Formation of Fischer-Type Aminocarbenes by a Double C−H Bond Activation of a Methylamino Group[⊥]

M. Carmen Carrión,[†] Ernesto García-Vaquero,[†] Félix A. Jalón,[†] Blanca R. Manzano,*[,†] Walter Weissensteiner,[‡] and Kurt Mereiter[§]

Departamento de Química Inorgánica, Orgánica y Bioquímica−IRICA, Universidad de Castilla−La Mancha, Avenida C. J. Cela, 10, 13071 Ciudad Real, Spain, Institut für Organische Chemie, Universität Wien, Währinger Strasse 38, A-1090 Vienna, Austria, and Department of Chemistry, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, Austria

Received April 7, 2006

The reaction at room temperature of $[RuCl_2(PPh_3)_3]$ and the ferrocenyl aminophosphine ligand PAPF leads to the product $[RuCl_2(PPh_3)(PAPF)]$, **1c**, in equilibrium with the starting materials. A shift of the reaction toward the formation of **1c** was observed with temperature. At 130 °C, **1c** was transformed into the chelate aminocarbene complex $[RuCl_2(PPh_3)(PAPF\text{-}c)]$, **2**, after a double C−H activation of the aminomethyl fragment. Complex **2** exhibits in the solid state a strong agostic interaction (X-ray structure determination) that is also maintained in solution. An intermediate of the transformation of **1** into **2** has been observed in solution. When complex **2** is heated in DMSO, displacement of the PPh_3 ligand by DMSO takes place, while the agostic interaction remains unchanged. The similar complexes $[RuCl_2(PPh_3)(PN)]$, with the ligand PPFA or PTFA, did not undergo any transformation upon heating and the aminocarbene group was not formed.

Introduction

The preparation of chiral aminocarbenes is an important goal in organic synthesis and catalysis.[1] In particular, the preparation of chiral N-heterocyclic carbenes (NHC) and their application in the synthesis and study of the reactivity of metallic complexes is a current and very active research field. Indeed, a relatively large number of results can be found in this area in the literature.[2] Such metallic carbenes have been widely tested in catalytic reactions.[3] In contrast to this significant activity, the preparation of more classical chiral Fischer-type aminocarbenes is restricted to laborious methods that limit the applicability of these systems. In principle, a reasonable way to prepare chiral aminocarbenes is through the double C−H activation of methylamino derivatives, but the direct activation of methyl groups to give aminocarbenes is a difficult process that has only rarely been reported in the literature,[4] with the exception of studies involving carbonyl clusters of Os.[5] Although difficult, it seems more favorable to convert alkenes,[6] THF,[7] aldimines, and aminals or amides[8] to carbenes. The formation of aminocarbenes by the attack of a nitrogen atom at the α carbon of a Ru−vinylidene moiety has also been described.[9] The difficulty in transforming an aminomethyl group to an aminocarbene arises due to the need for double C−H activation of the aminomethyl

[⊥] This paper is dedicated to Prof. Victor Riera on the occasion of his 70th birthday.

* To whom correspondence should be addressed. E-mail: blanca.manzano@uclm.es.

[†] Universidad de Castilla−La Mancha.

[‡] Universität Wien.

[§] Vienna University of Technology.

(1) (a) Winter, M. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 5, pp 155−214. (b) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, pp 469−547. (c) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61. (d) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (e) Zaragoza-Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999. (f) Wang, C. C.; Wang, Y.; Liu, H. J.; Lin, K. J.; Chou, L. K.; Chan, K. *J. Phys. Chem.* **1997**, *47*, 8887. (g) Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177. (h) Comely, A. C.; Gibson, S. E.; Sur, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 109. (i) Barluenga, J.; Fananas, F. J. *Tetrahedron* **2000**, *56*, 4597. (j) Hegedus, L. S. *Coord. Chem. Rev.* **2000**, *204*, 199, and references therein.

(2) (a) Lappert, M. F. In *Transition Metal Chemistry*; Müller, A., Diemann, E., Eds.; Verlag Chemie: Weiheim, Germany, 1981. (b) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162. (c) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *8*, 1125. (d) Bolm, C.; Kesselgruber, M.; Raabe, G. *Organometallics* **2002**, *21*, 707. (e) Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878. (f) Perry, M. C.; Cui, X.; Burgess, K. *Tetrahedron: Asymmetry* **2002**, *13*, 1969. (g) Rivas, F. M.; Giessert, A.; Diver, S. T. *J. Org. Chem.* **2002**, *67*, 1708. (h) Rivas, F. M.; Riaz, U.; Giessert, A.; Smulik, J. A.; Diver, A. T. *Org. Lett.* **2001**, *3*, 2673. (i) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R. *Organometallics* **2003**, *22*, 4384.

(3) (a) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451. (b) Diaz-Requejo, M. M.; Perez, P. J. *J. Organomet. Chem.* **2005**, *690*, 5441. (c) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978. (d) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. (e) Zinn, F. K.; Viciu, M. S.; Nolan, S. P. *Ann. Rep. Prog. Chem., Sect. B: Org. Chem.* **2004**, *100*, 231. (f) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (g) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130. (h) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951. (i) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290 (j) Gischig, S.; Togni, A. *Organometallics* **2004**, *23*, 2479.

(4) Kuznetsov, V.; Lough, A. J.; Gusev, D. G. *Chem. Commun.* **2002**, 2432.

(5) (a) Adams, R. D. *Chem. Rev.* **1989**, *89*, 1703. (b) Adams, R. D.; Babin, J. E.; Kin, H. S.; Tanner, J. T.; Wolfe, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 3426.

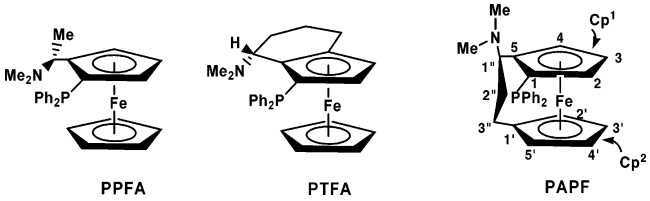
(6) (a) Coalter, J. N.; Spivak, G. J.; Gerard, H.; Clot, E.; Davidson, E. R.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 9388. (b) Holtcamp, M. W.; Labinger, K. G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (c) Coalter, J. N.; Ferrado, G.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 835.

(7) (a) Lueke, H. F.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2517. (b) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2158. (c) Fernando-Miguel, G.; Coalter, J. N.; Gerard, H.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2002**, *26*, 687.

(8) (a) Standfest-Hauser, C. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **2002**, *21*, 4891. (b) Standfest-Hauser, C. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **2003**, 1883. (c) Vyklický, L.; Dvoráková, H.; Dvorák, D. *Organometallics* **2001**, *20*, 5419.

10.1021/om060314g CCC: $33.50 © 2006 American Chemical Society
Publication on Web 08/09/2006

Chart 1



group. In principle, the process could start with an initial agostic C−H···metal interaction that, after C−H activation, would lead to an alkylhydride intermediate. This intermediate should evolve selectively toward a second C−H activation. This mechanistic route has been demonstrated for one Ru complex[10] but seems to be a difficult process in the majority of metallic systems. Ru complexes are known to form easily agostic C−H···Ru interactions[11] and to stabilize the intermediates of an N*C*−*H*[12] and even a double N*C*−*H* bond activation.[13]

On the basis of the information outlined above, the goal of the present work was the preparation of Fischer-type aminocarbene derivatives from unsaturated 16-electron chiral Ru complexes of formula $[RuCl_2(PPh_3)(PN)]$, where PN are the aminophosphine ligands derived from ferrocene (see Chart 1). The corresponding complexes with this formula bearing PTFA[14] and PPFA[15] ligands have been prepared previously by ourselves and other authors. Formally, a double CH activation of the methylamino groups of these compounds could lead to the formation of the aforementioned aminocarbenes. The ligands shown in Chart 1 are similar in terms of the relative dispositions of the P and N donor ligands but differ in the rigidity of the backbone. The ligands are arranged in Chart 1 from the least to the most rigid structure according to our experience in the NMR analysis in solution of different Pd and Ru complexes.[14,16] The ability of the ferrocenyl fragments to stabilize carbenes, both of the Fischer[17] and the N-heterocyclic[3i,18] types, was demonstrated in previous studies.

Results and Discussion

Synthesis. As reported previously[14,15] the reaction of $[RuCl_2(PPh_3)_3]$ with PPFA or PTFA in toluene at room temperature leads to complexes with the formula $[RuCl_2(PPh_3)(PN)]$ together with free PPh_3 (first step in Scheme 1, PN = PPFA, **1a**; PTFA, **1b**). When the reaction was carried out in refluxing toluene, the complexes $[RuCl_2(PPh_3)(PN)]$ were recovered as the sole products. The same result was obtained upon heating solutions of the isolated complexes. Consequently, activation of the aminomethyl group was not observed.

Different results were obtained when the more rigid ligand PAPF was used. The reaction between $[RuCl_2(PPh_3)_3]$ and PAPF at room temperature gave the product $[RuCl_2(PPh_3)(PAPF)]$, **1c** but this was in equilibrium with the starting materials (see Scheme 1). The existence of such an equilibrium was confirmed by monitoring the relative ratios of **1c** and the free ligands PPh_3 and PAPF in the ^{31}P NMR spectra between 90 and 20 °C. The reaction mixture was initially heated at 90 °C, and the equilibrium constant was determined at this temperature. The equilibrium constants were also determined at 80 and 60 °C (see Experimental Section). A clear shift in the reaction toward the formation of **1c** and free PPh_3 was observed when the temperature was higher. Consequently, the temperature of the reaction medium was increased in order to favor the formation of **1c** or even activate the methyl group. When the reaction was monitored by ^{31}P and ^{1}H NMR spectroscopy, chemical changes were not observed up to 100 °C. However, at 110 °C the slow transformation of **1c** to give the chelate aminocarbene **2** was observed. Given this information, the reaction was carried out at 130 °C in a closed Fisher-Porter tube in which this temperature could be achieved in toluene. Under these conditions, **2** was formed in excellent yield after 12 h. However, under these conditions the complexes **1a** and **1b** did not undergo any transformation.

To shed light on the mechanism of this process, we monitored this reaction in toluene-d_6 by ^{1}H NMR spectroscopy at 110 °C during 6 h. This experiment, together with the ^{31}P NMR resonances of **1c** and **2**, provides evidence for the presence of a minor component in the reaction medium. The spectrum showed three mutually coupled resonances, two with a J_{PP} constant typical of phosphines in a mutually *trans* arrangement (see Figure 1). In the ^{1}H NMR spectrum, apart from **1c**, evidence for another complex with coordinated dimethylamino groups was not found. We propose that this minor component is $[RuCl_2(PPh_3)_2(\kappa^1\text{-}P\text{-PAPF})]$, I (the disposition of the ligands proposed in Scheme 2 is speculative), and this could be formed from **1c** by displacement of the NMe_2 group by PPh_3. It is interesting to note that in this intermediate the NMe_2 group could be able to contact the Ru center and undergo the two necessary *C*−*H* activations that would give rise to **2**. A reasonable but speculative mechanism for the change from **1c** to **2** is depicted in Scheme 2. After decoordination of the dimethylamino group in **1c**, the rigidity of the ligand would probably allow this group to be in close proximity to the unsaturated metal center and the formation of a $MeNCH_2$-*H*···Ru agostic interaction would be possible (formation of II). Subsequent oxidative addition could lead to an alkyl hydride (III), and this—after a second C−H

(9) (a) Yam, V. W. W.; Chu, B. W. K.; Cheung, K. K. *Chem. Commun.* **1998**, 2261. (b) Yam, V. W. W.; Chu, B. W. K.; Ko, C. C.; Cheung, K. K. *Dalton Trans.* **2001**, 1911. (c) Tomon, T.; Ooyama, D.; Wada, T.; Shiren, K.; Tanaka, K. *Chem. Commun.* **2001**, 1100. (d) Rüba, E.; Hummel, A.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **2002**, *21*, 4955. (e) Yam, V. W. W.; Ko, C. C.; Chu, B. W. K.; Zhu, N. *J. Chem. Soc., Dalton Trans.* **2003**, 3914.

(10) Dong-Heon, L.; Chen, J.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2002**, 213.

(11) (a) Milstein, D. *Pure Appl. Chem.* **2003**, *75*, 445. (b) Sabo-Etienne, S.; Chaudret, B. *Mod. Coord. Chem.* **2002**, 45.

(12) (a) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956. (b) Liptau, P.; Carmona, D.; Oro, L. A.; Lahoz, F. J.; Kehr, G.; Erker, G. *Eur. J. Inorg. Chem.* **2004**, 4586.

(13) Ingleson, M. J.; Yang, X.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2005**, *127*, 10846.

(14) Jalón, F. A.; López-Agenjo, A.; Manzano, B. R.; Moreno-Lara, M.; Rodríguez, A.; Sturm, T.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1999**, 4031.

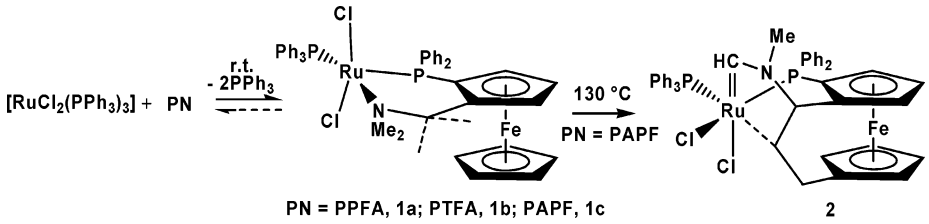
(15) Rodgers, G. E.; Cullen, W. R.; James, B. R. *Can. J. Chem.* **1983**, *61*, 4.

(16) Gómez-de la Torre, F.; Jalón, F. A.; López-Agenjo, A.; Manzano, B. R.; Rodríguez, A.; Sturm, T.; Weissensteiner, W.; Martínez-Ripoll, M. *Organometallics* **1998**, *17*, 4634.

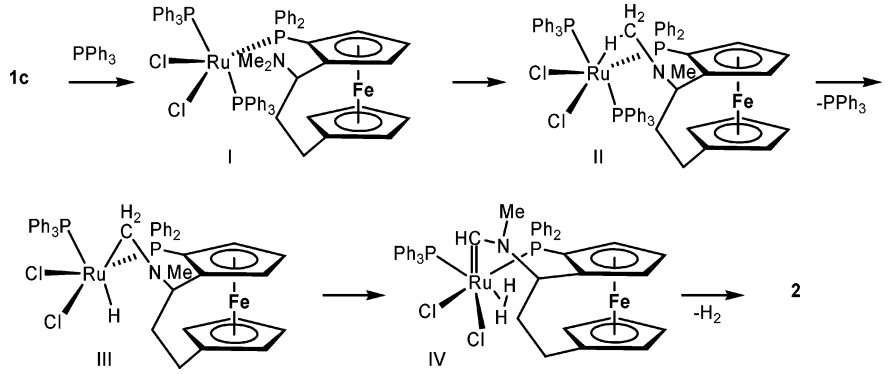
(17) A selection of more recent papers: (a) López-Cortes, J. G.; Contreras de la Cruz, L. F.; Ortega-Alfaro, M. C.; Toscano, R. A.; Alvarez-Toledano, C.; Rudler, H. *J. Organomet. Chem.* **2005**, *690*, 2229. (b) Klimova, E. I.; Klimova, T.; Ruiz-Ramírez, L.; Mendez-Stivalet, J. M.; Hernández-Ortega, S.; Martínez-García, M. *Russ. Chem. Bull.* **2004**, *53*, 834. (c) Barluenga, J.; Vicente, R.; Barrio, P.; López, L. A.; Tomas, M. *J. Am. Chem. Soc.* **2004**, *126*, 5974. (d) Meca, L.; Dvorak, D.; Ludvik, J.; Cisarova, I.; Stepnicka, P. *Organometallics* **2004**, *23*, 2541. (e) Fernández, I.; Mancheno, M. J.; Gómez-Gallego, M.; Sierra, M. A.; Lejon, T.; Hansen, L. K. *Organometallics* **2004**, *23*, 1851. (f) Sierra, M. A.; Mancheno, M. J.; del Amo, J. C.; Fernández, I.; Gómez-Gallego, M.; Rosario-Torres, M. *Organometallics* **2003**, *22*, 384.

(18) A selection of more recent papers: (a) Viciano, M.; Mas-Marza, E.; Poyatos, M.; Sanau, M.; Crabtree, R. H.; Peris, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 444. (b) Coleman, K. S.; Turberville, S.; Pascu, S. I.; Green, M. L. H. *J. Organomet. Chem.* **2005**, *690*, 653. (c) Ramnial, T.; McKenzie, I.; Gorodetsky, B.; Tsang, E. M. W.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 1054. (d) Seo, H.; K.; Bo, Y.; Lee, J. H.; Park, H.-J.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 4783. (e) Demirhan, F.; Yildirim, O.; Cetinkaya, B. *Turk. Trans. Met. Chem.* **2003**, *28*, 558.

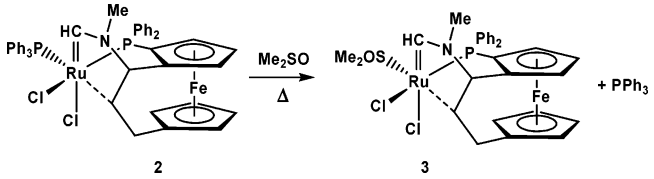
Scheme 1



Scheme 2



Scheme 3



activation (formation of IV) and H_2 liberation—would form the aminocarbene fragment of **2**, which also exhibits an agostic interaction (see below).

When **2** was dissolved in DMSO-d_6, a transformation was not observed at room temperature or even after heating 1 h at 55 °C. However, at 75 °C a slow transformation began to take place. A new product, **3**, appeared, and after 2 h at 95 °C the ratio **2**:**3** was 6:7. According to the NMR studies (see below), **3** may be formulated as [$RuCl_2$(DMSO-d_6)(PAPF-c)] (PAPF-c = aminocarbene derived from PAPF) formed after the replacement of PPh_3 by DMSO-d_6, with the coordination mode of the ferrocenyl ligand unchanged (see Scheme 3). The transformation between **2** and **3** is reversible and **3** reverts slowly in the NMR tube to give **2** when the temperature is lowered. After 2 days at room temperature, the ratio **2**:**3** is 9:7, while after 4 days it is 2:1, indicating that probably the equilibrium ratio has not been achieved. It is worth noting that the agostic interaction in complex **2** is not replaced by DMSO even at high temperature. Furthermore, the displacement of a strong donor ligand such as PPh_3 takes place with the agostic interaction remaining unaffected. This reflects a high stability of the moiety "Ru-(PAPF-c)".

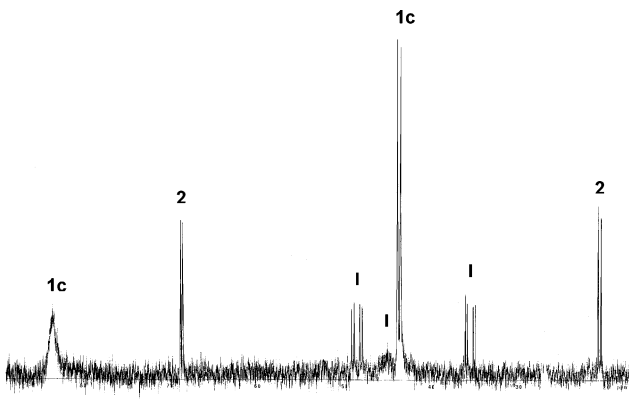


Figure 1. $^{31}P\{^1H\}$ NMR spectra (toluene-d_6, 110 °C) corresponding to the transformation of **1c** into **2**.

The different behavior exhibited by the PAPF ligand when compared with the other two is worthy of note. The complexes [$RuCl_2(PPh_3)$(PN)] with PPFA and PTFA seem to be highly stable. In the case of PAPF, a lower coordinating ability is observed for the ligand if we take into account the existence of the equilibrium in the formation of **1c** and the detection at high temperature of a species in which the dimethylamino group is uncoordinated. As previously stated, this lack of coordination would allow the activation of the methylamino group. It is possible that the steric requirements of the PAPF ligand related to its rigid backbone could be the origin of the relative tendency of the NMe_2 group of complex **1c** to become decoordinated. Besides, as stated above, the rigidity of the ligand backbone could allow access of this group to the metal center and this could, in turn, be activated.

Structural Characterization. Complexes **1c**, **2**, and **3** were characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (also by $^{13}C\{^1H\}$ in the case of **1c** and **2**). A complete assignment of the resonances was possible thanks to techniques such as bidimensional $^1H-^1H$ and $^1H-^{13}C$ g-HSQC, selective ^{31}P decoupled ^1H NMR spectra, monodimensional NOE experiments, and consideration of the characteristic pattern of these types of complexes (see information in Experimental Section).

If the ^1H and $^{13}C\{^1H\}$ NMR data for **1c** and **2** are compared, one significant difference is observed concerning the number of aminomethyl groups, and this is apparent for both nuclei. Two different groups are observed for **1c**, and this is due to the coordination of the N donor atom, which makes the two methyl groups diastereotopic. In contrast, only one type of methyl group is observed for **2**. For this complex a characteristic carbene resonance is observed in the ^1H NMR spectrum at 8.93 ppm, which integrates as one proton, and at 252.91 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Another salient difference in the ^1H NMR spectra of these complexes is the existence in **2** of a resonance

at −3.62 ppm, which can be attributed to one of the $H^{2''}$ protons of the chain of the PAPF ligand. This anomalous chemical shift can be explained by the existence of an agostic interaction with the corresponding C−H bond. In the $^{13}C\{^1H\}$ NMR spectrum, the carbon resonance of this bond appears at 46.86 ppm as a triplet with a J_{CP} of 16.5 Hz. In the proton-coupled ^{13}C NMR spectrum this signal exhibits two different J_{CH} coupling constants of 138.3 and 103.3 Hz. The former value is comparable to that expected for a conventional alkylic CH bond (for instance $J_{CH^{3''}}$ = 130 Hz), but the reduction in the latter value must be due to the agostic interaction. This indicates that the agostic interaction for one of the C−H bonds of the $C^{2''}H_2$ unit, which is observed in the solid state (see below), is maintained in solution. In the ^1H NMR spectra, both complexes show the expected seven resonances for the Cp protons, but a noteworthy difference is observed: a shift to low frequency (2.14 ppm) of one of the resonances in **1c** but not in **2**. This difference is due to the conformation that the ligand is forced to adopt when it is *P,N*-bidentate. As described previously,[16,19] when this ligand (or similar diphosphines) are coordinated to a transition metal in a chelate fashion, one phenyl ring of the diphenyl phosphino group is forced to be in close proximity to Cp[2] and this is very effective at shielding the cyclopentadienyl $H^{5'}$ proton of this ring. As a result, this signal appears at very low frequency (δ = 2−2.7 ppm). This anomalous chemical shift indicates chelate *P,N*-coordination of the ligands and also reflects their high level of rigidity. In the free ligands the signal for this proton appears in the normal range for cyclopentadienyl protons. The absence of this high-field shift for $H^{5'}$ in the case of **2** reflects a different conformation of the diphenylphosphino unit in this complex. In the case of **2**, several phenylic resonances appear broad. For instance, at room temperature one *ortho* proton resonance of the ferrocenyl PPh_2 group is broad, while the other is sharp. The former signal is resolved as a defined triplet when the sample is heated to 45 °C. This indicates the possibility that steric hindrance exists in the complex, and this prevents complete free rotation of the phenylic ring of the ferrocenyl ligand.

The ^1H NMR spectrum of **3** is quite similar to that of **2**. Comparable signals are observed for the ferrocenyl ligand, although changes in the chemical shifts are observed. This shift is considerable in the case of the aminomethyl group (about 0.5 ppm) and in the carbene and agostic protons (about 2 ppm). As expected, the coupling of these protons with the phosphorus atom of PPh_3, as observed in the case of **2**, is not seen in **3**. The steric hindrance in this derivative seems to be less marked than in **2** because the *ortho* phenylic signal, which is separated from the rest, appears as a well-defined multiplet that is transformed into an apparent doublet after decoupling of the PAPF-c phosphorus.

The $^{31}P\{^1H\}$ NMR spectra of compounds **1c** and **2** at room temperature are characterized by the presence of two doublets corresponding to the two nonequivalent phosphines arranged in a *cis* disposition. One of the resonances is shifted to significantly higher frequency as compared to the other. According to the selectively ^{31}P-decoupled ^1H NMR spectra, these signals correspond to the PAPF in **1c** and the PPh_3 resonance in **2**. This fact can be interpreted in terms of the high donor ability of these P donor centers. In the case of **1c**, and according to the known structure of the analogous complex $[RuCl_2(PPh_3)(iso\text{-}PFA)]$ [iso-PFA = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3\text{-}(CHMeNMe_2)P(i\text{-}Pr_2\text{-}1,2)]$,[20] a distorted square pyramidal geometry is expected. If the P atom of the PPFA ligand is located in the apical position (similar to the aforementioned complex), the P atom should be a strong donor center. In **2** the P atom of the ferrocenyl ligand is disposed *trans* to the weak donor agostic interaction, as evidenced by the X-ray structure (see below). In both cases, a shift to higher frequencies is expected for these P atoms.

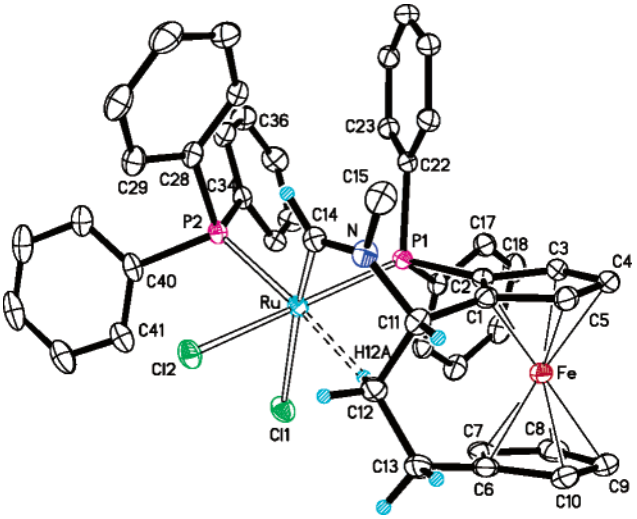


Figure 2. Structural view of **2** showing 30% displacement ellipsoids (aromatic and CH_3 hydrogen atoms and CH_2Cl_2 molecules omitted for clarity). Selected bond lengths and angles (Å, deg): Ru−C(14) 1.957(3), Ru−P(1) 2.349(1), Ru−P(2) 2.267(1), Ru−Cl(1) 2.509(1), Ru−Cl(2) 2.475(1), Ru−C(12) 2.644(3), Ru−H(12a) 1.919, P(2)−Ru−C(14) 93.26(8), P(2)−Ru−P(1) 100.01(3), P(2)−Ru−Cl(1) 99.34(3), P(2)−Ru−Cl(2) 85.52(3), P(2)−Ru−H(12a) 176.1, C(14)−Ru−H(12a) 88.5, Ru−H(12a)−C(12) 128.6.

In the case of **3**, only a singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum, and this is in accordance with the proposed displacement of the PPh_3 ligand. The absence of coordination in the PPh_3 unit was confirmed by the fact that couplings did not disappear in the ^1H NMR spectrum of **3** after selective irradiation of the free PPh_3 resonance.

As we were not able to isolate **3** in a pure form, we performed a MALDI mass spectrum of a mixture of **2** and **3** (see Experimental Section). Fortunately, a peak corresponding to **3** after the loss of one chloride was clearly observed.

X-ray Diffraction Analysis for $2\cdot 2CH_2Cl_2$. The X-ray crystal structure of the solvate $\mathbf{2}\cdot 2CH_2Cl_2$ consists of a neutral Ru complex with two CH_2Cl_2 molecules of crystallization per complex. The molecular structure of **2** is presented in Figure 2 with the atom-labeling scheme and a selection of bond lengths and angles. Two chlorides, a PPh_3, and a phosphinoaminocarbene ligand, PAPF-c, are coordinated to the Ru atom. This is consistent with the proposed double C−H activation experienced by PAPF, which is transformed in this way into a chelating phosphinoaminocarbene. Importantly, an agostic interaction completes the coordination sphere of Ru, and this environment is a distorted octahedron. Although some examples of agostic interactions in complexes with NHC ligands have been

(19) (a) Carrión, M. C.; Jalón, F. A.; López-Agenjo, A.; Manzano, B. R.; Weissensteiner, W.; Mereiter, K. *J. Organomet. Chem.* **2006**, *691*, 1369. (b) Jalón, F. A.; Manzano, B. R.; Gómez-de la Torre, F.; López-Agenjo, A. M.; Rodríguez, A. M.; Weissensteiner, W.; Sturm, T.; Mahía, J.; Maestro, M. *J. Chem. Soc., Dalton Trans* **2001**, 2417 (c) Mernyi, A.; Kratky, C.; Weissensteiner, W.; Widhalm, M. *J. Organomet. Chem.* **1996**, *508*, 209. (d) Sturm, T.; Weissensteiner, W.; Mereiter, K.; Kégl, T.; Jeges, G.; Petolz, G.; Kollár, L. *J. Organomet. Chem.* **2000**, *595*, 93.

(20) Hampton, C. R. S. M.; Butler, I. R.; Cullen, W. R.; James, B. R.; Charland, J. P.; Simpson, J. *Inorg. Chem.* **1992**, *31*, 5509.

described,[3i,21] to the best of our knowledge **2** is the first example in which a Fischer-type aminocarbene ligand also exhibits an agostic interaction. Taking into account the origin of the aminocarbene group, this interaction can be considered as the beginning of a third C−H activation. Such interactions have also been described in $RuCl_2L_3$ complexes.[3i,22] Two agostic interactions have been observed in $RuCl_2L_2$ complexes,[23] and two nonclassical agostic interactions (involving two C−H bonds of each methyl group) have been described[24] in $RuCl_2[PPh_2(2,6\text{-}Me_2C_6H_3)]_2$. Other examples include cationic derivatives of the type[25] $[RuXL_4]^+$ or[26] $[RuXL_3]^+$ and clusters or dimetallic complexes.[27] The relatively short Ru−C(12) [2.644(3) Å] and Ru−H(12a) (1.919 Å) distances indicate that the agostic interaction is strong.[23,24,26b]

The PPh_3 ligand is *trans* to this agostic interaction, and this makes the Ru−P(2) bond distance particularly short [2.267(1) Å] as compared with the Ru−P(1) bond distance of 2.349(1) Å. This structural information is consistent with the chemical shift of the PPh_3 group in the ^{31}P NMR spectrum.

As far as the aminocarbene unit is concerned, the Ru−C(14) [1.957(3) Å] and C(14)−N [1.309(3) Å] bond distances and the Ru−C(14)−N [122.9(2)°] angle are in the expected range for this type of Ru carbene compounds (Ru−C distances are usually in the range 1.91−2.04 Å, N−C in the range 1.26−1.36 Å, and Ru−C−N angles in the range 115−142°).[8a,b,9,28]

The transformation of the aminomethyl group into the aminocarbene fragment leads to significant changes in the conformation of the coordinated ferrocenyl ligand. The apical orientation of the dimethylamino group (or the PR_2 groups in the analogous diphosphine ligands) (see Chart 1) means that the metal is clearly located above the upper Cp plane. This forces the phosphorus atom to orientate the electron pair toward the metal position by rotating the PPh_2 unit about the C(Cp)−P bond, which at the same time places one phenyl ring in close proximity to the lower Cp ring.[16,19] In the carbene ligand, coordination through the carbon atom means that the metal is located below the upper Cp ring and the phenyl group is no longer orientated toward the lower Cp ring (see Figure 2). This situation is consistent with the chemical shifts found for the $H^{5'}$ proton in **1** and **2**, as explained in the NMR section (see above).

In conclusion, we have been able to transform a dimethylamino group into an aminocarbene in a PAPF Ru complex. The idea that an uncoordianted methylamino group forced to be in close proximity to an unsaturated center could give rise to an aminocarbene unit may lead to future developments in this field. The new aminocarbene complex obtained contains a very stable agostic interaction that is not displaced by DMSO at high temperature. Instead, the PPh_3 ligand is substituted by the coordinating solvent.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were predried and distilled over appropriate drying agents and degassed before use.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were recorded on Varian UNITY INOVA 500 and Varian UNITY 300 spectrometers. ^1H NMR spectra selectively decoupled from ^{31}P were also registered. Coupling constants are in Hz. Chemical shifts (ppm) are given relative to TMS (^1H, ^{13}C NMR), taking as reference the signal of the deuterated solvent that has been used. For the ^{31}P NMR, H_3PO_4 (85%) has been used as reference. $^1H-^1H$ COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. The NOE difference spectra: recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5−10 dB. $^1H-^{13}C$ g-HSQC spectra: standard pulse sequence with an acquisition time of 0.1 s, pulse width 11 ms, relaxation delay 1 s, number of scans 8, number of increments 256. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer. The MALDI mass spectra was recorded in a Bruker MicroFlex. s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. If not specified, the $^{13}C\{^1H\}$ NMR resonances are singlets. $RuCl_2(PPh_3)_3$[29] was prepared according to literature, and the ligands PPFA,[30] PTFA,[31] and PAPF[19c] were prepared as previously described.

[$RuCl_2(PPh_3)$(PAPF)] (1c). A solution of 13.2 mg of [$RuCl_2(PPh_3)_3$] (0.014 mmol) and 6.2 mg of racemic PAPF (0.014 mmol) was prepared in a NMR tube in toluene-d_8. This tube was introduced in the NMR probe and heated until 80 °C. After 1 h of reaction the ^1H and ^{31}P NMR detected the presence of the resonances of **1c**, which were assigned by comparing with the corresponding signals of the starting materials and those of PPh_3. ^1H NMR (toluene-d_8, 80 °C): 8.28 (2H, dd, J_{HH} = 7.8, J_{HP} = 11.2, H_{ortho}Ph-PAPF), 4.21 (Cp^1), 4.12 (2H, Cp^1), 3.84 (Cp^2), 3.73 (Cp^2), 3.66 (Cp^2), 2.14 (Cp^2,$H^{5'}$); 3.10, 2.94 (NMe_2) ppm. $^{13}C\{^1H\}$ NMR (toluene-d_8, 80 °C): 136.80 (d, J_{CP} = 10.8, C_{ortho}Ph-PAPF), 75.26 (Cp^1); 73.45 (Cp^2,$C^{5'}$), 72.00 (Cp^2), 71.80 (Cp^1), 71.10 (Cp^2), 67.53(Cp^2), 67.49 (Cp^1), 55.74 (NCH_3), 51.42 (NCH_3), 42.42 (CH_2), 38.35 (CH_2) ppm. ^{31}P NMR (toluene-d_8, 80 °C): 82.9 (d, J_{CP} = 45.0, PAPF), 43.7 (d, PPh_3) ppm.

[$RuCl_2(PPh_3)$(PAPF-c)] (2). [$RuCl_2(PPh_3)_3$] (0.1534 g, 0.16 mmol) and racemic PAPF (80 mg, 0.176 mmol) were solved in 10 mL of toluene. This solution was introduced in a Fisher-Porter tube

(21) (a) Burling, S.; Kociok-Köhn, G.; Mahon, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2005**, *24*, 5868. (b) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

(22) (a) La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778. (b) Goicoechea, J. M.; Mahon, M. F.; Whittlesey, M. K.; Kumar, P. G. A.; Pregosin, P. S. *Dalton Trans.* **2005**, 588. (c) Major, Q.; Lough, A. J.; Gusev, D. G. *Organometallics* **2005**, *24*, 2492.

(23) Baratta, W.; Herdtweck, E.; Rigo, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1629.

(24) Baratta, W.; Mealli, C.; Herdtweck, E.; Ienco, A.; Mason, S. A.; Rigo, P. *J. Am. Chem. Soc.* **2004**, *126*, 5549.

(25) (a) Bennett, M. A.; Goh, L. Y.; McMahon, I. J.; Mitchell, T. R. B.; Robertson, G. B.; Turney, T. W.; Wickramasinghe, W. A. *Organometallics* **1992**, *11*, 3069. (b) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekas, R.; Sillanpaa, R.; Casabo, J. *Chem. Commun.* **1992**, 1281. (c) Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2000**, *122*, 11230.

(26) (a) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398. (b) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087.

(27) (a) Brown, D. B.; Cripps, M.; Johnson, B. F. G.; Martin, C. M.; Braga, D.; Grepioni, F. *Chem. Commun.* **1996**, 1425. (b) Kuhlman, R.; Streib, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5813. (c) Kuhlman, R.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 3188. (d) Zhongli, H.; Plasseraud, L.; Moldes, I.; Dahan, F.; Neibecker, D.; Etienne, M.; Mathieu, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 916.

(28) (a) Clark, G. R. *J. Organomet. Chem.* **1977**, *134*, 51. (b) Adams, H. M.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, *394*, 349. (c) Bianchini, C.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Organometallics* **1999**, *18*, 2376. (d) Wing-Wah, V.; Chu, B. W.-W.; Ko, C.-C.; Cheung, K.-K. *J. Chem. Soc., Dalton Trans.* **2001**, 1911. (e) Fillaut, J.-L.; de los Rios, I.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Eur. J. Inorg. Chem.* **2002**, 935.

(29) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(30) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

(31) Jedlicka, B.; Widhalm, M.; Weissensteiner, W. *Chem. Commun.* **1993**, 1329.

and heated at 130 °C for 15 h. The solution was stirred during this time. The resulting orange solution was transferred to a Schlenk flask and evaporated to dryness. The resulting oil was triturated with diethyl ether (2 × 5 mL), and an orange powder was obtained (103 mg, 0.117 mmol, 73%). Monocrystals of **2** suitable for an X-ray analysis were obtained by diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. ^{1}H NMR (DMSO-d_6, rt): 8.93 (d, $J_{H-P(PPh3)} = 4.4$, −N=C*H*−); 8.70 (bm, H_{ortho}Ph−PAPF-c), 8.4, 7.9, 7.2, 7.1, 6.8 (bs, Ph); 7.6, 7.5, 7.4, 7.32, 6.95, 5.43 (t, $J_{HH} = 8.3$ H_{ortho}Ph−PAPF-c); 5.75, 4.36, 3.84, 3.13 (bs, Cp^2); 4.85, 4.21, 3.39 (s, Cp^1); 4.47 (d, $J_{HH} = 12.2$, H$^{1''}$); 3.73 (m, H$^{2''}$); 3.18 (s, N*Me*); 2.63 (m, H$^{3''}$); 2.03 (m, H$^{3''}$); −3.62 (m, H$^{2''}_{agost}$) ppm. ^{13}C-{^{1}H} NMR (DMSO-d_6, rt): 252.91 (t, $J_{CP} = 14.6$, −N=*C*(H)−); 141.04 (d, $J_{CP} = 49.4$, C_{ipso}); 136.35 (d, $J_{CP} = 9.2$, C_{ortho}); 134.38 (d, $J_{CP} = 36.0$, C_{ipso}); 133.94 (d, $J_{CP} = 19.5$, C_{ortho}); 134.38 (d, $J_{CP} = 36.0$, C_{ipso}); 133.94 (d, $J_{CP} = 19.5$, C_{ortho}); 132.73 (d, $J_{CP} = 3.0$, C_{para}); 132.18 (d, $J_{CP} = 9.8$, C_{meta}); 131.55 (d, $J_{CP} = 7.9$, C_{ortho}); 130.92 (C_{para}); 129.6 (d, $J_{CP} = 24.4$, C_{ipso}); 129.46 (d, $J_{CP} = 11.6$, C_{meta}); 129.44 (C_{para}); 128.39 (d, $J_{CP} = 9.2$, C_{meta}); 127.69 (d, $J_{CP} = 9.8$, C_{meta}); Cp^2: 87.81 (C$^{1'}$), 73.17, 71.57, 71.11, 69.55; Cp^1: 85.11 (d, $J_{CP} = 11.6$, C^2); 76.85 (d, $J_{CP} = 45.17$, C^1), 75.36 (d, $J_{CP} = 5.5$), 73.44, 71.66 (d, $J_{CP} = 5.5$); 64.38 (C$^{1''}$); 50.31 (N*Me*); 46.86 (t, $J_{CP} = 16.5$, C$^{2''}$); 25.53 (C$^{3''}$) ppm. ^{31}P NMR ($CDCl_3$, rt): 66.76 (d, $J_{PP} = 34.2$); 21.42 (d) ppm. Anal. Calcd for $C_{45}H_{41}Cl_2FeNP_2Ru$: C, 61.03; H, 1.58; N, 4.67. Found: C, 61.15; H, 1.63; N, 4.73.

Transformation of 2 into 3. Complex **2** (4 mg, 0.004 mmol) was solved in 0.5 mL of DMSO-d_6 in an NMR tube. At room temperature no changes were observed. At 75 °C a new product, **3**, appeared. After 2 h at 95 °C, the ratio **2**:**3** was 6:7. ^{1}H NMR data for **3**: 11.00 (s, −N=C*H*−); 8.48 (dd, $J_{HH} = 8.1$, $J_{HP} = 11.4$, H_{ortho}Ph−PAPF-c); 7.65−7.35 (m, Ph); 5.37 (s, Cp^2); 4.94 (s, Cp^1); 4.56 (d, $J_{HH} = 12.1$, H$^{1''}$); 4.41 (s, Cp^2); 4.39 (t, $J_{HH} = 2.6$,Cp^1); 3.94 (s, Cp^2), 3.70 (s, Cp^1); 3.64 (s, N*Me*); 3.61 (s, Cp^2); −5.78 (bs, H$^{2''}_{agost}$) ppm. ^{31}P NMR (DMSO-d_6, rt) data for **3**: 31.44 (s) ppm. MALDI mass spectra of a mixture of **2** and **3**: $m/z = 850$, [RuCl(PPh_3)(PAPF-c)]$^+$; 673, [RuCl(DMSO-d_6)(PAPF-c) + H]$^+$; 452, [PAPF-c + H]$^+$.

Determination of Equilibrium Constants for the Formation of 1c and Monitoring of the Chemical Evolution of 1c to 2. The equilibrium constant of the reaction [$RuCl_2(PPh_3)_3$] + PAPF ↔ [$RuCl_2(PPh_3)$(PAPF)], **1c**, + 2 PPh_3 was determined at 60, 80, and 90 °C by monitoring the evolution of the different species by ^{31}P NMR spectroscopy. [$RuCl_2(PPh_3)_3$] (18.8 mg, 19.6 mmol) and PAPF (9.1 mg, 19.6 mmol) were suspended in 0.5 mL of toluene-d_8 in an NMR tube equipped with a Young valve. This sample was first heated to 90 °C in the NMR probe. ^{31}P NMR spectra, with 240 scans, were recorded every 5 min during a total time of 105 min. The stabilization of the corresponding integrations was achieved after 56 min. The same procedure was followed to calculate the respective integrations at 80 and 60 °C, lowering the temperature in the NMR probe. The equilibrium constants were calculated, on the basis of the corresponding integrations, according to the equation $K_{eq} = [\mathbf{1c}][PPh_3]^2/[RuCl_2(PPh_3)_3][PAPF]$. The **1c**:$PPh_3$:PAPF ratios determined were the following: 21.9:100:28.4 (90 °C); 18.5:100:28.8 (80 °C); 15.8:100:38.5 (60 °C). The calculated constants were as follows: 271 (90 °C); 223 (80 °C); 106 (60 °C). The calculation of the equilibrium constants at 20 and 40 °C, by the same procedure, gives values practically identical for the two temperatures and above those expected considering the linear decay of K_{eq} vs temperature followed by the preceding data. As a consequence, we estimate that below 40 °C the equilibrium is not achieved during the NMR time of the experiments.

The evolution of the stated solution was followed at 110 °C during 6 h by ^{31}P NMR spectroscopy. The corresponding resonances of **2** (see below) were observed as minor signals. In addition, other small resonances were observed such as two doublets of doublets at 48.7 ppm ($J_{PP} = 115.5$, 36.6 Hz) and 36.1 ppm ($J_{PP} = 115.5$, 92.2 Hz) and a broad signal at about 45 ppm. These signals were assigned to the intermediate species I.

X-ray Structure Determination. Orange crystals of $C_{45}H_{41}Cl_2FeNP_2Ru\cdot 2CH_2Cl_2$ (complex **2**) were obtained by diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) by 0.3° ω-scan frames covering a complete sphere of the reciprocal space.[32] After data integration with the program SAINT, corrections for crystal decay, absorption, and $\lambda/2$ effects were applied with the program SADABS.[32] The structure was solved with direct methods using the program SHELXS-97.[33] Structure refinement on F^2 was carried out with the program SHELXL-97.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Salient crystal data are as follows: $C_{47}H_{45}Cl_6FeNP_2Ru$, $M_r = 1055.40$, orthorhombic, space group $Pca2_1$ (No. 29), $T = 223(2)$ K, $a = 24.633(5)$ Å, $b = 11.588(3)$ Å, $c = 15.585(4)$ Å, $V = 4448.7(19)$ Å^3, $Z = 4$, $\mu = 1.133$ mm^{-1}. Of 62 074 reflections collected up to $\theta = 30°$, 12 798 were independent ($R_{int} = 0.042$) and 11 000 were observed ($I > 2\sigma(I)$); number of refined parameters: 524; final R indices: R1 = 0.042 (all data), wR2 = 0.080 (all data).

Acknowledgment. We gratefully acknowledge the Subdirección General de Cooperación Internacional for an "Acción Integrada" project (HU-2003-0020) as well as Österreichischer Akademischer Austauschdienst for the "Acción Integrada" project 20/2004. Financial support from the Spanish DGES/MCyT (CTQ2005-01430/BQU) and from the J. Castilla-La Mancha-FEDER Funds (PBI-05-003) is acknowledged.

Supporting Information Available: X-ray data of complex **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060314G

(32) Bruker, Programs *SMART*, version 5.054; *SAINT*, version 6.2.9; *SADABS* version 2.03; *XPREP*, version 5.1; *SHELXTL*, version 5.1; Bruker AXS Inc.: Madison, WI, 2001.

(33) Sheldrick, G. M. *SHELX-97*, Program System for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997.