

The Allenylidene Complex [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ as a Precursor of Novel Pyrido[1,2-*a*]pyrimidinyl and 1,3-Thiazinyl Complexes

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Received May 15, 2000

The allenylidene complex [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ (**1**) reacts with 2-aminopyridine to give a mixture of the complexes [Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]BF₄ (**2**) and [Ru(η^5 -C₅H₅){C(CH=CPh₂)=NHC(CH₂)₄N}(CO)(PⁱPr₃)]BF₄ (**3**). The molar ratio of the isomers in the mixture depends on the reaction temperature. At temperatures lower than -30 °C, isomer **2** is the main reaction product, while at 0 °C an inverse relationship is observed. The structure of **2** has been determined by an X-ray investigation, revealing a Ru–C(bicycle) distance of 2.08(1) Å. Treatment of **2** with sodium methoxide results in the deprotonation of the NH group of the heterocycle to give the pyrido[1,2-*a*]pyrimidinyl derivative Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyrido[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃) (**4**), which has been also characterized by an X-ray diffraction analysis. In this case, the study reveals a Ru–C(bicycle) distance of 2.097(5) Å. The deprotonation of **2** is reversible. Thus, the addition of HBF₄·OEt₂ to dichloromethane solutions of **4** regenerates **2**. Similarly, the treatment of **4** with methyl trifluoromethanesulfonate affords [Ru(η^5 -C₅H₅){1-methyl-2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]CF₃SO₃ (**5**). Complex **1** also reacts with thioisonicotinamide. The reaction yields [Ru(η^5 -C₅H₅){4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazinium-6-yl}(CO)(PⁱPr₃)]BF₄ (**6**), which in the presence of sodium methoxide affords Ru(η^5 -C₅H₅){4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazin-6-yl}(CO)(PⁱPr₃) (**7**). The structure of **7** has been determined by an X-ray investigation, revealing a Ru–C(cycle) distance of 2.067(4) Å. The deprotonation of **6** is also reversible. Thus, the addition of HBF₄·OEt₂ to dichloromethane solutions of **7** regenerates **6**. Similarly, treatment of **7** with methyl trifluoromethanesulfonate gives [Ru(η^5 -C₅H₅){3-methyl-4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazinium-6-yl}(CO)(PⁱPr₃)]CF₃SO₃ (**8**).

Introduction

Transition-metal allenylidene complexes have attracted a great deal of attention in recent years as a new type of organometallic intermediate that may have unusual reactivity in stoichiometric¹ and catalytic² processes.

EHT-MO calculations³ indicate that allenylidenes coordinate to metal centers as σ -donor and π -acceptor ligands. The interaction between the HOMO of the allenylidene and the LUMO of the metallic fragment produces a lower charge transfer than the interaction

between the HOMO of the metallic fragment and the LUMO of the allenylidene. Thus, the π -acceptor component of the metal–allenylidene bond is stronger than the σ -donor one. As a result of this bonding situation, the reactivity of the C₃ organic unit strongly depends on the particular metallic fragment stabilizing the allenylidene ligand.

The majority of allenylidene complexes have only donor ligands which somewhat reduce the electrophilicity of the allenylidene. In 1996 we reported the synthesis of the complex [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ (**1**), containing a carbonyl group.⁴ The presence of this ligand may seem trivial; however, its

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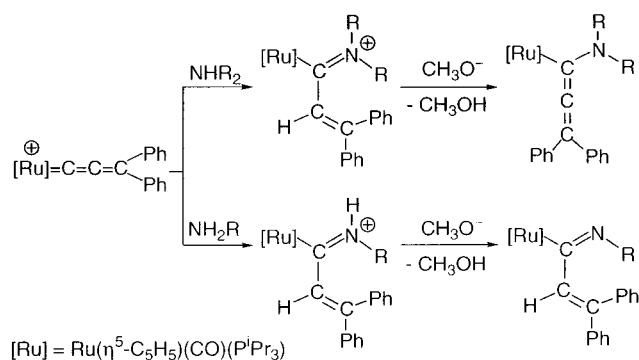
(1) (a) Werner, H. *Chem. Commun.* **1997**, 903. (b) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (c) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178*, 409.

(2) (a) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315. (b) Picquet, M.; Touchard, D.; Bruneau, C.; Dixneuf, P. H. *New J. Chem.* **1999**, 141. (c) Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 601. (d) Harlow, K. J.; Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1999**, 285.

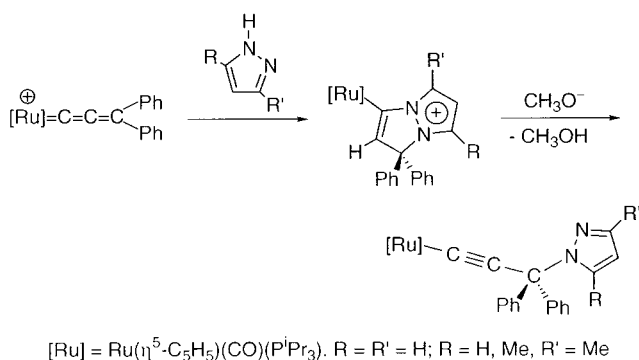
(3) (a) Berke, H.; Huttner, G.; Von Seyerl, J. *Z. Naturforsch.* **1981**, *36B*, 1277. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A.; Schrickel, J. *Organometallics* **1996**, *15*, 3556. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826.

(4) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

Scheme 1



Scheme 2



π -acidic nature enhances the reactivity associated with the allenylidene spine.^{3d,4,5} Thus, in contrast to other allenylidene complexes of the iron triad, the diphenylallenylidene ligand of **1** adds the N–H bond of secondary and primary amines at the C_α – C_β double bond to afford azoniabutadienyl derivatives of the types $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=NR_2\}(CO)(P^iPr_3)]BF_4$ and $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=NHR\}(CO)(P^iPr_3)]BF_4$, respectively. Treatment of the tertiary azoniabutadienyl complexes with sodium methoxide produces the deprotonation of the $CH=CPh_2$ group of the unsaturated η^1 -carbon donor ligand and the formation of the corresponding aminoallenyl derivatives, while under the same conditions the deprotonation of the secondary azoniabutadienyl compounds occurs at the nitrogen atom, and as a result, azabutadienyl derivatives are formed (Scheme 1).^{5f}

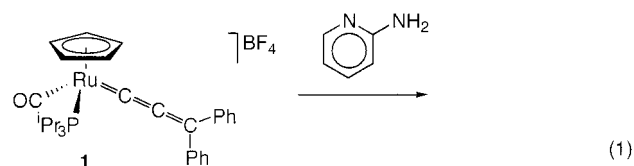
In reactions with secondary amines containing a second nitrogen atom, the diphenylallenylidene ligand of **1** is active not only at the C_α – C_β double bond but also at the C_γ atom. Thus, the addition of pyrazoles to solutions of **1** leads to pyrazolo[1,2-*a*]pyrazolyl complexes, which yield functionalized alkynyl derivatives by treatment with sodium methoxide (Scheme 2).^{5b}

Interest in the behavior of the diphenylallenylidene ligand of **1** in the presence of primary amines containing a second heteroatom led us to investigate the reactivity of **1** toward 2-aminopyridine and thioisonicotinamide.

In this paper, we report the synthesis and characterization of pyrido[1,2-*a*]pyrimidinyl- and 1,3-thiazinylruthenium complexes, two types of organometallic compounds unknown until now.

Results and Discussion

1. Reactions of $[Ru(\eta^5-C_5H_5)(C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ with 2-Aminopyridine. Treatment of dichloromethane solutions of **1** with 1.1 equiv of 2-aminopyridine leads to yellow solutions. After removal of the solvent, the $^{31}P\{^1H\}$ NMR spectrum of the residue in chloroform-*d* shows two singlets at 62.3 and 62.6 ppm, which corresponds to the pyridinium[1,2-*a*]pyrimidinyl and azoniabutadienyl derivatives $[Ru(\eta^5-C_5H_5)\{2,2\text{-diphenyl-}2H\text{-pyridinium}[1,2\text{-}a\text{]pyrimidin-4-yl}\}(CO)(P^iPr_3)]BF_4$ (**2**) and $[Ru(\eta^5-C_5H_5)\{C(CH=CPh_2)=NH-C(CH_3)_2N\}(CO)(P^iPr_3)]BF_4$ (**3**), respectively. The molar ratio of the isomers in the mixture depends on the reaction temperature. At temperatures lower than $-30^\circ C$, isomer **2** is the main reaction product, while at $0^\circ C$ an inverse relationship is observed (eq 1).



T (°C)	2		3
-55	4	:	1
-30	1.4	:	1
0	1	:	3.5

At first glance, the formation of **2** could be rationalized as the addition of one of the two NH bonds of the amine to the C_β – C_γ double bond of the allenylidene ligand of **1** and the subsequent coordination of the nitrogen atom of the pyridine group to the C_α atom. The formation of **3** can be rationalized as the addition of one of the two NH bonds of the amine to the C_α – C_β double bond of the allenylidene ligand of **1**, in agreement with the reactions collected in Scheme 1. The orientations observed for the additions ($N \rightarrow C_\alpha$ or C_γ and $H \rightarrow C_\beta$) agree well with EHT-MO calculations on transition-metal allenylidene complexes, indicating that the C_α and C_γ atoms are electrophilic centers, while the C_β atom is a nucleophile.³

According to the data collected in eq 1, one could think that the addition of primary amines containing a second nitrogen atom occurs not only at the C_α – C_β double bond of the allenylidene but also at the C_β – C_γ double bond. The first addition should be favored at low temperature, while the second one should be favored at high temper-

(5) (a) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297. (b) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567. (c) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4959. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434. (e) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606. (f) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995. (g) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **2000**, *19*, 4.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complexes [Ru(η^5 -C₅H₅){2,2-diphenyl-2H-pyridinium[1,2-a]pyrimidin-4-yl}(CO)(PⁱPr₃)]BF₄ (2**) and Ru(η^5 -C₅H₅){2,2-diphenyl-2H-pyrido[1,2-a]pyrimidin-4-yl}(CO)(PⁱPr₃) (**4**)**

	2	4		2	4
Ru ^a -P	2.356(3)	2.3520(14)	N(1)-C(26)	1.38(1)	1.376(6)
Ru-C(1)	2.26(1)	2.266(6)	N(2)-C(9)	1.45(1)	1.467(6)
Ru-C(2)	2.25(1)	2.276(7)	N(2)-C(22)	1.35(1)	1.284(6)
Ru-C(3)	2.25(1)	2.251(6)	C(7)-C(8)	1.36(1)	1.332(6)
Ru-C(4)	2.26(1)	2.222(6)	C(8)-C(9)	1.46(1)	1.515(6)
Ru-C(5)	2.23(1)	2.242(7)	C(9)-C(10)	1.55(2)	1.539(6)
Ru-C(6)	1.84(1)	1.835(5)	C(9)-C(16)	1.57(1)	1.557(6)
Ru-C(7)	2.08(1)	2.097(5)	C(22)-C(23)	1.43(2)	1.439(6)
C(6)-O	1.16(1)	1.152(5)	C(23)-C(24)	1.33(2)	1.324(7)
N(1)-C(7)	1.45(1)	1.442(6)	C(24)-C(25)	1.38(2)	1.420(7)
N(1)-C(22)	1.37(1)	1.421(6)	C(25)-C(26)	1.34(2)	1.349(7)
M(1) ^b -Ru-P	130.3(2)	129.8(2)	N(2)-C(9)-C(16)	109.8(8)	108.2(4)
M(1)-Ru-C(6)	125.5(4)	126.2(3)	N(2)-C(22)-C(23)	122(1)	120.9(5)
M(1)-Ru-C(7)	117.9(2)	118.3(3)	C(7)-N(1)-C(22)	119.6(9)	118.2(4)
P-Ru-C(6)	86.2(4)	85.57(16)	C(7)-N(1)-C(26)	121.1(9)	122.4(4)
P-Ru-C(7)	92.4(3)	91.18(13)	C(7)-C(8)-C(9)	126.9(10)	123.9(5)
C(6)-Ru-C(7)	94.6(5)	95.9(2)	C(8)-C(9)-C(10)	115.0(9)	114.2(4)
Ru-C(7)-N(1)	122.7(7)	122.9(3)	C(8)-C(9)-C(16)	108.6(8)	106.0(4)
Ru-C(7)-C(8)	124.1(8)	123.4(4)	C(9)-N(2)-C(22)	121.0(9)	117.1(4)
N(1)-C(7)-C(8)	113.1(9)	113.6(4)	C(10)-C(9)-C(16)	108.1(9)	110.0(4)
N(1)-C(22)-C(23)	118(1)	115.8(4)	C(22)-C(23)-C(24)	119(1)	121.7(5)
N(1)-C(22)-N(2)	119.3(10)	123.3(4)	C(23)-C(24)-C(25)	119(1)	120.7(5)
N(1)-C(26)-C(25)	120(1)	122.9(5)	C(24)-C(25)-C(26)	120(1)	118.3(5)
N(2)-C(9)-C(8)	106.0(9)	109.9(4)	C(26)-N(1)-C(22)	119.3(9)	119.1(4)
N(2)-C(9)-C(10)	109.3(8)	109.3(8)			

^a Ru, P, and O in this table stand for Ru(1), P(1), and O(1) in Figure 1. ^b M(1) is the centroid of the C(1)–C(5) Cp carbon atoms.

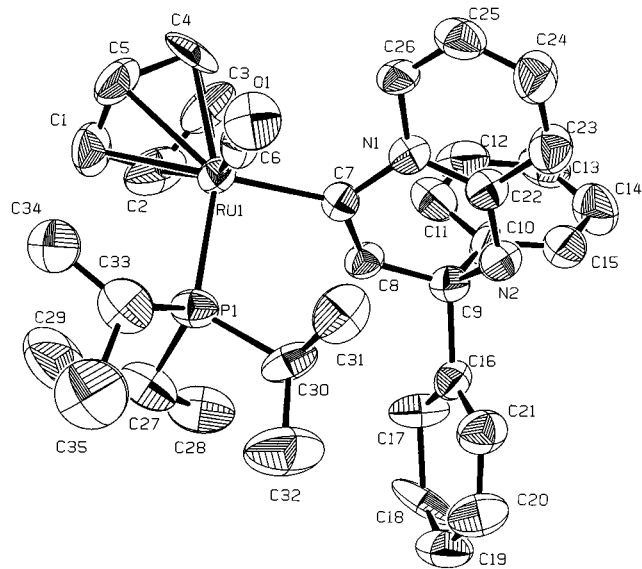


Figure 1. Molecular diagram of the cation of **2**, [Ru(η^5 -C₅H₅){2,2-diphenyl-2H-pyridinium[1,2-a]pyrimidin-4-yl}(CO)(PⁱPr₃)]⁺. Thermal ellipsoids are shown at 50% probability.

ature. This trivial conclusion is probably incorrect. It should be noted that 2-aminopyridine also exists in the imino tautomeric form and that this tautomeric equilibrium is highly dependent on the temperature.⁶ On this basis, the formation of **2** can be rationalized as the addition of the endocyclic NH bond of the imino form at the C_α-C_β double bond of the allenylidene ligand and the subsequent coordination of the exocyclic nitrogen atom to the C_γ atom.

In addition, it should be noted that the pyridinic nitrogen atom of **3** is not coordinated to the C_γ atom of

the azoniabutadienyl ligand. At first glance, it could be argued that this is due to the large steric hindrance experienced by the phenyl and pyridinyl groups. However, we have previously observed that complex **1** reacts with pyridine-2-thiol to give [Ru(η^5 -C₅H₅){C=CHC(Ph)₂N(CH)₄CS}(CO)(PⁱPr₃)]BF₄ containing a N(pyridinyl)-CPh₂ bond.^{5b} Therefore, the instability of the product resulting from the intramolecular cyclization of **3** should be related to the electronic structure of its condensed heterocycles.

Isomer **2** was obtained as pure yellow crystals in 66% yield, by crystallization in dichloromethane-diethyl ether of the crude product obtained from the reaction of **1** with 2-aminopyridine at -55 °C, and characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation of **2** is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying one face of the octahedron, and the angles formed by the triisopropylphosphine, the carbonyl group, and the heterocycle are close to 90°.

The unsaturated η^1 -carbon ligand can be described as a 2,2-diphenyl-2H-pyridinium[1,2-a]pyrimidin-4-yl group. The C(7)-C(8)-C(9)-N(2)-C(22)-N(1) ring has a twisted conformation. If the C(8) and C(22) atoms are situated in the ideal least-squares plane through the six atoms of the ring (the deviations from this plane (Å) are 0.03(1) (C(8)) and -0.01(1) (C(22))), the C(7) and N(2) atoms lie 0.158(9) and 0.193(9) Å above, respectively, while the C(9) and N(1) atoms lie 0.25(1) and 0.143(8) Å below, respectively. In contrast, the ring N(1)-C(22)-C(23)-C(24)-C(25)-C(26) is almost planar. The deviations from the best plane (Å) are 0.033(8) (N(1)), -0.04(1) (C(22)), 0.00(1) (C(23)),

(6) (a) Katritzky, A. R.; Lagowski, J. M. *Adv. Heterocycl. Chem.* **1963**, *1*, 341. (b) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. In *The Tautomerism of Heterocycles: Advances in Heterocyclic Chemistry*; Academic Press: New York, 1976; Supplement 1, Chapter 2.

0.07(2) (C(24)), -0.03(1) (C(25)), and -0.02(1) (C(26)). The dihedral angle formed by the least-squares planes through the atoms of both cycles is 13.6°.

The Ru–C(7) distance (2.08(1) Å) lies within the range 2.03(1)⁷–2.141(3) Å,⁸ where a Ru–C(sp²) single bond has been proposed to exist. In accordance with the sp² hybridization for C(7), the angles Ru–C(7)–N(1) and Ru–C(7)–C(8) are 122.7(7) and 124.1(8)°, respectively.

The structural parameters obtained for the C(7)–C(8)–C(9)–N(2)–C(22)–N(1) ring support the electronic structure proposed in eq 1. The C(7)–C(8) distance of 1.36(1) Å is in agreement with the sample mean of carbon–carbon bond lengths for double bonds (1.32(1) Å),⁹ whereas the C(8)–C(9) bond length (1.46(1) Å) is statistically identical with the sample mean of the C(sp²)–C(sp³) single-bond distance (1.48(3) Å).⁹ The C(7)–N(1) and C(9)–N(2) bond lengths are identical (1.45(1) Å) and agree well with C–N single bonds. However, the N(1)–C(22) (1.37(1) Å) and N(2)–C(22) (1.35(1) Å) distances are intermediate between those found for C–N double bonds in Schiff bases, hydrazones, and related compounds (about 1.29 Å) and those expected for a C–N single bond, suggesting electron delocalization over N(1), C(22), and N(2).

The structural parameters obtained for the N(1)–C(22)–C(23)–C(24)–C(25)–C(26) ring are also in accordance with the electronic structure proposed in eq 1 for this cycle. The N(1)–C(26) distance (1.38(1) Å) is similar to the N(1)–C(22) one, indicating electron delocalization over C(26), N(1), and C(22). Furthermore, the C(26)–C(25) (1.34(2) Å), C(25)–C(24) (1.38(2) Å), and C(24)–C(23) (1.33(2) Å) distances suggest that the electron delocalization also reaches to C(25), C(24), and C(23). The C(23)–C(22) bond length of 1.43(2) Å indicates a C(23)–C(22) single bond.

In agreement with the presence of a hydrogen atom bonded to N(2) in the complex, the IR spectrum of **2** in Nujol shows a ν(NH) band at 3328 cm⁻¹. In the ¹H NMR spectrum, the NH resonance appears at 8.56 ppm as a singlet. In addition, it should be mentioned that there exists another singlet at 5.50 ppm, corresponding to the C(8)–H resonance. In the ¹³C{¹H} NMR spectrum, the most noticeable feature is the presence of a doublet at 145.8 ppm, with a *J*(CP) value of 12.0 Hz, due to the C(7) resonance.

Complex **3** was characterized by IR and ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectroscopy. In the IR spectrum in Nujol, the most noticeable absorption is a ν(NH) band, which appears at 3283 cm⁻¹. In the ¹H NMR spectrum, the NH resonance is observed as a broad singlet at 11.22 ppm. The ¹³C{¹H} NMR spectrum strongly supports the presence of an azoniabutadienyl ligand in **3**, showing the RuC resonance at 255.1 ppm, as a doublet with a *J*(CP) of 8.4 Hz. The chemical shift and *J*(CP) values of this resonance agree well with those reported for previously synthesized azoniabutadienyl complexes.^{5f}

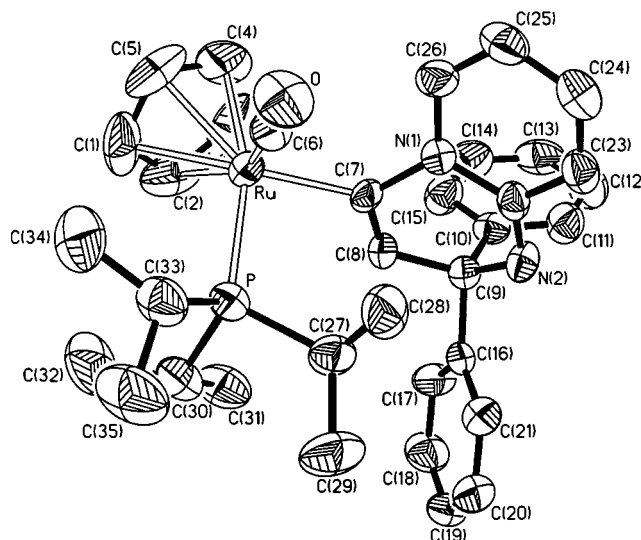
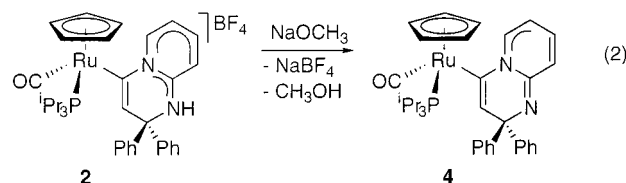


Figure 2. Molecular diagram of the complex Ru(η⁵-C₅H₅)-{2,2-diphenyl-2H-pyrido[1,2-a]pyrimidin-4-yl}(CO)(P^tPr₃) (**4**). Thermal ellipsoids are shown at 50% probability.

As a consequence of the participation of N(2) in the N(1)–C(22)–N(2) electron delocalization, the N(2)H hydrogen atom of **2** is relatively acidic. Thus, treatment of tetrahydrofuran suspensions of **2** with sodium methoxide leads to the pyrido[1,2-a]pyrimidinyl complex Ru(η⁵-C₅H₅){2,2-diphenyl-2H-pyrido[1,2-a]pyrimidin-4-yl}(CO)(P^tPr₃) (**4**), as a result of the deprotonation of the N(2) atom of **2** (eq 2).



Complex **4** was isolated as yellow crystals in 60% yield and, as for **2**, characterized by an X-ray crystallographic study. Figure 2 gives a view of the molecular geometry. Selected bond distances and angles are listed in Table 1.

Similarly to **2**, the geometry around the ruthenium center of **4** is close to octahedral, with the cyclopentadienyl ligand occupying one face of the octahedron, and the angles formed by the triisopropylphosphine, carbonyl group, and the bicycle are close to 90°.

The conformation of the cycle containing the two nitrogen atoms is twisted, as in **2**, with the related atoms lying in positions similar to those previously mentioned for the case of **2**, whereas the cycle containing only one heteroatom is almost planar. The dihedral angle formed by the least-squares planes through the atoms of both cycles is 17.7°.

The Ru–C(7) distance of 2.097(5) Å compares well with the bond length in **2** and agrees with a Ru–C(sp²) single bond. The angles Ru–C(7)–C(8) = 123.4(4)° and Ru–C(7)–N(1) = 122.9(3)° support the sp² hybridization for C(7).

The structural parameters obtained for the bicycle reveal the high electronic perturbation undergone by both cycles, as a result of the deprotonation. In contrast to **2**, the cycle of **4** containing the two nitrogen atoms

(7) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1987**, *326*, 413.

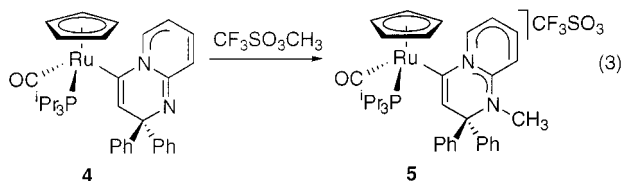
(8) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685.

(9) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

does not show any zone of electron delocalization. The deprotonation of N(2) gives rise to a C=N double bond between N(2) and the ring junction carbon atom (N(2)–C(22) distance 1.284(6) Å) and the loss of electron delocalization in the bond between this atom and N(1) (N(1)–C(22) distance 1.421(6) Å). The effect of the deprotonation in the cycle containing only one nitrogen atom is the reduction of the electron delocalization from N(1)–C(26)–C(25)–C(24)–C(23) in **2** to N(1)–C(26)–C(25) in **4** and the formation of the C(24)–C(23) double bond in **4** (C(23)–C(24) distance 1.324(7) Å).

The most noticeable feature in the IR spectrum of **4** is the absence of any ν (NH) band. In the ¹H NMR spectrum, the resonance corresponding to the RuC=CH proton appears at 4.94 ppm as a singlet. The ¹³C{¹H} NMR spectrum shows the resonance due to the RuC= carbon atom at 140.2 ppm, as a doublet with a J (CP) value of 13.7 Hz.

The reaction shown in eq 2 is reversible. Thus, addition of 1.1 equiv of HBF₄·OEt₂ to dichloromethane solutions of **4** regenerates **2** as a consequence of the protonation of N(2). Similarly, treatment of **4** with methyl trifluoromethanesulfonate affords the *N*-methylpyridinium[1,2-*a*]pyrimidinyl complex [Ru(η^5 -C₅H₅)-{1-methyl-2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]CF₃SO₃ (**5**), which was isolated as a yellow solid in 65% yield (eq 3).



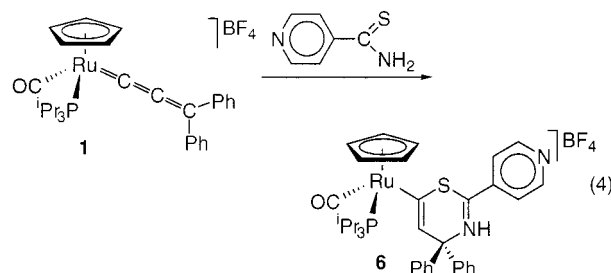
The presence of the [CF₃SO₃][−] anion in **5** is supported by its IR spectrum, which contains the characteristic stretching bands of the free anion¹⁰ at 1277, 1262, 1144, and 1030 cm^{−1}. In the ¹H NMR spectrum, the most noticeable resonances are two singlets at 5.42 and 2.96, with a 1:3 intensity ratio, corresponding to the RuC=CH proton and methyl group, respectively. The ¹³C{¹H} NMR spectrum shows the resonance due to the RuC= carbon atom at 145.3 ppm, as a broad signal.

From a methodological point of view, it should be mentioned that in organic chemistry, the reaction of 2-aminopyridine with 1,3-bifunctional compounds is a useful synthetic method for the preparation of pyrido[1,2-*a*]pyrimidines.¹¹ Thus, aromatic salts of pyrido[1,2-*a*]pyrimidines have been prepared from 1,3-dioxo compounds¹² or their acetal and ketal equivalents^{12c,13} in acidic media. The reactions of β -oxo acetals and β -chlorovinyl aldehydes with 6-unsubstituted 2-aminopyridines give 4-substituted salts, whereas 2-substituted salts are formed from 6-substituted 2-aminopyridines.^{12a} The reactions with β -chlorovinyl ketones afford either

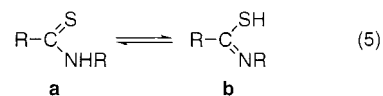
4-substituted or 2-substituted pyridinium[1,2-*a*]pyrimidines.¹⁴

In addition, it should be noted that the pyrazolo[1,2-*a*]pyrazolyl compounds shown in Scheme 2 and **2** (eq 2) behave differently in the presence of sodium methoxide. While the former compounds undergo ring opening as a consequence of the deprotonation of the RuC=CH proton, the deprotonation of **2** occurs at the N(2) nitrogen atom without ring opening. This difference in behavior appears to suggest that, in contrast to the heterocycles formed by addition of secondary amines with a second nitrogen atom to the allenylidene of **1**, the heterocycles resulting from the addition of primary amines with a second nitrogen atom are stable in basic medium. The reason for the stability of the latter seems to be the presence of a hydrogen atom in the nonring junction nitrogen atom. The behavior of both types of heterocycles toward the deprotonation can be related with the behavior of tertiary and secondary azoniabutadienyl complexes. The pyrazolo[1,2-*a*]pyrazolyl and tertiary azoniabutadienyl compounds, which are derived from secondary amines, undergo deprotonation at the RuC=CH carbon atom, while pyridinium[1,2-*a*]pyrimidinyl and secondary azoniabutadienyl complexes, which come from primary amines, undergo deprotonation at the nitrogen atom.

2. Reactions of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ with Thioisonicotinamide. Treatment of dichloromethane solutions of **1** with 1.1 equiv of thioisonicotinamide, under reflux, affords after 3 h the 1,3-thiazinium-6-yl-ruthenium complex [Ru(η^5 -C₅H₅)-{4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazinium-6-yl}(CO)(PⁱPr₃)]BF₄ (**6**), which was isolated as an orange solid in 86% yield, according to eq 4.



The formation of **6** with the nitrogen atom bonded to the Ph₂C carbon atom can be rationalized, formally, as the addition of one of the two NH bonds of the thioamide at the C _{β} –C _{γ} double bond of the allenylidene ligand of **1**, followed by the coordination of the sulfur atom to the C _{α} atom of the resulting vinylidene. However, it should be taken into account that primary and secondary thioamides have the tautomeric forms shown in eq 5.¹⁵



Furthermore, the addition of HXR (X = O, S, NR') molecules to the C _{α} –C _{β} double bond of the allenylidene ligand of **1** is a well-known process,^{4,5f} while there are

(10) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17.

(11) Hermecz, I.; Vasvári-Debrecezy, L.; Mátyus, P. In *Comprehensive Heterocyclic Chemistry II, A Review of the Literature 1982–1995*; Jones, G., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 8, Chapter 8.23.

(12) (a) Sawyer, J. R. H.; Wibberley, D. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1138. (b) Potts, K. T.; Dugas, R.; Surapaneni, C. R. *J. Heterocycl. Chem.* **1973**, *10*, 821. (c) Dennin, F.; Blondeau, D.; Sliwa, H. *Tetrahedron Lett.*, **1991**, *32*, 4307.

(13) (a) Pollak, A.; Stanovnik, B.; Tisler, M. *J. Org. Chem.* **1971**, *36*, 2457. (b) Tamura, S.; Ono, M. *Chem. Pharm. Bull.* **1978**, *26*, 3167.

(14) Fischer, G. W. *Z. Chem.* **1978**, *18*, 121; *Chem. Abstr.* **1978**, *89*, 23666.

(15) Walter, W.; Voss, J. In *The Chemistry of Amides*; Patai, S., Ed.; Interscience: London, 1970; Chapter 8.

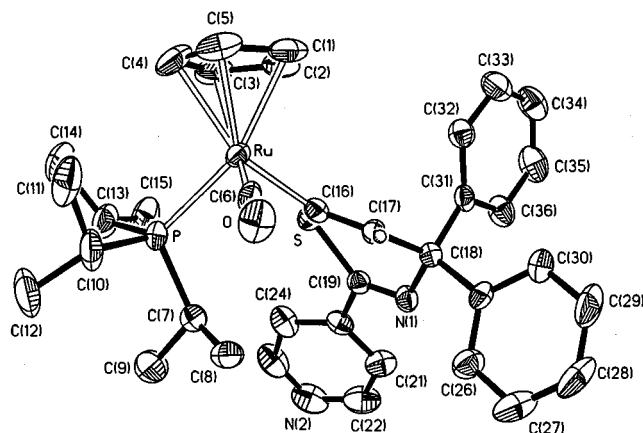


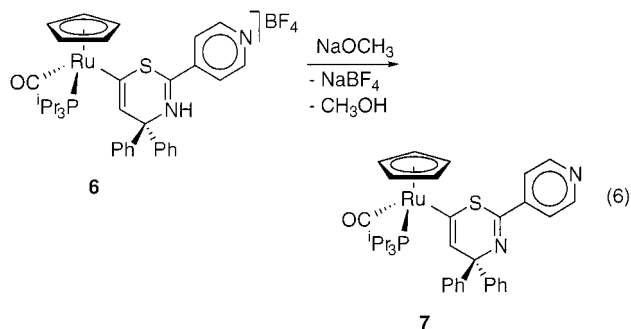
Figure 3. Molecular diagram of the complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-}\{4,4\text{-diphenyl-2-(}p\text{-pyridinyl)-4H-1,3-thiazin-6-yl}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**7**). Thermal ellipsoids are shown at 50% probability.

no precedents for the addition of primary amines to the $\text{C}_\beta\text{-C}_\gamma$ double bond. Therefore, the addition of the S-H bond of the imidothiol form **b** to the $\text{C}_\alpha\text{-C}_\beta$ double bond of the allenylidene ligand of **1**, followed by the coordination of the nitrogen atom to the C_γ atom of the resulting thiocarbene intermediate, seems to be the most reasonable way to explain the formation of **6**.

Moreover, since the formation of an isomer of **6** containing the nitrogen atom bonded to the RuC carbon atom is not observed, eq 4 suggests that the addition of SH bonds to the $\text{C}_\alpha\text{-C}_\beta$ double bond of the allenylidene ligand of **1** is favored with regard to the addition of NH bonds.

The most noticeable feature in the IR spectrum of **6** in Nujol is the presence of a $\nu(\text{NH})$ band at 3249 cm^{-1} . In the ^1H NMR spectrum, the NH resonance appears at 8.95 ppm, as a broad signal, whereas the resonance due to the $\text{RuC}=\text{CH}$ proton is observed as a singlet at 5.70 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows the RuC resonance at 130.9 as a doublet with a $J(\text{CP})$ value of 14.2 Hz.

Similarly to **2**, the nitrogen atom of **6** undergoes deprotonation in basic medium. Thus, the treatment of tetrahydrofuran suspensions of **6** with sodium methoxide leads to the thiazinyl derivative $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-}\{4,4\text{-diphenyl-2-(}p\text{-pyridinyl)-4H-1,3-thiazin-6-yl}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**7**), which was isolated as a yellow solid in 60% yield, according to eq 6.



Complex **7** was characterized by an X-ray crystallographic study. Figure 3 shows a view of the molecular geometry. Selected bond distances and angles are collected in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-}\{4,4\text{-diphenyl-2-(}p\text{-pyridinyl)-4H-1,3-thiazin-6-yl}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**7**)

Ru-P	2.3056(14)	S-C(19)	1.757(4)
Ru-C(1)	2.226(4)	N(1)-C(18)	1.464(4)
Ru-C(2)	2.256(4)	N(1)-C(19)	1.259(5)
Ru-C(3)	2.251(4)	N(2)-C(22)	1.318(7)
Ru-C(4)	2.234(4)	N(2)-C(23)	1.313(6)
Ru-C(5)	2.212(4)	C(16)-C(17)	1.313(5)
Ru-C(6)	1.813(4)	C(17)-C(18)	1.512(5)
Ru-C(16)	2.067(4)	C(18)-C(25)	1.521(5)
C(6)-O	1.146(5)	C(18)-C(31)	1.528(5)
S-C(16)	1.762(4)	C(19)-C(20)	1.474(5)
M(1) ^a -Ru-P	128.49(15)	C(16)-C(17)-C(18)	124.5(3)
M(1)-Ru-C(6)	125.08(19)	N(1)-C(18)-C(17)	110.4(3)
M(1)-Ru-C(16)	119.16(17)	C(17)-C(18)-C(25)	108.9(3)
P-Ru-C(6)	88.05(13)	C(17)-C(18)-C(31)	112.0(3)
P-Ru-C(16)	95.11(10)	C(25)-C(18)-C(31)	110.5(3)
C(6)-Ru-C(16)	91.02(15)	C(18)-N(1)-C(19)	118.2(3)
Ru-C(16)-C(17)	128.6(3)	N(1)-C(19)-S	124.9(3)
Ru-C(16)-S	114.63(18)	N(1)-C(19)-C(20)	117.5(3)
S-C(16)-C(17)	116.1(3)	S-C(19)-C(20)	117.4(3)

^a M(1) is the centroid of the C(1)-C(5) Cp carbon atoms.

Similarly to **2** and **4**, the geometry around the ruthenium center in **7** is close to octahedral with the cyclopentadienyl ligand occupying one face of the octahedron. The angles formed by the triisopropylphosphine, the carbonyl group, and the thiazinyl ligand are close to 90° .

The thiazine skeleton maintains a boat conformation with the C(16), C(17), N(1), and C(19) atoms lying in a plane (the deviations from this plane are $-0.013(3)$, $0.014(3)$, $-0.012(3)$, and $0.015(4)$ Å, respectively) and the C(18) and S atoms situated $0.536(3)$ and $0.4734(9)$ Å above the plane, respectively.

The Ru-C(16) distance of $2.067(4)$ Å compares well with the Ru-C(7) distances in **2** and **4** and supports a Ru-C(sp²) single bond. The angles Ru-C(16)-C(17) = $128.6(3)^\circ$ and Ru-C(16)-S = $114.63(14)^\circ$ support the sp² hybridization for C(16).

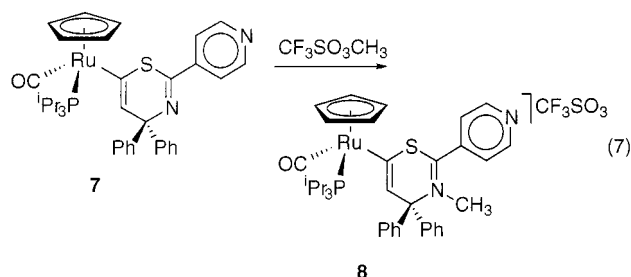
The structural parameters within the thiazine ring agree well with those found in organic thiazines.¹⁶ The C(16)-C(17) ($1.313(5)$ Å) and C(19)-N(1) ($1.259(5)$ Å) bond lengths support the double-bond character of these bonds, whereas the C(16)-S ($1.762(4)$ Å), S-C(19) ($1.757(4)$ Å), N(1)-C(18) ($1.464(4)$ Å), and C(17)-C(18) ($1.512(5)$ Å) distances indicate single bonds between these atoms.

In agreement with the structure shown in Figure 3, the ^1H NMR spectrum of **7** contains a singlet at 6.08 ppm due to the C(17)-H resonance, and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a doublet at 132.2 ppm, with a $J(\text{CP})$ value of 13.8 Hz, corresponding to C(16).

The deprotonation of **6** is reversible. Thus, the addition of 1.1 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ to dichloromethane solutions of **7** regenerates **6**. Similarly, the treatment of dichloromethane solutions of **7** with 1.1 equiv of methyl trifluoromethanesulfonate yields the *N*-methylthiazinium derivative $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{-}\{3\text{-methyl-4,4-}$

(16) (a) Yokoyama, M.; Nakamura, M.; Ohteki, H.; Imamoto, T.; Yamaguchi, K. *J. Org. Chem.* **1982**, *47*, 1090. (b) Bakasse, M.; Duguay, G.; Quiniou, H.; Toupet, L. *Tetrahedron* **1988**, *44*, 139. (c) Tea, C. G.; Pradère, J. P.; Bujoli, B.; Quiniou, H.; Toupet, L. *Bull. Soc. Chim. Fr.* **1987**, 149. (d) Quiniou, H.; Guilloton, O. *Adv. Heterocycl. Chem.* **1990**, *50*, 85.

diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazinium-6-yl}(CO)-(PⁱPr₃)]CF₃SO₃ (**8**), which was isolated as an orange solid in 76% yield (eq 7).



The IR spectrum of **8**, in Nujol, shows the characteristic stretching bands of the [CF₃SO₃]⁻ anion at 1275, 1260, 1161, and 1030 cm⁻¹. In the ¹H NMR spectrum, the most noticeable resonances are two singlets at 5.79 and 4.55 ppm, with a 1:3 intensity ratio, corresponding to the RuC=CH proton and methyl group, respectively. The ¹³C{¹H} NMR spectrum contains a resonance due to the RuC= carbon atom, which appears at 132.3 ppm as a doublet with a *J*(CP) value of 13.8 Hz.

As a consequence of the discovery of the cephalosporins and the enormous developments occurring in the chemistry of these antibiotics since the 1940s, the 1,3-thiazine nucleus has become one of the most important six-membered heterocycles.^{16d} The syntheses of 1,3-thiazines have been classified in four types ([3 + 3], [4 + 2], [5 + 1], and [6 + 0]) according to the composition of the assembling units.¹⁷ The reaction shown in eq 4 is a novel [3 + 3] synthesis, where an allenylidene derivative is used as the C₃ reagent for the first time.

Concluding Remarks

This study has revealed the existence of two new types of η^1 -carbon unsaturated ligands and the ability of the unsaturated chain of the allenylidene ligand of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ to act as a C₃ reagent in condensation reactions with 2-aminopyridine and thioisonicotinamide.

Reactions of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ with the above-mentioned organic molecules leads to the derivatives [Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]BF₄ and [Ru(η^5 -C₅H₅){4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazinium-6-yl}(CO)(PⁱPr₃)]BF₄, which react with sodium methoxide to give the corresponding pyrido[1,2-*a*]pyrimidinyl and 1,3-thiazinyl complexes and, in contrast to the previously reported pyrazolo[1,2-*a*]pyrazolyl related compounds, do not undergo ring opening.

In conclusion, the allenylidene ligand of [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ undergoes 1,2,3-diheterocyclization reactions with primary amines containing a second heteroatom and thioamides, similar to those with secondary amines with a second heteroatom. However, the resulting cycles from the primary amines are stable in basic medium, as a consequence of the presence of a NH bond in one of the heterocycles, which can be deprotonated, preventing the ring opening.

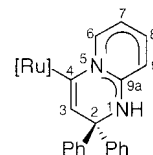
Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material [Ru(η^5 -C₅H₅)(C=C=CPh₂)(CO)(PⁱPr₃)]BF₄ (**1**) was prepared by the published method.¹⁰

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me₄Si (¹H and ¹³C) and 85% H₃PO₄ (³¹P). Coupling constants, *J*, are given in hertz.

Preparation of [Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]BF₄ (2**) and [Ru(η^5 -C₅H₅){C(CH=CPh₂)=NHC(CH₃)₄N}(CO)(PⁱPr₃)]BF₄ (**3**).** A dark red solution of **1** (295 mg, 0.47 mmol) in 5 mL of dichloromethane at -55 °C was treated with 2-aminopyridine (49 mg, 0.52 mmol), and the mixture was stirred for 10 min. The solution became yellow and the solvent was removed in vacuo, giving a yellow residue. The ³¹P{¹H} NMR (CDCl₃) spectrum of this residue shows the presence of complexes **2** and **3** in a molar ratio of 4:1. The residue was washed with diethyl ether to afford a yellow solid, which was crystallized, at room temperature, from dichloromethane/diethyl ether to give yellow crystals of complex **2**. Yield: 251 mg (66%). Anal. Calcd for C₃₅H₄₂BF₄N₂OPRu·CH₂Cl₂: C, 51.87; H, 5.22; N, 3.46. Found: C, 51.89; H, 5.22; N, 3.63.

Spectroscopic Data for **2**.



IR (Nujol, cm⁻¹): ν (NH) 3328 (m), ν (CO) 1935 (s), ν (C=N, C=C, Ph) 1646 (m), 1592 (s), 1516 (m), ν (BF₄) 1093 (br). ¹H NMR (300 MHz, 20 °C, CDCl₃, plus COSY): δ 8.68 (d, 1H, *J*(H₆H₇) = 6.9, H₆), 8.56 (s, 1H, NH), 7.28–7.12 (m, 12H, H₈, H₉, and Ph), 6.60 (ddd, 1H, *J*(H₆H₇) = *J*(H₇H₈) = 6.9, *J*(H₇H₉) = 2.1, H₇), 5.50 (s, 1H, H₃), 5.30 (s, 5H, Cp), 2.13 (m, 3H, PCHCH₃), 0.89 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.7, PCHCH₃), 0.86 (dd, 9H, *J*(PH) = 6.9, *J*(PH) = 13.8, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, CDCl₃): δ 62.3 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, CDCl₃, plus DEPT): δ 206.5 (d, *J*(PC) = 21.1, CO), 151.3 (s, C_{9a}), 145.8 (d, *J*(PC) = 12.0, C₄), 145.2, 144.7 (both s, C_{ipso-Ph}), 141.0, 140.3, 115.5, 112.2 (all s, C₆-C₉), 134.4 (br s, C₃), 128.9, 128.6, 127.9, 127.2, 126.5 (all s, Ph), 85.7 (s, Cp), 62.3 (s, C₂), 25.5 (d, *J*(PC) = 21.7, PCHCH₃), 19.6, 18.8 (both s, PCHCH₃). MS (FAB⁺): *m/z* 639 (M⁺).

Spectroscopic Data for **3.** IR (Nujol, cm⁻¹): ν (NH) 3283 (m), ν (CO) 1952 (s), ν (C=N) 1592 (m), ν (BF₄) 1090 (br). ¹H NMR (300 MHz, 20 °C, CDCl₃): δ 11.22 (br s, 1H, NH), 8.17 (d, *J*(HH) = 4.8, 1H, py), 7.74 (m, 1H, py) 7.54–6.90 (m, 13H, Ph + 2H, py + =CH), 5.04 (s, 5H, Cp), 2.31 (m, 3H, PCHCH₃), 1.29 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.4, PCHCH₃), 1.26 (dd, 9H, *J*(PH) = 6.6, *J*(PH) = 13.5, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, CDCl₃): δ 62.6 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, CDCl₃): δ 255.1 (d, *J*(PC) = 8.4, RuC), 203.8 (d, *J*(PC) = 16.1, CO), 148.0, 139.1, 130.2, 128.2, 128.0, 122.9, 117.4 (all s, Ph + py + CH=CPh₂), 87.5 (s, Cp), 29.1 (d, *J*(PC) = 23.4, PCHCH₃), 19.8, 19.5 (both s, PCHCH₃). All attempts to obtain complex **3** analytically pure from the reaction mixture of **2** and **3** by either fractional crystallization or column chromatography were unsuccessful.

Preparation of Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyrido[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃) (4**).** A yellow suspension of **2** (160 mg, 0.22 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (24 mg, 0.44 mmol) and stirred for 1 h. The solvent was removed in vacuo. Toluene (10 mL) was added, and the suspension was filtered to eliminate sodium tetrafluoroborate. Solvent was evaporated, and the residue was washed with pentane to afford a yellow solid.

(17) Sainsbury, M. In *Comprehensive Heterocyclic Chemistry II, A Review of the Literature 1982–1995*; Boulton, A. J., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 6, Chapter 6.07.

Table 3. Crystal Data and Data Collection and Refinement Details for [Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]BF₄ (2), Ru(η^5 -C₅H₅){2,2-diphenyl-2*H*-pyrido[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃) (4), and Ru(η^5 -C₅H₅){4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazin-6-yl}(CO)(PⁱPr₃) (7)

	2	4	7
Crystal Data			
formula	C ₃₅ H ₄₂ BF ₄ N ₂ OPRu·CH ₂ Cl ₂	C ₃₅ H ₄₁ N ₂ OPRu	C ₃₆ H ₄₁ N ₂ OPRuS·1/2C ₇ H ₈
mol wt	810.52	637.74	727.88
color and habit	yellow prism	yellow prism	yellow prism
symmetry, space group	monoclinic, <i>P2</i> ₁	monoclinic, <i>P2</i> ₁ / <i>n</i>	monoclinic, <i>P2</i> ₁ / <i>c</i>
<i>a</i> , Å	10.207(3)	11.726(2)	14.688(9)
<i>b</i> , Å	17.975(9)	17.719(3)	13.419(5)
<i>c</i> , Å	10.305(5)	15.393(3)	17.696(8)
β , deg	98.11(3)	103.18(2)	102.65(3)
<i>V</i> , Å ³ ; <i>Z</i>	1871(1); 2	3114(1); 4	3403(3); 4
<i>D</i> _{calcd} , g cm ⁻³	1.438	1.360	1.421
Data Collection and Refinement			
diffractometer	AFC6S-Rigaku	Bruker Siemens STOE AED-2	Bruker Siemens-P4
λ (Mo K α), Å	0.710 73	0.710 73	0.710 73
monochromator	graphite oriented	graphite oriented	graphite oriented
μ , mm ⁻¹	0.646	0.58	0.604
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 50$
temp, K	298.0(2)	298.0(2)	173.0(2)
no. of data collect	3427	6747	7219
no. of unique data		5430 (<i>R</i> _{int} = 0.0451)	5880 (<i>R</i> _{int} = 0.0204)
no. of obsd data	2733		
no. of params refined	393	371	419
<i>R</i> ¹ ^a	0.0537 (<i>F</i> > 3 σ (<i>F</i>))	0.0528 (<i>F</i> ² > 2 σ (<i>F</i> ²))	0.0390 (<i>F</i> ² > 2 σ (<i>F</i> ²))
w <i>R</i> ² ^b (all data)		0.0984	0.1082
GOF	2.364	0.995	1.009

$$^a R1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

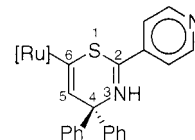
Yield: 84 mg (60%). Anal. Calcd for C₃₅H₄₁N₂OPRu: C, 65.91; H, 6.48; N, 4.39. Found: C, 65.98; H, 6.39; N, 4.52. IR (Nujol, cm⁻¹): ν (CO) 1918 (s), ν (C=N, C=C, Ph) 1639 (m), 1592 (s), 1530 (m). ¹H NMR (300 MHz, 20 °C, C₆D₆, plus COSY): δ 7.86 (d, 1H, *J*(H₆H₇) = 6.9, H₆), 7.80–7.00 (m, 10H, Ph), 6.78 (d, 1H, *J*(H₈H₉) = 9.0, H₉), 6.32 (ddd, 1H, *J*(H₈H₉) = 9.0, *J*(H₇H₈) = 6.9, *J*(H₆H₈) = 1.5, H₈), 5.53 (dd, 1H, *J*(H₆H₇) = *J*(H₇H₈) = 6.9, H₇), 4.94 (s, 1H, H₃), 4.88 (s, 5H, Cp), 2.00 (m, 3H, PCHCH₃), 0.77 (dd, 9H, *J*(PH) = 6.6, *J*(PH) = 13.5, PCHCH₃), 0.64 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 12.9, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, C₆D₆): δ 65.6 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, C₆D₆, plus HETCOR): δ 207.9 (d, *J*(PC) = 21.7, CO), 152.5 (s, C_{9a}), 151.9, 150.6 (both s, C_{ipso-Ph}), 140.2 (d, *J*(PC) = 13.7, C₄), 138.9 (s, C₆), 130.5 (s, C₈), 129.3 (s, C₃), 128.6, 128.5, 128.4, 127.6, 126.0, 125.1 (all s, Ph), 123.1 (s, C₉), 101.6 (s, C₇), 85.8 (s, Cp), 66.2 (s, C₂), 26.0 (d, *J*(PC) = 23, PCHCH₃), 19.9, 19.3 (both s, PCHCH₃). MS (FAB⁺): *m/z* 639 (M⁺ + H).

Reaction of 4 with HBF₄. A solution of 4 (12.8 mg, 0.02 mmol) in 0.5 mL of dichloromethane-*d*₂ was treated with 2.8 μ L (0.02 mmol) of HBF₄·OEt₂. The ¹H and ³¹P{¹H} NMR spectra recorded after 2 min showed only the presence of 2.

Preparation of [Ru(η^5 -C₅H₅){1-methyl-2,2-diphenyl-2*H*-pyridinium[1,2-*a*]pyrimidin-4-yl}(CO)(PⁱPr₃)]CF₃SO₃ (5). A yellow solution of 4 (145 mg, 0.22 mmol) in 5 mL of dichloromethane was treated with methyl trifluoromethanesulfonate (27 μ L, 0.24 mmol), and the mixture was stirred for 5 min. The solvent was removed in vacuo, and the residue was washed with diethyl ether to afford a yellow solid. Yield: 104 mg (65%). Anal. Calcd for C₃₇H₄₄F₃N₂O₄PRuS: C, 55.42; H, 5.53; N, 3.49; S, 4.00. Found: C, 55.74; H, 5.68; N, 3.23; S, 4.19. IR (Nujol, cm⁻¹): ν (CO) 1927 (s), ν (C=N, C=C, Ph) 1630 (m), 1585 (m), 1500 (m), and ν (SO₃) 1277 (vs), 1262 (vs), 1144 (s), 1030 (s). ¹H NMR (300 MHz, 20 °C, CDCl₃): δ 9.14 (br s, 1H, H₆), 7.82 (m, 1H, py), 7.39–7.10 (m, 12H, Ph + 2H, py), 6.97 (m, 1H, py), 5.42 (br s, 1H, H₃), 5.25 (s, 5H, Cp), 2.96 (s, 3H, NCH₃), 2.12 (m, 3H, PCHCH₃), 0.90 (m, 18H, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, CDCl₃): δ 62.8 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, CDCl₃): δ 206.3 (d, *J*(PC) = 21.6, CO), 151.4 (s, C_{9a}), 145.3 (br, C₄), 143.4, 142.9, 112.7, 112.2 (all s,

C₆–C₉), 142.0, 139.5 (both s, C_{ipso-Ph}), 135.0 (s, C₃), 128.9, 128.8, 128.5, 128.1, 127.7 (all s, Ph), 120.9 (q, *J*(CF) = 322, CF₃), 85.9 (s, Cp), 69.2 (s, C₂), 36.24 (s, NCH₃), 25.3 (d, *J*(PC) = 19.8, PCHCH₃), 19.4, 18.7 (both s, PCHCH₃). MS (FAB⁺): *m/z* 653 (M⁺).

Preparation of [Ru(η^5 -C₅H₅){4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazin-6-yl}(CO)(PⁱPr₃)]BF₄ (6).



A dark red solution of 1 (395 mg, 0.63 mmol) in 12 mL of dichloromethane was treated with thioisonicotinamide (96 mg, 0.69 mmol), and the mixture was refluxed for 3 h. The solvent was removed in vacuo, and the residue was washed with diethyl ether to afford an orange solid. Yield: 410 mg (86%). Anal. Calcd for C₃₆H₄₂BF₄N₂OPRuS: C, 56.18; H, 5.50; N, 3.64; S, 4.17. Found: C, 56.10; H, 5.57; N, 3.59; S, 4.25. IR (Nujol, cm⁻¹): ν (NH) 3249 (w), ν (CO) 1909 (s), ν (C=N, C=C, Ph) 1638 (m), 1620 (m), 1575 (m). ¹H NMR (300 MHz, 20 °C, CDCl₃): δ 8.95 (br, 1H, NH), 8.68 (d, 2H, *J*(HH) = 6.5, py), 8.08 (d, 2H, *J*(HH) = 6.5, py), 7.31–7.10 (m, 10H, Ph), 5.70 (s, 1H, =CH), 5.19 (s, 5H, Cp), 2.20 (m, 3H, PCHCH₃), 1.04 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHCH₃), 1.02 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 13.8, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, CDCl₃): δ 66.4 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, CDCl₃): δ 207.0 (d, *J*(PC) = 19.3, CO), 158.5 (s, SCN), 148.6 (s, C_{p-py}), 148.1 (s, C_{o-py}), 147.9, 147.7 (both s, C_{ipso-Ph}), 130.9 (d, *J*(PC) = 14.2, RuC), 128.2 (s, =CH), 127.9, 127.8, 127.7, 126.3, 126.2 (all s, Ph), 121.9 (s, C_{m-py}), 85.7 (s, Cp), 70.8 (s, CPh₂), 26.8 (d, *J*(PC) = 23.5, PCHCH₃), 19.9, 19.4 (both s, PCHCH₃). MS (FAB⁺): *m/z* 683 (M⁺).

Preparation of Ru(η^5 -C₅H₅){4,4-diphenyl-2-(*p*-pyridinyl)-4*H*-1,3-thiazin-6-yl}(CO)(PⁱPr₃) (7). An orange suspension of 6 (410 mg, 0.54 mmol) in 15 mL of tetrahydrofuran was treated with sodium methoxide (58 mg, 1.08 mmol) and

stirred for 1 h. The solvent was removed in vacuo. Toluene (10 mL) was added, and the suspension was filtered to eliminate sodium tetrafluoroborate. The solution was concentrated to ca. 1 mL, and 10 mL of pentane was added to afford a yellow solid, which was washed with pentane. Yield: 175 mg (60%). Anal. Calcd for C₃₆H₄₁N₂OPRuS: C, 63.42; H, 6.06; N, 4.11; S, 4.70. Found: C, 63.28; H, 5.95; N, 4.01; S, 4.93. IR (Nujol, cm⁻¹): ν (CO) 1920 (s), ν (C=N, C=C, Ph) 1580 (m), 1580 (m), 1575 (m), 1550 (m). ¹H NMR (300 MHz, 20 °C, C₆D₆): δ 8.60 (d, 2H, J (HH) = 4.5, py), 7.85 (d, 2H, J (HH) = 4.5, py), 7.73 (m, 4H, Ph), 7.28–7.00 (m, 6H, Ph), 6.08 (s, 1H, =CH), 4.88 (s, 5H, Cp), 1.95 (m, 3H, PCHCH₃), 0.83 (dd, 9H, J (HH) = 7.2, J (PH) = 14.1, PCHCH₃), 0.76 (dd, 9H, J (HH) = 6.2, J (PH) = 13.2, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, C₆D₆): δ 67.1 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, CD₂Cl₂): δ 207.6 (d, J (PC) = 19.3, CO), 159.3 (s, SCN), 150.4 (s, C_{*o*}-py), 149.6, 148.8 (both s, C_{*ipso*}-Ph), 145.8 (s, C_{*p*}-py), 132.2 (d, J (PC) = 13.8, RuC), 130.7 (s, =CH), 128.3, 128.1, 127.9, 126.4, 126.3 (all s, Ph), 121.3 (s, C_{*m*}-py), 86.2 (s, Cp), 70.9 (s, CPh₂), 27.4 (d, J (PC) = 23.0, PCHCH₃), 20.3, 19.8 (both s, PCHCH₃). MS (FAB⁺): m/z 683 (M⁺ + H).

Reaction of 7 with HBF₄. A solution of 7 (13.4 mg, 0.02 mmol) in 0.5 mL of dichloromethane-*d*₂ was treated with 2.8 μ L (0.02 mmol) of HBF₄·OEt₂. The ¹H and ³¹P{¹H} NMR spectra recorded after 2 min showed only the presence of 6.

Preparation of [Ru(η^5 -C₅H₅){3-methyl-4,4-diphenyl-2-(*p*-pyridinyl)-4H-1,3-thiazinium-6-yl}(CO)(PⁱPr₃)]-CF₃SO₃ (8). A yellow-brown solution of 7 (78 mg, 0.11 mmol) in 5 mL of dichloromethane was treated with methyl trifluoromethanesulfonate (15 μ L, 0.13 mmol), and it was stirred for 5 min. The red solution obtained was concentrated to ca. 2 mL, and addition of 12 mL of diethyl ether caused the precipitation of an orange solid. Yield: 75 mg (76%). Anal. Calcd for C₃₈H₄₄F₃N₂O₄PRuS₂: C, 53.95; H, 5.24; N, 3.31; S, 7.58. Found: C, 53.90; H, 5.21; N, 3.40; S, 7.63. IR (Nujol, cm⁻¹): ν (CO) 1925 (s), ν (C=N, C=C, Ph) 1645 (m), 1562 (m), ν (SO₃) and ν (CF₃) 1275 (vs), 1260 (vs), 1161 (s), 1030 (s). ¹H NMR (300 MHz, 20 °C, CDCl₃): δ 8.93 (d, 2H, J (HH) = 6.8, py), 8.55 (d, 2H, J (HH) = 6.8, py), 7.38–7.24 (m, 10H, Ph), 5.79 (s, 1H, =CH), 5.31 (s, 5H, Cp), 4.55 (s, 3H, NCH₃), 2.29 (m, 3H, PCHCH₃), 1.15 (dd, 9H, J (HH) = 7.5, J (PH) = 14.4, PCHCH₃), 1.13 (dd, 9H, J (HH) = 6.9, J (PH) = 13.8, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 20 °C, CD₂Cl₂): δ 65.2 (s). ¹³C{¹H} NMR (75.4 MHz, 20 °C, CD₂Cl₂): δ 207.2 (d, J (PC) = 19.3,

CO), 157.8 (br, SCN), 152.5 (br, C_{*p*}-py), 147.8, 147.4 (both br, C_{*ipso*}-Ph), 145.9 (s, C_{*o*}-py), 132.3 (d, J (PC) = 13.8, RuC), 129.7 (s, =CH), 128.2, 128.1, 127.9, 127.0, 126.9 (all s, Ph), 125.2 (s, C_{*m*}-py), 121.0 (q, J (CF) = 321, CF₃), 86.0 (s, Cp), 71.7 (s, CPh₂), 48.5 (s, NCH₃), 27.3 (d, J (PC) = 23.5, PCHCH₃), 19.9, 19.4 (both s, PCHCH₃). MS (FAB⁺): m/z 697 (M⁺).

Crystal Data for 2, 4, and 7. Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to AFC6S-Rigaku (2; T = 298.0(2) K), Bruker-Siemens-STOE AED-2 (4; T = 298.0(2) K), and Bruker-Siemens P4 (7; T = 173.0(2) K) automatic diffractometers (Mo K α radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit cell parameters were determined by least-squares fitting from the settings of high-angle reflections. Data were collected by the $\omega/2\theta$ scan method. Lorentz and polarization corrections were applied. Decay were monitored by measuring three standard reflections throughout data collection. Shift corrections for decay and absorption (semiempirical ψ -scan method) were also applied.

The structures were solved by Patterson methods and refined by full-matrix least squares on F (2)¹⁸ or F^2 (4 and 7).¹⁹ Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were observed or included at idealized positions. For 2 and 7, crystallization solvent molecules (dichloromethane and disordered toluene, respectively) were also detected, included in the refinement, and refined isotropically. Crystal data and details of the data collection and refinement are given in Table 3.

Acknowledgment. We acknowledge financial support from the DGES of Spain (Project PB98-1591).

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for 2, 4, and 7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000415T

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

(19) TEXSAN Single-Crystal Structure Analysis Software, version 5.0; Molecular Structure Corp., The Woodlands, TX, 1989.