

Addition of Secondary and Primary Amines to the Allenylidene Ligand of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$: Synthesis of Azoniabutadienyl, Aminoallenyl, and Azabutadienyl Derivatives of Ruthenium(II)

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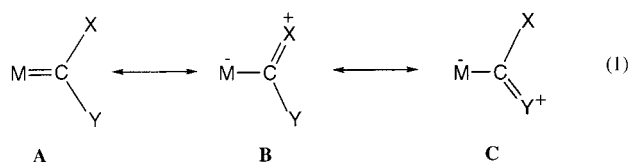
Received June 17, 1999

The allenylidene complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**1**) reacts with diethylamine and piperidine to give the azoniabutadienyl derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NEt}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**2**) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NCH}_2(\text{CH}_2)_3\text{CH}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**3**), respectively. The molecular structure of **2** has been determined by X-ray crystallography. The geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face. The Ru–C_α bond length is 2.063(6) Å, whereas the C_α–N distance is 1.306(7) Å. Treatment of **2** and **3** with sodium methoxide produces the deprotonation of the CH=CPh₂ fragment to afford the aminoallenyl derivatives

$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NET}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**4**) and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NCH}_2(\text{CH}_2)_3\text{CH}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**5**). Complex **1** also reacts with *n*-propylamine and aniline. In this case, the reaction products are $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NH}^n\text{Pr}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**6**) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**7**). Treatment of **6** and **7** with sodium methoxide produces the deprotonation of the nitrogen atom of the unsaturated η¹-carbon ligand, to give the azabutadienyl compounds $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{N}^n\text{Pr}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**8**) and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**9**), respectively. The ellipticities of the Ru–C_α and C_α–N bonds of the model compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}_2\}(\text{CO})(\text{PH}_3)]^+$ (**10**), $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NH}_2)=\text{C}=\text{CH}_2\}(\text{CO})(\text{PH}_3)$ (**11**), and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}\}(\text{CO})(\text{PH}_3)$ (**12**) have been studied using the AIMPAC series of programs. The obtained values are 0.07 and 0.12 (**10**), 0.05 and 0.07 (**11**), and 0.07 and 0.10 (**12**), respectively.

Introduction

Carbene complexes of the chromium triad have proven to be attractive reagents in modern organic synthesis,¹ in particular, the alkenylalkoxycarbene and alkenylaminocarbene derivatives.² X-ray diffraction,³ spectroscopic,⁴ and theoretical⁵ studies indicate that for an adequate description of the bonding situation in these types of compounds the three resonance structures



shown in eq 1 must be considered. For aminocarbene complexes (X = N) the structure B is a major contributor.

Since the advent of Grubbs' ROMP catalyst $\text{RuCl}_2(\text{CHCH}=\text{CPh}_2)(\text{PR}_3)_2$ ⁶ a great deal of interest has been

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(1) (a) Dötz, K. H. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983; p 191. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Schwindt, M. A.; Müller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143.

(2) (a) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbit, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784. (b) Barluenga, J. *Pure Appl. Chem.* **1996**, *68*, 543.

(3) Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983; p 73.

(4) (a) Fischer, H.; Kreissl, F. R. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983; p 69. (b) Hafner, A.; Hegedus, L. S.; de Weck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

(5) Hoffmann, P. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983; p 113.

(6) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (c) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503. (d) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 4707. (e) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311. (f) Nguyen, S. T.; Grubbs, R. H. *J. Organomet. Chem.* **1995**, *497*, 195. (g) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867. (h) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001. (i) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. (j) Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 4088.

given to the synthesis of alkenylcarbenes of the iron triad.⁷ However, as far as we know, alkenylaminocarbenes of ruthenium have not been previously reported.

Aminocarbene complexes are usually prepared by exchange processes involving the displacement with secondary and primary amines of alkoxy groups from alkoxy-carbenes,⁸ or by addition of these amines to vinylidene precursors.⁹ In 1993, Fischer and co-workers reported that also (diarylallenylidene)pentacarbonylchromium and -tungsten complexes react with secondary and primary amines to afford alkenylaminocarbene derivatives.¹⁰

Diarylallenylidene complexes of the iron triad have attracted a great deal of attention in recent years, as a new type of organometallic intermediate that may have unusual reactivity in stoichiometric¹¹ and catalytic¹² processes. The reactivity of these types of compounds strongly depends on the particular metallic fragment which stabilizes the allenylidene unit. Thus, three different behaviors have been observed.

The diphenylallenylidene ligand of the complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{C}=\text{C}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)$ shows nucleophilic character, reacting with HBF_4 and dimethyl acetylenedicarboxylate to give $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{CCH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)]\text{BF}_4$ and $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{\text{C}=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})=\text{C}=\text{CPh}_2\}(\text{P}^i\text{Pr}_3)]$, respectively.¹³ In contrast, the cationic compounds $[\text{Os}\{\text{C}[\text{C}(\text{O})\text{OMe}]=\text{CH}_2\}(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$,¹⁴ $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{C}=\text{C}=\text{CPh}_2)\text{L}_2]\text{PF}_6$ ($\text{L}_2 = 2\text{PPh}_3$,

dppe , dppm),¹⁵ $[\text{RuCl}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppm})_2]\text{PF}_6$,¹⁶ $[\text{Ru}(\eta^5\text{-C}_n\text{H}_m)(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)\{\kappa^1\text{-Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Bu}^t\}]\text{PF}_6$ ($\text{C}_n\text{H}_m = \text{C}_5\text{H}_5$, C_9H_7),¹⁷ and $[\text{RuCl}(\text{C}=\text{C}=\text{CPh}_2)\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]\text{PF}_6$ ¹⁸ have a moderate electrophilic character. These complexes do not undergo intermolecular addition of weak nucleophilic reagents (i.e. water and alcohols), and the reactions with strong nucleophiles lead to functionalized alkynyl compounds as a result of the regioselective addition of the reagents at the C_γ atom of the allene ligand. Diphenylallenylidene groups stabilized by less basic metallic fragments, such as $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{P}^i\text{Pr}_3)]^+$,¹⁹ $[\text{Ru}(\eta^5\text{-C}_9\text{H}_4\text{Me}_3)(\text{CO})(\text{PPh}_3)]^+$,²⁰ and $[\text{RuCl}(\eta^6\text{-C}_6\text{H}_4\text{X}_2)(\text{PMe}_3)]^+$ ($\text{X} = \text{H}$, Me)²¹ show stronger electrophilic character and add alcohols at the $\text{C}_\alpha\text{-C}_\beta$ double bond of the allenylidene moiety to afford α,β -unsaturated alkoxy-carbene derivatives.

Because EHT-MO calculations on transition-metal allenylidene complexes indicate that the C_α and C_β atoms are electrophilic and nucleophilic centers, respectively,^{15a,22} and the H-O hydrogen atom of alcohols is electrophilic, it has been proposed that the transition state for the RXH additions to allenylidene ligands requires a heteroatom- C_α interaction, which labilizes the H-X bond, favoring the migration of the H-X hydrogen atom to the C_β atom of the allenylidene ligand.^{22c} In agreement with this, it has been recently observed that the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ adds PRPh_2 ($\text{R} = \text{H}$, Me , Ph) selectively at the C_α atom to afford the derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{PRPh}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$.²³ Surprisingly, the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{PPhPh}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ is stable and does not evolve by migration of the H-P hydrogen atom to the C_β atom of the allenylidene unit. Interest in the behavior of the diphenylallenylidene ligand in the presence of EHR_2 ($\text{E} =$ group 15 donor atom) molecules, and in the synthesis of "aminocarbenes" of ruthenium, led us to investigate the reactivity of the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ toward secondary and primary amines. In this paper, we report the synthesis and characterization of the first azoniabutadienyl, aminoallenyl, and azabutadienyl complexes of ruthenium(II).

(7) (a) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Chem. Commun.* **1989**, 219. (b) Devanne, D.; Dixneuf, P. H. *Chem. Commun.* **1990**, 641. (c) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (d) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258. (e) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (f) Ruiz, N.; Péron, D.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 1095. (g) Kühn, J.; Schollmeyer, D.; Rück-Braun, K. *Chem. Ber.* **1997**, *130*, 1647. (h) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919. (i) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (j) Xia, H. P.; Jia, G. *Organometallics* **1997**, *16*, 1. (k) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. *J. Organomet. Chem.* **1997**, *538*, 31. (l) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M. *Organometallics* **1998**, *17*, 3707. (m) Harlow, K. J.; Hill, A. I.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **1998**, *17*, 1916. (n) Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M. P.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500. (o) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4959. (p) Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177.

(8) Kreissl, F. R. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983; p 151.

(9) (a) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (b) Morran, P. D.; Mawby, R. J.; Wilson, G. D.; Moore, M. H. *Chem. Commun.* **1996**, 261. (c) Bianchini, C.; Purches, G.; Zanobini, F.; Peruzzini, M. *Inorg. Chim. Acta* **1998**, *272*, 1. (d) Yam, V. W.-W.; Chu, B. W.-K.; Cheung, K.-K. *Chem. Commun.* **1998**, 2261.

(10) Fischer, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133.

(11) (a) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (b) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178*, 409. (c) Buriez, B.; Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. *T. Organometallics* **1999**, *18*, 1504.

(12) (a) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (b) Trost, B. M.; Flygare, J. A. *Tetrahedron Lett.* **1994**, *35*, 4059. (c) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315. (d) Picquet, M.; Touchard, D.; Bruneau, C.; Dixneuf, P. H. *New J. Chem.* **1999**, 141. (e) Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. *T. Chem. Commun.* **1999**, 601. (f) Harlow, K. J.; Hill, A. F.; Wilton-Ely, J. D. E. *J. Chem. Soc., Dalton Trans.* **1999**, 285.

(13) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479.

(14) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373.

(15) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453.

(16) (a) Pirio, N.; Touchard, D.; Toupel, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980. (b) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920.

(17) Crochet, P.; Demerseman, B.; Vallejo, M. I.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 5406.

(18) Wolinska, A.; Touchard, D.; Dixneuf, P. J.; Romero, A. J. *Organomet. Chem.* **1991**, *420*, 217.

(19) (a) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297.

(20) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 2483.

(21) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809.

(22) (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) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *15*, 55826.

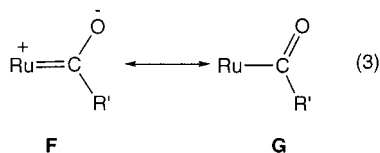
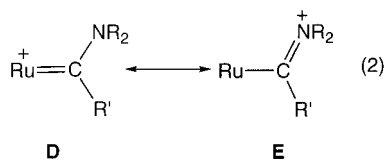
(23) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434.

BF₄ (2.010(6) Å),⁷⁰ and [Ru(η⁵-C₅Me₅)(μ-SⁱPr)₂(μ-C₁₈H₁₅)]-BF₄ (2.04(3), 1.98(2) Å),²⁸ where a ruthenium–carbon bond between single and double has been proposed.

The Ru–C(7) distance lies between those reported for the allenyl derivatives Ru(η⁵-C₅H₅){C(C≡CPh)=C=CPh₂}(CO)(PⁱPr₃) (2.004(5) Å)^{22c} and [Ru(η⁵-C₅H₅){C(PHPh₂)=C=CPh₂}(CO)(PⁱPr₃) (2.139(5) Å),²³ where a Ru–C(sp²) single bond is proposed to exist.

The difference between the N(1)–C(7) distance (1.306(7) Å) and the separations between the nitrogen atom and the ethyl groups is very illustrative. The N(1)–C(22) (1.506(9) Å) and N(1)–C(24) (1.476(7) Å) distances are statistically identical and agree well with a C–N single bond, while the N(1)–C(7) bond length compares well with the N–C double-bond length found in Schiff bases, hydrazones, and related compounds (about 1.29 Å). The angles around N(1) are between 114.3(5) and 123.2(5)°, whereas the angles around C(7) are between 114.9(5) and 127.5(4)°.

If we extrapolate eq 1 to the case of complex **2**, we obtain eq 2. The previously mentioned structural pa-



rameters indicate not only that the resonance structure E (related to B in eq 1) is the major contributor to the structure of **2** but also that the contribution of the resonance structure D (related to A in eq 1) is not really relevant. The contribution of the latter is similar to the contribution of the resonance structure F (eq 3) to the structure of the previously reported acyl compound Ru(η⁵-C₅H₅){C(O)CH=CPh₂}(CO)(PⁱPr₃).¹⁹

The similarity between the acyl ligand and the unsaturated η¹-carbon donor ligand of **2** is surprising. The Ru–C(7) bond length and the C(8)–C(9) olefinic bond distance (1.339(7) Å) are exactly the same as the related parameters in the acyl complex (2.060(2) Å and 1.333(4) Å, respectively). Moreover, the C(sp²)–C(sp²) single-bond distance (C(7)–C(8) = 1.481(7) Å) in **2** and the related bond length in the acyl complex (1.502(3) Å) are statistically identical. The above-mentioned C–C double-bond and C(sp²)–C(sp²) single-bond values agree well with the mean values described for double and single C(sp²)–C(sp²) bonds (1.34 and 1.48 Å, respectively),²⁹ which indicates that the delocalization of π-electron density along the X–C–CH–CPh₂ (X = N, O) chain is not appreciable in both compounds.

The similarity between the acyl ligand and the unsaturated η¹-carbon donor ligand of **2** is also revealed by comparison of the ¹³C{¹H} NMR spectra of both

compounds. In the ¹³C{¹H} NMR spectrum of **2**, the C_α resonance appears as a doublet at 240.8 ppm, with a C–P coupling constant of 9.7 Hz, and the C_β and C_γ resonances are observed as singlets at 141.4 and 137.7 ppm, respectively. These chemical shifts are similar to those observed in the ¹³C{¹H} NMR spectrum of Ru(η⁵-C₅H₅){C(O)(CH=CPh₂)}(CO)(PⁱPr₃) for the related resonances 249.5, 144.5, and 130.6 ppm.

In agreement with the presence of a C–N double bond in the azoniabutadienyl ligand of **2** the IR spectrum of this complex in Nujol shows a ν(C=N) band at 1499 cm⁻¹. In the ¹H NMR spectrum the most noticeable resonances are a singlet at 6.69 ppm corresponding to the =CH proton and four multiplets between 4.35 and 3.76 ppm, due to the four CH₂ protons of the ethyl groups. The presence of two inequivalent ethyl groups in the spectrum agrees with a double bond between the atoms C(7) and N(1). This double bond prevents the rotation of the NET₂ unit in solution at room temperature. The total blockage was confirmed by a NOE experiment. Saturation of the =CH resonance increases the intensity (2.8%) of only one CH₂ multiplet.

The spectroscopic data of **3** agree with those of **2**. In the ¹³C{¹H} NMR spectrum, the C_α resonance appears as a doublet at 237.4 ppm, with a C–P coupling constant of 9.7 Hz, while the C_β and C_γ resonances are observed as singlets at 137.9 and 141.9 ppm, respectively. In the IR spectrum in Nujol the ν(C=N) band is observed at 1500 cm⁻¹. The ¹H NMR spectrum shows a singlet at 6.54 ppm corresponding to the =CH proton.

Treatment of **2** and **3** with sodium methoxide in tetrahydrofuran produces the deprotonation of the CH=CPh₂ group of the azoniabutadienyl ligands to give the aminoallenyl derivatives Ru(η⁵-C₅H₅){C(NEt₂)=C=CPh₂}(CO)(PⁱPr₃) (**4**) and [Ru(η⁵-C₅H₅){C(NCH₂(CH₂)₃CH₂)=C=CPh₂}(CO)(PⁱPr)₃ (**5**), which were isolated as yellow solids in 85 and 80% yields, respectively (Scheme 1). Characteristic spectroscopic features of **4** and **5** are the C=C=C stretching frequency in the IR spectra at 1963 (**4**) and 1935 cm⁻¹ (**5**) and three resonances in the ¹³C{¹H} NMR spectra at 199.5 (d, J(PC) = 2.7 Hz), 117.2 (d, J(PC) = 13.2 Hz), and 101.2 (s) ppm (**4**) and at 198.1 (d, J(PC) = 2.7 Hz), 120.8 (d, J(PC) 12.0 Hz), and 101.5 (s) (**5**) ppm for the C_β, C_α, and C_γ allenyl carbon atoms, respectively.

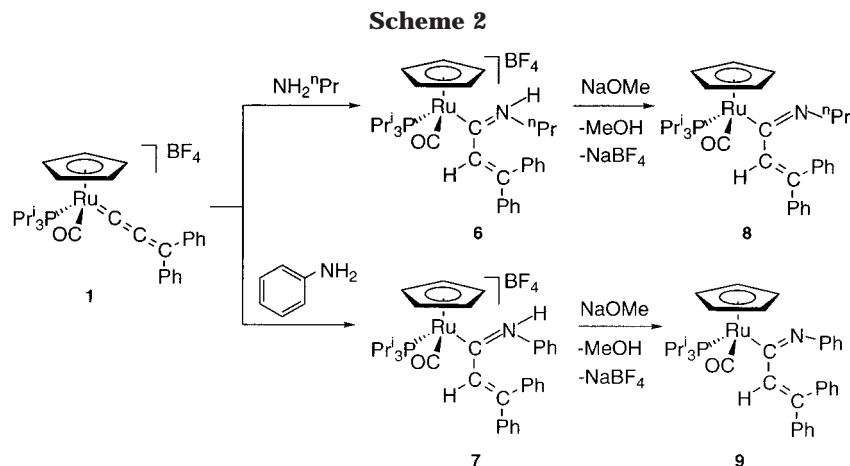
Although a variety of η¹-allenyl transition-metal compounds have been previously reported,^{19,22c,23,30} the aminoallenyl derivatives of ruthenium are unknown.

2. Reactions of [Ru(η⁵-C₅H₅)(C=C=CPh₂)(CO)-(PⁱPr₃)]BF₄ with Primary Amines. Complex **1** also reacts with primary amines. Similarly to the reactions with secondary amines, the addition at room temperature of 1 equiv of propylamine and aniline to dichloromethane solutions of **1** affords the azoniabutadienyl

(28) Matsuzaka, J.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36.

(29) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, 51.

(30) (a) Jacobs, T. L. In *The Chemistry of the Allenes*; Landor, S. R.; Ed.; Academic Press: London, 1982; Vol. 2, p 334. (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Chemistry*; Wiley-Interscience: New York, 1984. (c) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35. (d) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289. (e) Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185. (f) Wouters, J. M. A.; Klein, R. E.; Elsevier, C. J.; Häming, L.; Stam, C. H. *Organometallics* **1994**, *13*, 4586. (g) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L. *Organometallics* **1996**, *15*, 3670. (h) Esteruelas, M. A.; Lahoz, F. J.; Martín, M.; Oñate, E.; Oro, L. A. *Organometallics* **1997**, *16*, 4572. (i) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567.



compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NH}^n\text{Pr}\}(\text{CO})\text{-}(\text{P}^i\text{Pr}_3)\text{BF}_4$ (**6**) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NHPh}\}\text{-}(\text{CO})(\text{P}^i\text{Pr}_3)\text{BF}_4$ (**7**), respectively, which were isolated as yellow crystals in 90% yield (Scheme 2).

The spectroscopic data of **6** and **7** agree with those found for **2** and **3**. The IR spectrum of **6** in Nujol shows a $\nu(\text{NH})$ band at 3321 cm^{-1} and a $\nu(\text{C}=\text{N})$ band at 1529 cm^{-1} , in agreement with the presence of a C–N double bond in the azoniabutadienyl ligand. In the IR spectrum of **7** these bands appear at 3271 and 1592 cm^{-1} , respectively. In the ^1H NMR spectra, the most noticeable resonances are those due to the =NH and =CH protons, which are observed as singlets at 9.75 and 6.45 ppm (**6**) and at 11.13 and 6.70 ppm (**7**), respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra reflect the similarity between these compounds and the acyl derivatives $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{O})\text{CH}=\text{CR}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$. The resonances corresponding to the Ru–C carbon atoms appear as doublets at 242.2 (**6**) and 248.7 (**7**) ppm, with C–P coupling constants of 10.6 and 11.5 Hz, respectively. The resonances due to the CH= and =CPh₂ carbon atoms are observed as singlets at 133.7 and 138.8 ppm (**6**) and at 136.8 and 139.9 (**7**) ppm.

The stereochemistry at the C–N double bond of the azoniabutadienyl ligands of these compounds was inferred on the basis of NOE experiments. The saturation of the NH resonance of **6** increases the intensities of the cyclopentadienyl (11.5%), NCH₂ (6.8%), and CH₃ (PⁱPr₃, 12%) resonances, while the CH= resonance does not show an NOE effect. However, the saturation of the NCH₂ resonances increases the intensity of the CH= resonance (3.3%), while it has no effect on the cyclopentadienyl and triisopropylphosphine signals. Similarly to **6**, the saturation of the NH resonance of **7** increases the intensity (21.1%) of the cyclopentadienyl resonance.

Complexes **6** and **7** also undergo a deprotonation process in the presence of base. However, the deprotonation does not take place at the CH=CPh₂ olefinic group, as in the case of **2** and **3**, but at the nitrogen atom. Thus, the treatment of tetrahydrofuran solutions of **6** and **7** with 2 equiv of sodium methoxide leads to the azabutadienyl derivatives $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{N}^n\text{Pr}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**8**) and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**9**), which were isolated as yellow solids in 90% yield (Scheme 2). As far as we know, transition-metal complexes containing this type of unsaturated η^1 -carbon ligand have not been previously reported.

Complexes **8** and **9** were characterized by MS, elemental analysis, and IR and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. In the IR spectra in Nujol the most noticeable absorptions are the $\nu(\text{C}=\text{N})$ bands, which appear at 1605 (**8**) and 1542 (**9**) cm^{-1} . The ^1H NMR spectrum of **8** shows the CH= resonance as a singlet at 6.89 ppm and at 3.71 and 3.59 ppm (CH₂N) and at 1.89 and 1.73 ppm (CH₂) the CH₂ resonances of the *n*-propyl group. The saturation of the CH₂N resonances increases the intensity of both the phenyl (8.8%) and CH= (3.1%) resonances, while it has no effect on the cyclopentadienyl and triisopropyl signals. This NOE experiment strongly supports the *trans* disposition of the metallic fragment and the *n*-propyl group at the C–N double bond of the azabutadienyl ligand. In the NMR spectrum of **9** the CH resonance lies within the phenyl signals.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** shows a doublet at 193.0 ppm with a C–P coupling constant of 11.5 Hz, corresponding to the Ru–C atom, and singlets at 141.6 and 132.0 ppm due to the HC= and CPh₂ carbon atoms, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** agrees well with that of **8**; the Ru–C resonance appears as a doublet at 204.5 ppm with a C–P coupling constant of 9.0 Hz, whereas the HC= and =CPh₂ resonances are observed as singlets at 142.0 and 130.1 ppm.

3. Theoretical Analysis. We have previously shown that the addition of secondary and primary amines to the allenylidene ligand of **1** affords the complexes **2**, **3**, **6**, and **7**. At first glance, for an adequate description of the bonding situation in this type of compound, two resonance structures should be considered (eq 2), the aminocarbene (D) and the azoniabutadienyl (E). The structural parameters of **2** suggest that the azoniabutadienyl resonance form is the major contributor to the real structure of this type of compound and that the contribution of the aminocarbene resonance form is not very significant.

To reaffirm the formulation of **2**, **3**, **6**, and **7** as azoniabutadienyl complexes, we performed electronic structure calculations on $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}_2\}\text{-}(\text{CO})(\text{PH}_3)]^+$ (**10**), $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NH}_2)=\text{C}=\text{CH}_2\}(\text{CO})\text{-}(\text{PH}_3)$ (**11**), and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}\}(\text{CO})\text{-}(\text{PH}_3)$ (**12**) as simplified models of the azoniabutadienyl derivatives **2**, **3**, **6**, and **7**, the aminoallenyl compounds **4** and **5**, and the azabutadienyl complexes **8** and **9**, respectively. For comparative purposes the electronic structure of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2)(\text{CO})(\text{PH}_3)]^+$ (**13**) was also

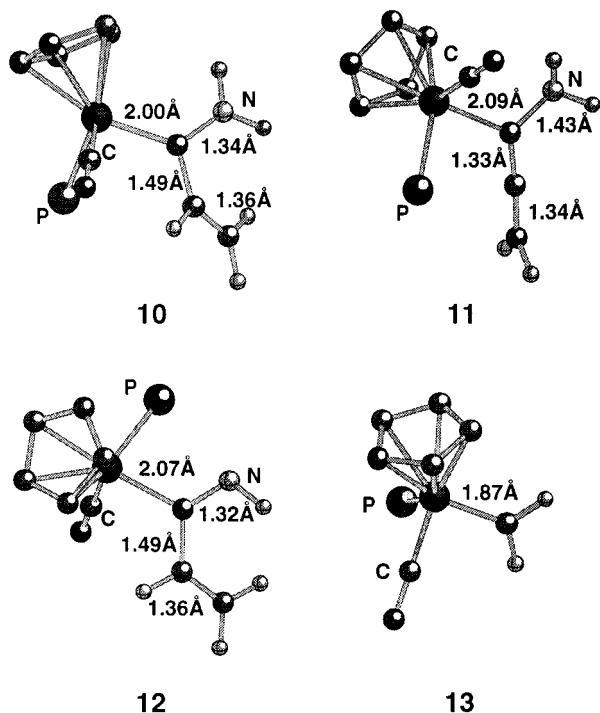


Figure 2. Optimized structures of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}_2\}(\text{CO})(\text{PH}_3)]^+$ (**10**), $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NH}_2)=\text{C}=\text{CH}_2\}(\text{CO})(\text{PH}_3)$ (**11**), $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}\}(\text{CO})(\text{PH}_3)$ (**12**), and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2)(\text{CO})(\text{PH}_3)]^+$ (**13**), obtained by ab initio calculations at the MP2 level.

calculated. Figure 2 shows the optimized structures at the MP2 level of the four model compounds.

The theoretical structure of **10** is in excellent agreement with the experimental X-ray structure of **2**. The main discrepancy is found in the Ru–C $_{\alpha}$ distance (2.00 Å), which is about 0.06 Å shorter than that determined from the X-ray diffraction study.

In addition, it should be noted that the C $_{\alpha}$ –N distance in **10** (1.34 Å) is only 0.02 Å longer than the calculated one for **12** (1.32 Å), while it is 0.09 Å shorter than the related parameter of **11**. This is remarkable and strongly supports the presence of a double bond between the C $_{\alpha}$ and N atoms of **10**.

The azoniabutadienyl character of the unsaturated η^1 -carbon donor ligand of **10** also seems to be clear from the point of view of the Ru–C $_{\alpha}$ distances. Although the Ru–C $_{\alpha}$ distance in **10** is 0.07 Å shorter than that of **12** (2.07 Å), it is 0.13 Å longer than the related parameter in the carbene model complex **13** (1.87 Å).

The C $_{\alpha}$ –C $_{\beta}$ and C $_{\beta}$ –C $_{\gamma}$ distances in **10** are identical with those found in **12** (1.49 and 1.36 Å, respectively) and agree with the expected ones for single and double C(sp 2)–C(sp 2) bonds. The C $_{\alpha}$ –C $_{\beta}$ (1.33 Å) and C $_{\beta}$ –C $_{\gamma}$ (1.34 Å) bond lengths in **11** are in agreement with those obtained from X-ray diffraction analysis in ruthenium 30i and rhodium 30h allenyl complexes.

The degree of π -character of a bond can be analyzed on the basis of Bader's atoms-in-molecules (AIM) theory. 31 At the bond critical point two of the eigenvalues (λ_1 and λ_2) of the Hessian (second derivatives matrix) of the electron density are negative. They correspond to perpendicular directions to the bond as the electron density

Table 2. Ellipticities of the Bonds Ru–C $_{\alpha}$, C $_{\alpha}$ –N, C $_{\alpha}$ –C $_{\beta}$, and C $_{\beta}$ –C $_{\gamma}$ of the Complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}_2\}(\text{CO})(\text{PH}_3)]^+$ (**10**), $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NH}_2)=\text{C}=\text{CH}_2\}(\text{CO})(\text{PH}_3)$ (**11**), $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}\}(\text{CO})(\text{PH}_3)$ (**12**), and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2)(\text{CO})(\text{PH}_3)]^+$ (**13**)

	Ru–C $_{\alpha}$	C $_{\alpha}$ –N	C $_{\alpha}$ –C $_{\beta}$	C $_{\beta}$ –C $_{\gamma}$
10	0.07	0.12	0.03	0.21
11	0.05	0.07	0.26	0.21
12	0.07	0.10	0.03	0.22
13	0.11			

reaches a maximum. The electron density is minimum along the bond path, and thus the corresponding eigenvalue λ_3 has a positive sign. When λ_1 and λ_2 are equal, the bond has cylindrical symmetry. However, when electronic charge is preferentially accumulated in a given plane along the bond path (as it is for a bond with π -character), then λ_1 and λ_2 have different values. If λ_2 is the value of smallest magnitude, then the quantity ϵ (eq 4), the ellipticity of the bond, provides a measure of the extent to which charge is preferentially accumulated in a given plane, and therefore of the grade of π -character of the bond:

$$\epsilon = \frac{\lambda_1}{\lambda_2} - 1 \quad (4)$$

To analyze the extent of double- or single-bond character in the metal–unsaturated η^1 -carbon ligand interactions and in the internal structures of these ligands in complexes **10–13**, we have studied the ellipticity of the Ru–C $_{\alpha}$, C $_{\alpha}$ –N, C $_{\alpha}$ –C $_{\beta}$, and C $_{\beta}$ –C $_{\gamma}$ bonds, using the AIMPA series of programs. The obtained results are collected in Table 2.

According to the ellipticities of the Ru–C $_{\alpha}$ and C $_{\alpha}$ –N bonds, the azoniabutadienyl character of **2**, **3**, **6** and **7** is unanswerable. The ellipticity of the Ru–C $_{\alpha}$ bond of **10** is similar to those of **11** and **12**, which without a shadow of a doubt correspond to Ru–C single bonds, while it is significantly smaller than the ellipticity of the Ru–C $_{\alpha}$ double bond of **13**. Moreover, the ellipticities of the C $_{\alpha}$ –N bonds of **10** and **12** are similar (the ellipticity of **10** is even higher than that of **12**) and are significantly higher than the ellipticity of the C $_{\alpha}$ –N single bond of the allenylamino complex **11**.

In agreement with the allenyl formulation of the unsaturated η^1 -carbon ligand of **11**, the ellipticities of the C $_{\alpha}$ –C $_{\beta}$ and C $_{\beta}$ –C $_{\gamma}$ bonds of this ligand are approximately equal and are 1 order of magnitude higher than the ellipticities of the C $_{\alpha}$ –C $_{\beta}$ single bonds of **10** and **12**. The ellipticities of the C $_{\beta}$ –C $_{\gamma}$ double bonds of **10** and **12** agree well with those corresponding to the C $_{\alpha}$ –C $_{\beta}$ and C $_{\beta}$ –C $_{\gamma}$ double bonds of **11**.

Concluding Remarks

This study has revealed a new finding in the chemistry of the diarylallenylidene complexes of the iron triad. The diphenylallenylidene ligand of the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ adds at the C $_{\alpha}$ –C $_{\beta}$ double bond the N–H bond of secondary and primary amines to afford azoniabutadienyl derivatives of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NR}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{N}(\text{R})\text{H}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$, respectively. Although, at first glance, an

(31) Bader, R. F. W. In *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.

important contribution of the aminocarbene resonance form to the structure of these compounds should be expected, the X-ray structure determination of the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NET}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ and the analysis of the ellipticities of the Ru–C $_{\alpha}$ and C $_{\alpha}$ –N bonds of the model compound $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CH}_2)=\text{NH}_2\}(\text{CO})(\text{PH}_3)]^+$ indicate that the contribution of this resonance form is not relevant. According to the values of the ellipticities 0.07, for the Ru–C $_{\alpha}$ bond, and 0.12, for the C $_{\alpha}$ –N bond, the respective single- and double-bond characters of the Ru–C $_{\alpha}$ and C $_{\alpha}$ –N bonds are unanswerable.

There is a marked difference, in the presence of bases, in behavior between the tertiary azoniabutadienyl complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NR}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ and the secondary azoniabutadienyl compounds $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{N}(\text{R})\text{H}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$. Treatment of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NR}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ 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 $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NR}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$. Under the same conditions, the deprotonation of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{N}(\text{R})\text{H}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ does not occur at the CH=CPh $_2$ group but at the nitrogen atom. Thus, the reactions of the latter with sodium methoxide lead to the azabutadienyl derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NR}\}(\text{CO})(\text{P}^i\text{Pr}_3)]$.

In conclusion, if the coligands are selected in such a way that the metallic fragment is poorly basic, the allenylidene ligand of diarylallenylidene complexes of the iron triad shows a strong electrophilic character. As a result, the reactions of these compounds with secondary and primary amines are a useful strategy to obtain tertiary and secondary azoniabutadienyl complexes, which are the entry to the synthesis of aminoallenyl and azabutadienyl derivatives, respectively.

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 $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**1**) was prepared by the published method.^{19a}

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me $_4$ Si (^1H and ^{13}C) and 85% H $_3$ PO $_4$ (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NET}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (2**).** A dark red solution of **1** (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with diethylamine (15 mg, 0.26 mmol), and the mixture was stirred for 5 min. The solution became yellow, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a yellow solid. Yield: 160 mg (95%). Anal. Calcd for C $_{34}$ H $_{47}$ BF $_4$ NO $^+$ Pr $_3$: C, 57.96; H, 6.74; N, 1.99. Found: C, 57.86; H, 6.73; N, 2.04. IR (Nujol, cm $^{-1}$): $\nu(\text{CO})$ 1926 (vs), $\nu(\text{C}=\text{N})$ 1499 (m), $\nu(\text{BF}_4)$ 1048 (vs, br). ^1H NMR (300 MHz, 293 K, CDCl $_3$): δ 7.50–6.90 (m, 10H, Ph), 6.69 (s, 1H, =CH), 4.68 (s, 5H, Cp), 4.32, 4.21, 4.05, and 3.88 (all m, 4H, NCH $_2$), 2.28 (m, 3H, PCHCH $_3$), 1.49 (t, 6H, *J*(HH) = 7.1, NCH $_2$ CH $_2$), 1.28 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 14.6, PCHCH $_3$), 1.26 (dd, 9H, *J*(HH) = 6.8, *J*(PH) = 13.6, PCHCH $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 293 K, CDCl $_3$): δ 62.4 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, 293 K, CDCl $_3$): δ 240.8 (d, *J*(PC) = 9.7, RuC), 204.4 (d, *J*(PC) = 18.0, CO), 141.4 (s, HC=), 138.8 and 137.5 (both s, C $_{\text{ipso}}$), 137.4 (s, CPh $_2$), 130.0, 129.1, 128.5, and 128.2 (all s, Ph), 86.0 (s, Cp), 55.5 and

48.7 (both s, NCH $_2$), 28.4 (d, *J*(PC) = 23.2, PCHCH $_3$), 19.9 and 19.7 (both s, PCHCH $_3$), 12.8 and 11.8 (both s, NCH $_2$ CH $_2$). MS (FAB $^+$): *m/z* 618 (M $^+$).

Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{NCH}_2\text{-(CH}_2\text{)}_3\text{CH}_2\}(\text{CO})(\text{P}^i\text{Pr})\text{BF}_4$ (3**).** A dark red solution of **1** (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with piperidine (15 mg, 0.26 mmol), and the mixture was stirred for 5 min. The solution became brown, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a brown solid, which was crystallized from dichloromethane/diethyl ether to give yellow crystals. Yield: 155 mg (90%). Anal. Calcd for C $_{35}$ H $_{47}$ BF $_4$ NO $^+$ Pr $_3$: C, 58.67; H, 6.61; N, 1.95. Found: C, 58.42; H, 6.22, N, 1.87. IR (Nujol, cm $^{-1}$): $\nu(\text{CO})$ 1947 (vs), $\nu(\text{C}=\text{N})$ 1500 (m), $\nu(\text{BF}_4)$, 1052 (vs, br). ^1H NMR (300 MHz, 293 K, CDCl $_3$): δ 7.50–7.00 (m, 10H, Ph), 6.54 (s, 1H, =CH), 4.65 (s, 5H, Cp), 4.32–4.00 (m, 4H, NCH $_2$), 2.29 (m, 3H, PCHCH $_3$), 1.85–1.62 (m, 4H, NCH $_2$ CH $_2$), 1.55 and 1.40 (both m, 2H, NCH $_2$ CH $_2$ CH $_2$), 1.20 (dd, 9H, *J*(HH) = 6.6, *J*(PH) = 15.0, PCHCH $_3$), 1.19 (dd, 9H, *J*(HH) = 6.6, *J*(PH) = 15.8, PCHCH $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 293 K, CDCl $_3$): δ 64.4 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, 293 K, CDCl $_3$): δ 237.4 (d, *J*(PC) = 9.7, RuC), 204.8 (d, *J*(PC) = 18.4, CO), 141.9 (s, CPh $_2$), 139.0 and 138.8 (both s, C $_{\text{ipso}}$), 137.9 (s, HC=), 130.4, 129.1, 128.8, 128.6, and 128.3 (all s, Ph), 86.6 (s, Cp), 60.5 and 56.1 (both s, NCH $_2$), 28.5 (d, *J*(PC) = 22.6, PCHCH $_3$), 26.3 and 26.1 (both s, NCH $_2$ CH $_2$), 22.3 (s, NCH $_2$ CH $_2$ CH $_2$), 19.9 and 19.7 (both s, PCHCH $_3$). MS (FAB $^+$): *m/z* 630 (M $^+$).

Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NET}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]$ (4**).** A yellow suspension of **2** (185 mg, 0.26 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (29 mg, 0.54 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. Yield: 140 mg (85%). Anal. Calcd for C $_{34}$ H $_{46}$ NO $^+$ Pr $_3$: C, 66.15; H, 7.61; N, 2.26. Found: C, 65.80; H, 7.41; N, 2.21. IR (Nujol, cm $^{-1}$): $\nu(\text{CO})$ 1917 (vs), $\nu(\text{C}=\text{C}=\text{C})$ 1963 (m). ^1H NMR (300 MHz, 293 K, CDCl $_3$): δ 7.60–7.00 (m, 10H, Ph), 4.91 (s, 5H, Cp), 3.32 (m, 4H, NCH $_2$), 2.05 (m, 3H, PCHCH $_3$) 1.01, (t, 6H, *J*(HH) = 7.1, NCH $_2$ CH $_2$), 0.96 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 13.8, PCHCH $_3$), 0.77 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.1, PCHCH $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 293 K, CDCl $_3$): δ 69.5 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, 293 K, CDCl $_3$): δ 208.6 (d, *J*(PC) = 22.4, CO), 199.5 (d, *J*(PC) = 2.7, C=C=C), 142.3 and 142.0 (both s, C $_{\text{ipso}}$), 128.8, 128.6, 125.2, 125.3, and 125.2 (all s, Ph), 117.2 (d, *J*(PC) = 13.2, RuC), 101.2 (s, CPh $_2$), 86.4 (s, Cp), 45.9 (s, NCH $_2$), 27.2 (d, *J*(PC) = 22.0, PCHCH $_3$), 20.0 and 19.4 (both s, PCHCH $_3$), 12.6 (s, NCH $_2$ CH $_2$). MS (FAB $^+$): *m/z* 618 (M $^+$).

Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{NCH}_2(\text{CH}_2)_3\text{CH}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]$ (5**).** A yellow suspension of **3** (185 mg, 0.26 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (29 mg, 0.54 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. Yield: 132 mg (80%). Anal. Calcd for C $_{35}$ H $_{46}$ NO $^+$ Pr $_3$: C, 66.86; H, 7.37; N, 2.23. Found: C, 66.45; H, 7.42, N, 2.12. IR (Nujol, cm $^{-1}$): $\nu(\text{C}=\text{C}=\text{C})$ 1934 (m), $\nu(\text{CO})$ 1929 (m). ^1H NMR (300 MHz, 293 K, CDCl $_3$): δ 7.80–7.00 (m, 10H, Ph), 4.87 (s, 5H, Cp), 3.39 and 2.96 (both m, 4H, NCH $_2$), 2.06 (m, 3H, PCHCH $_3$), 1.67 (m, 4H, NCH $_2$ CH $_2$), 1.50–1.10 (m, 2H, NCH $_2$ CH $_2$ CH $_2$), 1.00 (dd, 9H, *J*(HH) = 6.6, *J*(PH) = 15.0, PCHCH $_3$), 0.84 (dd, 9H, *J*(HH) = 6.6, *J*(PH) = 15.8, PCHCH $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 293 K, CDCl $_3$): δ 71.0 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, 293 K, CDCl $_3$): δ 207.9 (d, *J*(PC) = 20.4, CO), 198.1 (d, *J*(PC) = 2.7, C=C=C), 142.6 and 141.3 (both s, C $_{\text{ipso}}$), 128.6, 128.5, 125.5, and 125.4 (all s, Ph), 120.8 (d, *J*(PC) = 12.0, RuC), 101.5 (s, CPh $_2$), 86.6 (s, Cp), 55.8

(s, NCH₂), 27.3 (s, NCH₂CH₂), 27.1 (d, *J*(PC) = 19.4, PCHCH₃), 25.1 (s, NCH₂CH₂CH₂), 19.6 and 19.5 (both s, PCHCH₃). MS (FAB⁺): *m/z* 630 (M⁺).

Preparation of [Ru(η^5 -C₅H₅)₂{C(CH=CPh₂)=NHⁿPrⁿ}-CO)(PⁱPr₃)BF₄ (6). A dark red solution of **1** (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with *n*-propylamine (15 mg, 0.26 mmol), and the mixture was stirred for 5 min. The solution became brown, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a brown solid, which was crystallized from dichloromethane/diethyl ether to give yellow crystals. Yield: 150 mg (90%). Anal. Calcd for C₃₃H₄₅BF₄NOPRu: C, 57.39; H, 6.57; N, 2.03. Found: C, 57.02; H, 6.63; N, 1.91. IR (Nujol, cm⁻¹): ν (NH) 3321 (m), ν (CO) 1948 (vs), ν (C=N) 1529 (m), ν (BF₄) 1077 (vs, br). ¹H NMR (300 MHz, 293 K, CDCl₃): δ 9.75 (s, 1H, NH), 7.50–7.00 (m, 10H, Ph), 6.45 (s, 1H, =CH), 4.82 (s, 5H, Cp), 3.66 (m, 2H, NCH₂), 2.19 (m, 3H, PCHCH₃), 1.77 and 1.42 (both m, 2H, CH₂CH₂), 1.23 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.4, PCHCH₃), 1.22 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.1, PCHCH₃), 0.85 (t, 3H, *J*(HH) = 7.5, CH₂CH₂CH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, CDCl₃): δ 64.5 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃): δ 242.2 (d, *J*(PC) = 10.6, RuC), 204.5 (d, *J*(PC) = 16.5, CO), 141.3 and 140.7 (both s, C_{ipso}), 138.8 (s, CPh₂), 133.7 (s, HC=), 130.3, 128.9, 128.5, 128.4, and 128.3 (all s, Ph), 86.8 (s, Cp), 54.6 (s, NCH₂), 28.9 (d, *J*(PC) = 23.4, PCHCH₃), 21.5 (s, CH₂CH₂), 19.8 and 19.3 (both s, PCHCH₃), 11.03 (s, CH₂CH₂CH₃). MS (FAB⁺): *m/z* 604 (M⁺).

Preparation of [Ru(η^5 -C₅H₅)₂{C(CH=CPh₂)=NPh}-CO)(PⁱPr₃)BF₄ (7). A dark red solution of **1** (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with aniline (15 mg, 0.26 mmol), and the mixture was stirred for 5 min. The solution became brown, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a brown solid, which was crystallized from dichloromethane/diethyl ether to give yellow crystals. Yield: 157 mg (90%). Anal. Calcd for C₃₆H₄₃BF₄NOPRu: C, 59.67; H, 5.98; N, 1.86. Found: C, 59.20; H, 5.93; N, 1.84. IR (Nujol, cm⁻¹): ν (NH) 3271 (m), ν (CO) 1947 (vs), ν (C=N) 1592 (m), ν (BF₄) 1061 (vs, br). ¹H NMR (300 MHz, 293 K, CDCl₃): δ 11.13 (s, 1H, NH), 7.41–6.98 (m, 15H, Ph), 6.70 (s, 1H, =CH), 5.18 (s, 5H, Cp), 2.32 (m, 3H, PCHCH₃), 1.34 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHCH₃), 1.32 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.1, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, CDCl₃): δ 62.2 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃): δ 248.7 (d, *J*(PC) = 11.5, RuC), 204.5 (d, *J*(PC) = 17.0, CO), 141.5, 140.6, and 138.8 (all s, C_{ipso}), 139.9 (s, CPh₂), 136.8 (s, HC=), 130.53, 129.6, 129.5, 129.1, 128.8, 128.7, 128.4, 128.2, and 123.4 (all s, Ph), 87.8 (s, Cp), 29.4 (d, *J*(PC) = 23.4, PCHCH₃), 19.9 and 19.7 (both s, PCHCH₃). MS (FAB⁺): *m/z* 638 (M⁺).

Preparation of Ru(η^5 -C₅H₅)₂{C(CH=CPh₂)=NⁿPrⁿ}(CO)-(PⁱPr₃) (8). A brown suspension of **6** (185 mg, 0.27 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (29 mg, 0.54 mmol) and stirred for 1 h. The mixture became yellow, and 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. Yield: 145 mg (90%). Anal. Calcd for C₃₃H₄₄NOPRu: C, 65.75; H, 7.35; N, 2.32. Found: C, 65.62; H, 7.01; N, 2.21. IR (Nujol, cm⁻¹): ν (CO) 1948 (vs), ν (C=N) 1605 (m). ¹H NMR (300 MHz, 293 K, C₆D₆): δ 7.80–7.00 (m, 10H, Ph), 6.89 (s, 1H, =CH), 4.61 (s, 5H, Cp), 3.71 and 3.59 (both m, 2H, NCH₂), 2.16 (m, 3H, PCHCH₃), 1.89 and 1.72 (both m, 2H, NCH₂CH₂), 1.14 (m, 12H, CH₂CH₂CH₃ and PCHCH₃), 1.01 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.6, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, C₆D₆): δ 67.55 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, CDCl₃): δ 208.6 (d, *J*(PC) = 17.4, CO), 193.0 (d, *J*(PC) = 11.5, RuC), 144.8 (s, 2 C_{ipso}), 141.6 (s, HC=), 132.0 (s, CPh₂), 128.7, 128.5, 128.1, 127.5, and 126.5 (all s, Ph), 87.3 (s, Cp), 60.0 (s, CH₂N),

Table 3. Summary for Crystal Data Collection and Structure Analysis of [Ru(η^5 -C₅H₅)₂{C(CH=CPh₂)=NEt₂}(CO)(PⁱPr₃)BF₄ (2)

formula	C ₃₄ H ₄₇ BF ₄ NOPRu
fw	704.60
cryst size (mm)	0.42 × 0.18 × 0.14
cell measmts (25 rflns) (deg)	12.7 < 2 θ < 14.7
color, shape	yellow green, prism
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	9.084(2)
<i>b</i> (Å)	22.215(4)
<i>c</i> (Å)	17.224(2)
β (deg)	104.24(1)
<i>V</i> (Å ³)	3369(1)
<i>Z</i> (formula units)	4
λ (Mo K α) (Å)	0.71069
<i>F</i> (000)	1464
abs cor	Psi
transmissn factors	0.98–1.00
stds: no., interval	3 rflns, 100 rflns
decay (%)	–0.80
temp (K)	290(1)
scan method	$\omega/2\theta$
scan speed (ω) (deg min ⁻¹)	4
2 θ interval (deg)	5 < 2 θ < 50.1
no. of unique rflns	5610
no. of obsd rflns (<i>I</i> > 3 σ <i>I</i>)	3747
no. of params	388
rfln/param ratio	9.66
refinements	full-matrix least squares on <i>F</i>
<i>R</i> ^a	0.044
<i>R</i> _w (<i>w</i> = σ_F^{-2}) ^b	0.054
GOF	1.722
residual peaks (e Å ⁻³)	+0.65, –0.43

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

27.6 (d, *J*(PC) = 23.4, PCHCH₃), 25.0 (s, CH₂CH₂), 19.8 and 19.3 (both s, PCHCH₃), 12.6 (s, CH₂CH₂CH₃). MS (FAB⁺): *m/z* 604 (M⁺).

Preparation of Ru(η^5 -C₅H₅)₂{C(CH=CPh₂)=NPh}(CO)-(PⁱPr₃) (9). A brown suspension of **7** (185 mg, 0.26 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (29 mg, 0.54 mmol) and stirred for 1 h. The mixture became yellow, and 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. Yield: 150 mg (90%). Anal. Calcd for C₃₆H₄₂NOPRu: C, 67.90; H, 6.66; N, 2.19. Found: C, 67.50; H, 6.63; N, 2.26. IR (Nujol, cm⁻¹): ν (CO) 1908 (vs), ν (C=N) 1542. ¹H NMR (300 MHz, 293 K, CDCl₃) δ 7.51–6.70 (m, 15H, Ph), 4.69 (s, 5H, Cp), 2.14 (m, 3H, PCHCH₃), 1.07 (dd, 9H, *J*(HH) = 6.6, *J*(PH) = 13.2, PCHCH₃), 0.94 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.9, PCHCH₃). ³¹P{¹H} NMR (121.4 MHz, 293 K, C₆D₆): δ 67.5 (s). ¹³C{¹H} NMR (75.4 MHz, 293 K, C₆D₆): δ 208.2 (d, *J*(PC) = 15.0, CO), 204.5 (d, *J*(PC) = 9.0, RuC), 154.1 (s, NC_{ipso}), 142.0 (s, HC=), 144.6 and 141.2 (both s, C_{ipso}), 130.1 (s, CPh₂), 130.9, 128.7, 128.6, 128.4, 127.2, 126.8, 121.8, and 121.0 (all s, Ph), 87.8 (s, Cp), 29.4 (d, *J*(PC) = 23.4, PCHCH₃), 19.9 and 19.7 (both s, PCHCH₃). MS (FAB⁺): *m/z* 638 (M⁺).

Crystal Data for 2. A crystal suitable for X-ray diffraction analysis was mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer (*T* = 290 K, Mo K α radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 3. Data were collected by the $\omega/2\theta$ scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring 3 standard reflections every 100 measurements. Slight corrections for decay and absorption (semiempirical ψ method) were also applied.

The structure was solved by Patterson methods and subsequent expansion of the model using DIRDIF.³² Reflections having $I > 3\sigma(I)$ were used for structure refinement. Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were included at idealized positions and not refined. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN³³ software system and ORTEP³⁴ for plotting. Maximum and minimum peaks in the final difference Fourier maps were +0.65 and $-0.43 \text{ e } \text{Å}^{-3}$.

Appendix

The theoretical calculations were carried out through a series of partial optimizations on compounds **10–13**. The ligands Cp, CO, and PH₃ were kept frozen. The

(32) Beurskens, P. T.; DIRDIF; Technical Report 1984/1; Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1984.

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

(34) Johnson, C. K. ORTEP, A Thermal Ellipsoid Plotting Program; Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

calculations were carried out at the MP2 level using the program Gaussian 94.³⁵ The basis sets employed were LANL2DZ ECP for the Ru atom and 6-31G for the rest of the atoms.

Acknowledgment. We thank the DGES (PROJECT PB-95-0806, Programa de Promoción General del Conocimiento) for financial support.

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

OM9904706

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Ciolowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision D.3; Gaussian, Inc., Pittsburgh, PA, 1995.