

Synthesis and Structural Characterization of Stable Hydride–Alkylidene Complexes of Iridium(III)

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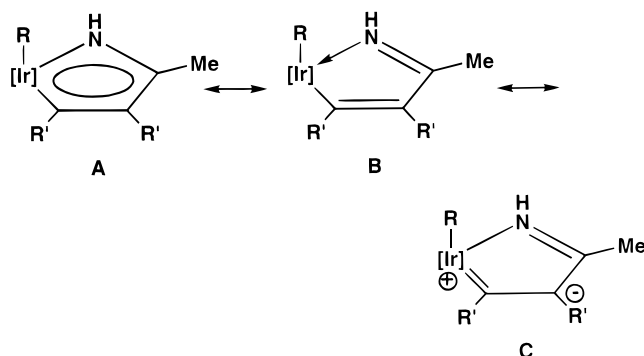
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Received April 23, 1998

Summary: The protonation of the iridapyrrole complex $\text{Tp}^{\text{Me}_2}(\text{H})\text{Ir}[\text{C}(\text{Me})=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NH}]$ allows the isolation of the two possible stereoisomers of the chelating Ir(III) alkylidene $[\text{Tp}^{\text{Me}_2}(\text{H})\text{Ir}(\text{H})\text{C}(\text{Me})\text{CH}(\text{Me})\text{C}(\text{Me})=\text{NH}][\text{BAR}'_4]^-$ (**2**; $\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$). They undergo easy and reversible hydride migration onto the electrophilic carbene atom.

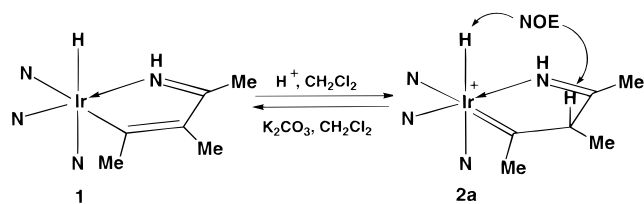
Alkylidene complexes of the late transition metals in high oxidation states have been postulated as reactive intermediates in several catalytic processes.¹ Recently, we have obtained the first alkylidene complexes of Ir(III), $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})\text{C}(\text{Me})\text{CH}(\text{Me})\text{C}(\text{Me})=\text{NH}]^+$, by protonation at C_β of the alkenyl derivatives $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{R})(\text{PMe}_3)$ ($\text{Tp}^{\text{Me}_2} = \text{hydrotris}(3,5\text{-dimethyl-1-pyrazolyl})\text{borate}$;² $\text{R} = \text{H, Et}$). These compounds are very reactive, albeit observable, species^{3,4} that undergo α -migratory insertion reactions at temperatures above -60°C .

Iridapyrrole complexes with a structure of type **A** ($\text{R} = \text{H, R}' = \text{Me}$; $\text{R} = \text{Et, R}' = \text{H}$) have also been prepared in our laboratory by the H_2O -catalyzed intramolecular coupling of alkenyl and acetonitrile ligands.⁵ Since they seem to exhibit considerable alkenyl character (canonic form **B**), protonation at C_β (see **C**) to generate new, cationic alkylidene complexes appeared feasible.^{3,6,7} In this contribution we wish to report preliminary results on this chemistry, including the structural characterization by X-ray methods of the first hydride–alkylidene



complex of a late transition metal in a high oxidation state, $[\text{Tp}^{\text{Me}_2}(\text{H})\text{Ir}(\text{H})\text{C}(\text{Me})\text{CH}(\text{Me})\text{C}(\text{Me})=\text{NH}]^+$ (**2a**), isolated as its BAR'_4^- salt ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$).⁸

Addition of 1 equiv of $[\text{H}(\text{OEt}_2)_2][\text{BAR}'_4]$ to a cold (-70°C) CH_2Cl_2 solution of $\text{Tp}^{\text{Me}_2}(\text{H})\text{Ir}(\text{C}(\text{Me})=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NH}$) (**1**),^{5b} produces the cationic hydride–alkylidene **2a** quantitatively (NMR, no intermediates observed) (eq 1).



(1)

Interestingly, compound **2a** rearranges in solution in the presence of small amounts of water to give the thermodynamically favored stereoisomer **2b** (eq 2), through a still undisclosed mechanism. Treatment of dichloromethane solutions of **2a** or **2b** with an excess of K_2CO_3 (20°C , 2 h) gives the hydride–iridapyrrole

(6) (a) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. (b) Bleeker, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1993**, *12*, 985. (c) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951. (d) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.

(7) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(8) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

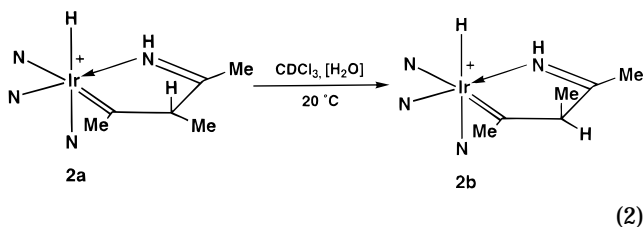
(1) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (b) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z. *J. Am. Chem. Soc., Chem. Commun.* **1996**, 1.

(2) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(3) Alías, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *J. Am. Chem. Soc.* **1998**, *120*, 5816.

(4) The alkylidene moiety is considered as a neutral ligand. For $\text{Ir}^{\text{III}}=\text{CH}_2$ complexes see: (a) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079. (b) Fryzuk, M. D.; Gao, X.; Rettig, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 3106. Ir(III)–alkylidene complexes have been postulated as reactive intermediates in stoichiometric and catalytic processes: (c) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (d) Thorn, D. L. *Organometallics* **1982**, *1*, 879. (e) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (f) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212. (g) France, M. B.; Feldman, J.; Grubbs, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1307. (h) Bleeker, J. R.; Behm, R. *J. Am. Chem. Soc.* **1997**, *119*, 8503.

(5) (a) Alvarado, Y.; Daff, P. J.; Pérez, P. J.; Poveda, M. L.; Sánchez-Delgado, R.; Carmona, E. *Organometallics* **1996**, *15*, 2192. (b) Complex **1** was obtained by heating the allylic species $\text{Tp}^{\text{Me}_2}(\text{H})\text{Ir}(\eta^3\text{-syn-C}_3\text{H}_4\text{-Me})$ (Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *6*, 860) in CH_3CN .



complex **1**, clearly demonstrating the reversibility of the protonation reaction.⁹

The formulation proposed for compounds **2** finds support in the observation of their characteristic NMR signals, notably a low-field ¹³C{¹H} resonance at *ca.* 325 ppm due to the α -carbon of the carbene ligand and a high-field ¹H signal in the proximity of δ -15 attributable to the hydride functionality.¹⁰ The stereochemistry of the kinetic isomer **2a** can be clearly inferred from 2D-NOESY spectra, which indicate that the protonation is stereospecific and occurs on the face of the ring adjacent to the hydride ligand. Further structural confirmation comes from the results of an X-ray study¹¹ carried out with **2a**. This shows (Figure 1) the expected planar geometry about C α . The Ir–C α bond distance of 1.80(3) Å is similar to the iridium–carbon bond length of 1.869(9) Å found in the Ir(I) methylidene complex [N(SiMe₂CH₂PPh₂)₂Ir=CH₂].^{4a} Complex **2a** is a very unusual example of a structurally characterized electrophilic hydrido–alkylidene complex with a *cis* distribution of these two ligands.¹² Somewhat related metallocyclic carbene units M=C–C–C–C have been studied by Jones and co-workers.¹³

Additionally with regard to the chemical reactivity of compounds **2**, it is worth pointing out that despite the correct position of the hydride ligand to migrate onto the alkylidene carbon (the Ir–H bond lies parallel to the $p\pi$ orbital of the carbene carbon), the effects of the α -migratory insertion reaction are not apparent. It should be noted, however, that because of the severe steric con-

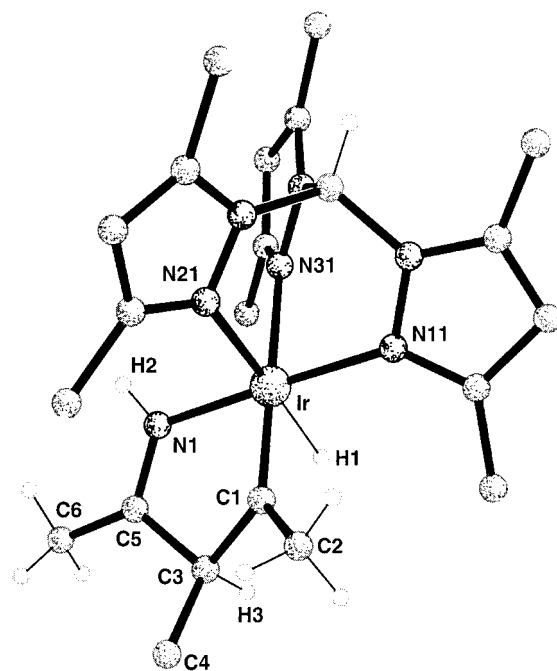
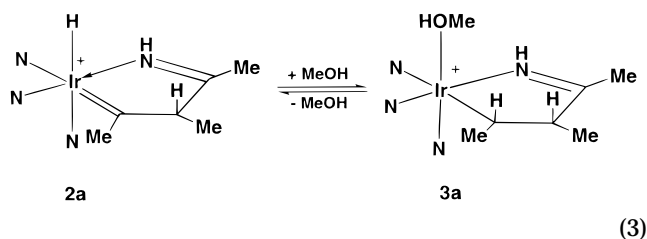


Figure 1. Molecular structure of complex **2a**. Selected bond lengths (Å) and angles (deg): Ir(1)–N(1), 2.01(2); Ir(1)–H(1), 2.03(14); Ir(1)–C(6), 1.80(3); C(4)–C(6)–Ir(1), 113(2); C(7)–C(6)–Ir(1), 128(3); C(4)–C(6)–C(7), 118(3).

straints a β -H elimination from the resulting alkyl intermediate is hindered: the ring β -H is too far from the metal center to yield an accessible transition state for the elimination reaction, and furthermore, the Me group bonded to the α -C of the ring would point, after the migration, to the side of the ring opposite with respect to the vacant coordination site created by this process. Therefore, α -H elimination (albeit nonproductive) should be favored over β -H elimination in the alkyl intermediates of these α -migratory insertion reactions.^{12a,14}

In accord with this line of argumentation, complexes **2a** and **2b** do not rearrange in dry, noncoordinating solvents. Nevertheless, in methanol solution α -migration is facile (eq 3) and yields the expected methanol adducts **3**. The process is stereospecific and reversible;



removal of the solvent under vacuum cleanly regenerates the alkylidene complexes **2**. Acetonitrile gives more stable adducts; the reaction of compounds **2** with NCMe results in the instantaneous, stereospecific formation of the adducts **4**, as shown in eq 4 for the **2a** \rightarrow **4a** transformation.¹⁵ These results represent an unusual observation of a *direct and reversible* α -H migration onto

(9) (a) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157. (b) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

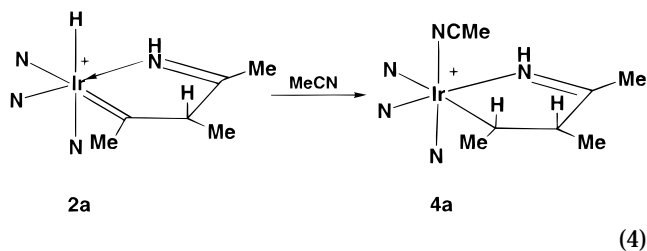
(10) A cold (-70 °C) solution of [H(OEt)₂][BAR₄] (0.14 g, 0.136 mmol) in CH₂Cl₂ (2 mL) was transferred onto a solution of complex **1** (0.08 g, 0.136 mmol) in CH₂Cl₂ (5 mL) cooled at the same temperature. After the mixture was stirred for 10 min, the cooling bath was removed and the solution reduced in volume to *ca.* 1 mL and cooled again to -70 °C. Light petroleum (10 mL) was then added and the resulting orange precipitate filtered and redissolved in a mixture of light petroleum–diethyl ether (3:1, 15 mL). The resulting solution was left overnight at -30 °C to give analytically pure complex **2a** as orange crystals in 60% yield. Anal. Calcd for C₅₃H₄₆B₂N₇F₂₄Ir: C, 43.88; H, 3.17; N, 6.75. Found: C, 43.52; H, 3.17; N, 6.40. Selected spectroscopic data are as follows: ¹H NMR (CDCl₃, 25 °C) δ -15.68 (s, 1H, IrH), 0.21 (qd, ³J_{HH} = 7.4, ⁴J_{HH} = 2 Hz, 1H, CHMe), 1.72 (d, ³J_{HH} = 7.4 Hz, 3H, CHMe), 9.89 (br s, 1H, NH); ¹³C{¹H} NMR (CDCl₃, 25 °C) δ 48.2 (CHMe), 82.2 (CHMe), 192.3 (C=NH), 324.5 (Ir=C). IR (Nujol) ν (IrH) 2152, ν (NH) 3320 cm⁻¹.

(11) Crystal data for **2a**·1/4CH₂Cl₂: triclinic, $P\bar{1}$, $a = 13.539(2)$ Å, $b = 15.486(4)$ Å, $c = 16.487(5)$ Å, $\alpha = 96.54(13)^\circ$, $\beta = 108.68(12)^\circ$, $\gamma = 92.75(14)^\circ$, $V = 3239(14)$ Å³, $Z = 2$, $D_c = 1.509$ Mg/m³, $R_1 = 0.1025$ for $I > 2\sigma(I)$, $wR_2 = 0.2700$. R indices (all data): $R_1 = 0.1709$, $wR_2 = 0.3092$.

(12) (a) Schrock, R. R.; Seidel, S. W.; Möscher-Zanetti, N. C.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195. For a *trans* configuration of these ligands see: (b) Werner, H.; Stüer, W.; Laubender, M.; Lehmann, C.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2236.

(13) (a) Crowther, D. J.; Zhang, Z.; Palenik, G. J.; Jones, W. M. *Organometallics* **1992**, *11*, 622. (b) Stenstrom, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079.

(14) For α -elimination processes in alkyl ligands see for example: (a) Turner, H. W.; Schrock, R. R.; Fellman, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (b) Parkin, G.; Bunel, E.; Burger, J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (c) Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620.

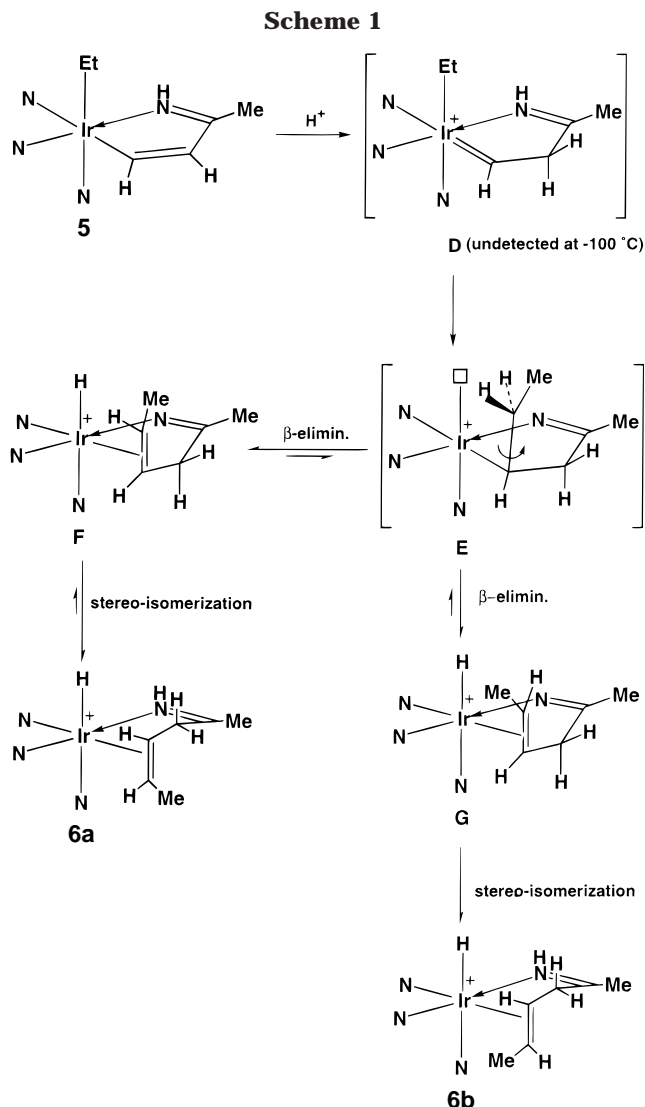


a well-defined electrophilic alkylidene carbon to give an alkyl ligand.¹⁶

Treatment of the ethyl–iridapyrrole complex $\text{Tp}^{\text{Me}_2}\text{-(Et)Ir}(\text{CH}=\text{CHC}(\text{Me})=\text{NH})$ (**5**)^{5a} with 1 equiv of $[\text{H}(\text{OEt}_2)_2][\text{BAr}_4']$ (CH_2Cl_2 , 20 °C) quantitatively gives rise (NMR) to the hydride–*cis*-olefin derivative **6a**, which slowly converts in solution, at 20 °C, into the thermodynamically more stable *trans* stereoisomer **6b** (Scheme 1). Complexes **6a**, **b** have been fully characterized by 1D and 2D NMR techniques;¹⁷ the structure of **6b** has been confirmed by X-ray studies to be reported elsewhere.

The reaction is expected to take place with initial formation of the cationic ethyl–alkylidene intermediate **D** (Scheme 1), but this species cannot be detected even when the protonation is effected at –100 °C (CD_2Cl_2). Clearly, β -H elimination from the migration product **E** is so facile in this case that the reaction proceeds to give the hydride–olefin complex **F**. An additional stereoisomerization step of the bonded olefin¹⁸ would give the observed product **6a**;^{5a} complex **6b** could then be formed from this stereoisomer, assuming the reversibility of the above processes.¹⁹

In conclusion, we have demonstrated that iridapyrrole complexes with a structure of type **A** ($\text{R} = \text{H}, \text{Et}$) undergo electrophilic attack by H^+ at the β -carbon of the ring in a stereospecific manner to give cationic, electrophilic alkylidene derivatives of Ir(III). When $\text{R} = \text{Et}$, α -Et



migration is followed by fast β -H elimination (**E** \rightarrow **F** or **G** in Scheme 1) but for $\text{R} = \text{H}$ the effects of the α -H migration are not observable because of the lack of accessible β -H elimination pathways in the purported alkyl intermediate. This has made possible not only the isolation of the first stable alkylidene complexes of a group 9 element in oxidation state +3 and the structural characterization by X-ray methods of one of these complexes but, moreover, the observation of a direct and reversible α -migration of a hydride ligand from the metal onto the electrophilic carbon atom of the carbene functionality.

Acknowledgment. The DGES (Projects PB96-0824 and PB94-1445) and the Junta de Andalucía are thanked for financial support. We also thank Dr. Y. Alvarado for some preliminary studies on the protonation of complex **5**. M.S. and F.M.A. thank the Spanish Ministerio de Educación y Ciencia for research grants.

Supporting Information Available: Text giving details of the X-ray diffraction study and tables giving crystal and refinement data, selected bond lengths and angles, atomic coordinates, and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

(15) Compound **1** (0.07 g, 0.12 mmol) was dissolved in a cold (–70 °C) mixture of CH_2Cl_2 – MeCN (2:1, 15 mL) and treated with a solution of $[\text{H}(\text{OEt}_2)_2][\text{BAr}_4']$ (0.12 g, 0.12 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was warmed slowly to room temperature and the solvent removed under reduced pressure. Workup as described above for **2a** furnished complex **4a** as a microcrystalline white solid. Yield: 0.08 g (45%). Anal. Calcd for $\text{C}_{55}\text{H}_{49}\text{B}_2\text{N}_8\text{F}_{24}\text{Ir}$: C, 44.29; H, 3.28; N, 7.51. Found: C, 44.16; H, 3.13; N, 7.68. Selected spectroscopic data are as follows: ^1H NMR (CDCl_3 , 25 °C) δ 0.68, 1.34 (d, $^3J_{\text{HH}} = 8$ Hz, 3H each, CHMe), 3.0 (m, $^3J_{\text{HH}} = 10$, $^3J_{\text{HMe}} = 8$, $^4J_{\text{HH}} = 2$ Hz, 1H, CHMe), 4.22 (dq, $^3J_{\text{HH}} = 10$, $^3J_{\text{HMe}} = 8$ Hz, 1H, IrCHMe), 8.63 (br s, 1H, NH); IR (Nujol) $\nu(\text{NH})$ 3346 cm^{-1} .

(16) For H-migration studies in Fischer's carbene complexes see: Michelin, R. A.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Organometallics* **1993**, *12*, 2372 and references therein.

(17) Complex **5** (0.06 g, 0.1 mmol) and $[\text{H}(\text{OEt}_2)_2][\text{BAr}_4']$ (0.10 g, 0.1 mmol) were dissolved together in CH_2Cl_2 (10 mL) at room temperature. The resulting colorless solution was stirred overnight and then evaporated in vacuo. Extraction into a mixture of petroleum ether–diethyl ether (1:1, 10 mL), concentration, and cooling at –30 °C afforded complex **6b** as a microcrystalline white solid. Yield: 0.09 g (60%). Anal. Calcd for $\text{C}_{53}\text{H}_{46}\text{B}_2\text{N}_7\text{F}_{24}\text{Ir}\cdot\text{Et}_2\text{O}$: C, 44.90; H, 3.67; N, 6.43. Found: C, 44.92; H, 3.64; N, 6.19. Selected spectroscopic data are as follows: ^1H NMR (CDCl_3 , 25 °C) δ –17.36 (s, 1H, IrH), 0.94 (d, $^3J_{\text{HH}} = 6$ Hz, 3H, CHMe), 3.24, 3.30 (AB spin system, $^2J_{\text{AB}} = 20$, $^3J_{\text{AH}} = 5.6$, $^4J_{\text{AH}} = 2$ Hz, 1H each, CH_2), 4.15 (dq, $^3J_{\text{HH}} = 12$, $^3J_{\text{HMe}} = 6$ Hz, 1H, CH_{olef}), 5.37 (dd, $^3J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 5.4$ Hz, 1H, CH_{olef}), 8.65 (br s, 1H, NH); IR (Nujol) $\nu(\text{IrH})$ 2200, $\nu(\text{NH})$ 3185 cm^{-1} .

(18) (a) Penag, T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174. (b) Casey, C. P.; Underiner, T. L.; Vosejka, P. C.; Slough, G. A.; Cavney, J. A.; Hayashi, R. K. *Organometallics* **1997**, *16*, 2189.

(19) Variable-temperature NMR and deuteration experiments are in good accord with the pathway showed in Scheme 1 and have also allowed the characterization of the hydride–olefin species **F** and **G**.