tetrahydrobenzo[*c*]thiophen-1-yl)-pyridine (41). A colorless solid. Mp (under air) 48—50 °C. ^1H NMR ($CDCl_3$) δ=1.00 (s, 6H, CH_3), 1.61 (t, *J*=6.7 Hz, 2H, CH_2), 2.50 (s, 2H, CH_2), 2.98 (t, *J*=6.7 Hz, 2H, CH_2), 6.92 (s, 1H, thienyl), 7.90 (dt, *J*=1.1, 5.1 Hz, 1H), 7.56 (d, *J*=8.4 Hz, 1H), 7.66 (dt, *J*=1.6, 8.1 Hz, 1H), 8.59 (d, *J*=5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=24.51 (CH_2), 27.66 (CH_3), 29.51 ($C(CH_3)_2$), 36.23 (CH_2), 40.45 (CH_2), 120.66 (Ar), 120.85 (Ar), 120.90 (Ar), 135.13 (Ar, quanternary), 136.19 (Ar), 137.13 (Ar, quaternary), 140.22 (Ar, quanternary), 149.43 (Ar), 153.66 (Ar, quaternary); IR (KBr) 2916 s, 1584 s, 1474 s, 1390 m, 1288 m, 1152 m, 858 m, 782 s cm^{-1}. MS *m/z* (% rel intensity) 244 ($M+1^+$; 21), 243 (M^+; 100), 228 (68). HRMS Calcd for $C_{15}H_{17}NS$: M, 243.1082. Found: *m/z* 243.1087. Anal. Found: C, 74.16; H, 7.35; N, 5.55%. Calcd for $C_{15}H_{17}NS$: C, 74.03; H, 7.04; N, 5.76 %.

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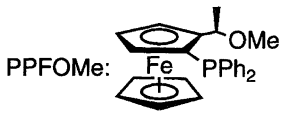

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