

## Preparation of Benzyl Azide Complexes of Iridium(III)

Gabriele Albertin,<sup>\*,†</sup> Stefano Antoniutti,<sup>†</sup> Daniela Baldan,<sup>†</sup> Jesús Castro,<sup>‡</sup> and Soledad García-Fontán<sup>‡</sup>*Dipartimento di Chimica, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy, and Departamento de Química Inorgánica, Facultad de Química, Universidade de Vigo, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain*

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Hydride complexes  $\text{IrHCl}_2(\text{P}(\text{Pr}_3)_2)_2$  (**1**) and  $\text{IrHCl}_2\text{P}_3$  (**2**) [ $\text{P} = \text{P}(\text{OEt})_3$  and  $\text{PPh}(\text{OEt})_2$ ] were prepared by allowing  $\text{IrHCl}_2(\text{P}(\text{Pr}_3)_2)_2$  to react with phosphite in refluxing benzene or toluene. Treatment of  $\text{IrHCl}_2\text{P}_3$ , first with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  and then with an excess of  $\text{ArCH}_2\text{N}_3$ , afforded benzyl azide complexes  $[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{Ar})\text{P}_3]\text{BPh}_4$  (**3**, **4**) [ $\text{Ar} = \text{C}_6\text{H}_5$ ,  $4\text{-CH}_3\text{C}_6\text{H}_4$ ;  $\text{P} = \text{P}(\text{OEt})_3$ ,  $\text{PPh}(\text{OEt})_2$ ]. Azide complexes reacted in  $\text{CH}_2\text{Cl}_2$  solution, leading to the imine derivative  $[\text{IrCl}_2\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_5\}\text{P}_3]\text{BPh}_4$  (**5**). The complexes were characterized by spectroscopy and X-ray crystal structure determination of  $[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{C}_6\text{H}_5)\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$  (**3a**) and  $[\text{IrCl}_2\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_5\}\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$  (**5a**). Both solid-state structure and  $^{15}\text{N}$  NMR data indicate that the azide is coordinated through the substituted  $\text{N}\gamma$  [ $\text{Ir}-\text{N}\gamma(\text{CH}_2\text{Ar})\text{NN}\alpha$ ] nitrogen atom.

## Introduction

Organic azides are interesting starting materials, used to prepare a multitude of organic and inorganic compounds.<sup>1</sup> One important aspect of their reactivity is the easy loss of nitrogen to generate the nitrene  $\text{RN}:$  moieties, which can give rise to a variety of reactions.<sup>1</sup> Transition metal complexes can favor the formation of  $\text{RN}:$ , which can then react with the same metal fragment to yield imido  $[\text{M}]=\text{NR}$  derivatives.<sup>2,3</sup>

In the first step of the interaction between  $\text{RN}_3$  and the metal fragment, organic azide was believed to  $\eta^1$ -coordinate to the metal center, but only in a few cases were the corresponding complexes isolated and characterized.<sup>4–6</sup>

These include Ta(V), V(V), and W(IV) mononuclear complexes containing a bent NNN moiety<sup>4</sup> (**[A]**, Chart 1) and Cu(I), Ag(I), and Pd(II) derivatives, with “linear” organo azide ligand<sup>5</sup> (**[B]**, **[C]**, Chart 1).

A mixed-metallic zirconium(IV)–iridium(III) complex, containing a bridging  $\text{PhNNN}$  group, is also reported<sup>6</sup> (**[D]**, Chart 1). The bent adducts **[A]** and **[D]** are best described as metal complexes containing a “diazonylimido” ligand, whereas in linear complexes the “azide” ligand may coordinate through either terminal  $\text{N}\alpha$  **[C]** or substituted  $\text{N}\gamma$  **[B]** nitrogen atoms.

We are interested in the chemistry of diazo and triazo complexes and have reported the synthesis and reactivity of hydrazine, diazene, diazenido, and triazene complexes of transition metals (Mn and Fe triads) containing phosphites  $\text{P}(\text{OR})_3$  and  $\text{PPh}(\text{OR})_2$  as supporting ligands.<sup>7,8</sup> As the  $d^6$  metal fragment containing these ligands has shown interesting properties in stabilizing azo species<sup>8</sup> such as  $\text{HN}=\text{CH}_2$ ,  $\text{NH}=\text{NH}$ ,  $\text{NH}_2\text{N}=\text{CH}_2$ , etc., we thought of extending our studies to organic azides, to test whether coordination on new metal fragments can take place. The results of a study

\* To whom correspondence should be addressed. E-mail: albertin@unive.it.

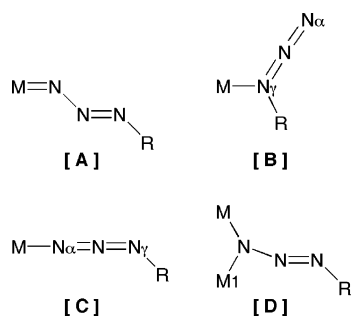
<sup>†</sup> Università Ca' Foscari Venezia.

<sup>‡</sup> Universidade de Vigo.

- (1) (a) *The Chemistry of the Azido Group*; Patai, S., Ed.; Interscience: New York, 1971. (b) *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984.
- (2) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239–482. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (d) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279–293.
- (3) (a) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025–1029. (b) Danopoulos, A. A.; Hay-Motherwell, R. S.; Wilkinson, G.; Cafferkey, S. M.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1997**, 3177–3184. (c) Barloy, L.; Gauvin, R. M.; Osborn, J. A.; Sizun, C.; Graff, R.; Kyritsakas, N. *Eur. J. Inorg. Chem.* **2001**, 1699–1707. (d) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322–323. (e) Heyduk, A. F.; Blackmore, K. J.; Ketterer, N. A.; Ziller, J. W. *Inorg. Chem.* **2005**, *44*, 468–470.

- (4) (a) Fickes, M. G.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6384–6385. (b) Proulx, G.; Bergman, R. G. *Organometallics* **1996**, *15*, 684–692. (c) Guillemot, G.; Solari, E.; Floriani, C.; Rizzoli, C. *Organometallics* **2001**, *20*, 607–615.
- (5) (a) Barz, M.; Herdtweck, E.; Thiel, W. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2262–2265. (b) Dias, H. V. R.; Polach, S. A.; Goh, S.-K.; Archibong, E. F.; Marynick, D. S. *Inorg. Chem.* **2000**, *39*, 3894–3901.
- (6) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 653–655.

Chart 1



on iridium, which allowed the isolation and full characterization of the first  $\eta^1$ -organic azide complexes for this metal, are reported here.

## Experimental Section

**General Comments.** All synthetic work was carried out in an inert atmosphere (Ar) using standard Schlenk techniques or a vacuum atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air but were stored in an inert atmosphere at  $-25\text{ }^\circ\text{C}$ . All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks.  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was a Pressure Chemical Co. product, used as received. Phosphine  $\text{PPh}(\text{OEt})_2$  was prepared by the method of Rabinowitz and Pellon,<sup>9</sup> while  $\text{P}(\text{OEt})_3$  was an Aldrich product purified by distillation under nitrogen. Alkyl<sup>10</sup> and aryl<sup>11</sup> azides were prepared following methods previously reported. The labeled  $\text{C}_6\text{H}_5\text{CH}_2^{15}\text{N}_3$  azide was prepared by following the same method,<sup>10</sup> by reacting  $\text{Na}[^{15}\text{NNN}]$  (98% enriched, CIL) with benzyl bromide,  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ . Equimolar mixtures of  $\text{C}_6\text{H}_5\text{CH}_2^{15}\text{NNN}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{NN}^{15}\text{N}$  were obtained. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer. NMR spectra ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) were obtained on AC200 or Avance 300 Bruker spectrometers at temperatures between  $-90$  and  $+30\text{ }^\circ\text{C}$ , unless otherwise noted.  $^1\text{H}$  and  $^{13}\text{C}$  spectra are referred to internal tetramethylsilane;  $^{31}\text{P}$ - $\{^1\text{H}\}$  chemical shifts are reported with respect to 85%  $\text{H}_3\text{PO}_4$ , while  $^{15}\text{N}$  shifts are with respect to  $\text{CH}_3^{15}\text{NO}_2$ , in both cases with downfield shifts considered positive. The COSY, HMQC, and HMBC NMR experiments were performed using their standard

programs. The iNMR software package<sup>12</sup> was used to treat NMR data. The conductivities of  $10^{-3}\text{ mol dm}^{-3}$  solutions of the complexes in  $\text{CH}_3\text{NO}_2$  at  $25\text{ }^\circ\text{C}$  were measured with a Radiometer CDM 83.

**Synthesis of Complexes.** Hydride complex  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  was prepared by following the reported method.<sup>13</sup>

**$\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  (1) [P =  $\text{P}(\text{OEt})_3$  (a),  $\text{PPh}(\text{OEt})_2$  (b)].** An excess of the appropriate phosphite (1.10 mmol) was added to a solution of  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  (0.15 g, 0.26 mmol) in 10 mL of benzene, and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). Cooling the resulting solution to  $-25\text{ }^\circ\text{C}$  yielded yellow crystals, which slowly separated out and were then filtered and crystallized from ethanol; yield  $\geq 70\%$ .

Anal. Calcd for  $\text{C}_{21}\text{H}_{52}\text{Cl}_2\text{IrO}_6\text{P}_3$  (**1a**): C, 33.33; H, 6.93; Cl, 9.37. Found: C, 33.19; H, 7.05; Cl, 9.18.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ): 4.15 (m, 12 H,  $\text{CH}_2$ ), 2.73 (m, 1 H, CH), 1.34, 1.29 (d, 6 H,  $\text{CH}_3$   $^i\text{Pr}$ ), 1.30, 1.25 (t, 18 H,  $\text{CH}_3$  OEt), ABCX spin syst,  $\delta_X -12.10$ ,  $J_{AX} = 255.0$ ,  $J_{BX} = 19.7$ ,  $J_{CX} = 10.8$  Hz (1 H, IrH).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ): ABC spin syst,  $\delta_A 85.2$ ,  $\delta_B 77.0$ ,  $\delta_C 0.57$ ,  $J_{AB} = 27.6$ ,  $J_{AC} = 27.3$ ,  $J_{BC} = 547.6$  Hz. IR (KBr):  $\nu_{\text{IrH}}$  2081 (m),  $\nu_{\text{IrCl}}$  320 (m)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{29}\text{H}_{52}\text{Cl}_2\text{IrO}_6\text{P}_3$  (**1b**): C, 42.44; H, 6.39; Cl, 8.64. Found: C, 42.69; H, 6.26; Cl, 8.49.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ): 7.92–7.31 (m, 10 H, Ph), 4.10, 3.89, 3.69 (m, 8 H,  $\text{CH}_2$ ), 2.64 (m, 1 H, CH), 1.30, 1.27 (d, 6 H,  $\text{CH}_3$   $^i\text{Pr}$ ), 1.25, 1.23 (t, 12 H,  $\text{CH}_3$  OEt), ABCX spin syst,  $\delta_X -12.41$ ,  $J_{AX} = 221.4$ ,  $J_{BX} = 467.3$ ,  $J_{CX} = 11.1$  Hz (1 H, IrH).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ): ABC spin syst,  $\delta_A 102.7$ ,  $\delta_B 98.0$ ,  $\delta_C 2.51$ ,  $J_{AB} = 17.7$ ,  $J_{AC} = 23.0$ ,  $J_{BC} = 467.3$  Hz. IR (KBr):  $\nu_{\text{IrH}}$  2126 (m),  $\nu_{\text{IrCl}}$  322 (m)  $\text{cm}^{-1}$ .

**$\text{IrHCl}_2\text{P}_3$  (2) [P =  $\text{P}(\text{OEt})_3$  (a),  $\text{PPh}(\text{OEt})_2$  (b)].** An excess of the appropriate phosphite (2.20 mmol) was added to a solution of  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  (0.30 g, 0.52 mmol) in 20 mL of toluene, and the reaction mixture was refluxed for 4 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (4 mL). Cooling the resulting solution to  $-25\text{ }^\circ\text{C}$  yielded yellow crystals, which slowly separated out in 1–2 days and were then collected and dried under vacuum; yield  $\geq 70\%$ .

Anal. Calcd for  $\text{C}_{18}\text{H}_{46}\text{Cl}_2\text{IrO}_6\text{P}_3$  (**2a**): C, 28.35; H, 6.08; Cl, 9.30. Found: C, 28.17; H, 6.15; Cl, 9.11.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ): 4.15 (m, 18 H,  $\text{CH}_2$ ), 1.24, 1.21 (t, 27 H,  $\text{CH}_3$ ),  $\text{AB}_2\text{X}$  spin syst,  $\delta_X -11.67$ ,  $J_{AX} = 366$ ,  $J_{BX} = 24$  Hz (1 H, IrH).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ):  $\text{AB}_2$  spin syst,  $\delta_A 84.8$ ,  $\delta_B 76.0$ ,  $J_{AB} = 53.0$  Hz. IR (KBr):  $\nu_{\text{IrH}}$  2051 (m),  $\nu_{\text{IrCl}}$  318 (m)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{30}\text{H}_{46}\text{Cl}_2\text{IrO}_6\text{P}_3$  (**2b**): C, 41.96; H, 5.40; Cl, 8.26. Found: C, 42.09; H, 5.28; Cl, 8.34.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ): 7.70, 7.36 (m, 15 H, Ph), 4.08, 3.90, 3.70 (m, 12 H,  $\text{CH}_2$ ), 1.26, 1.22 (t, 18 H,  $\text{CH}_3$ ),  $\text{AB}_2\text{X}$  spin syst,  $\delta_X -11.78$ ,  $J_{AX} = 318$ ,  $J_{BX} = 24$  Hz (1 H, IrH).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^\circ\text{C}$ ) ( $\delta$ ):  $\text{AB}_2$  spin syst,  $\delta_A 102.9$ ,  $\delta_B 97.9$ ,  $J_{AB} = 34.0$  Hz. IR (KBr):  $\nu_{\text{IrH}}$  2062 (m),  $\nu_{\text{IrCl}}$  323 (m)  $\text{cm}^{-1}$ .

**$[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{Ar})\text{P}_3]\text{BPh}_4$  (3, 4) [Ar =  $\text{C}_6\text{H}_5$  (3),  $4\text{-CH}_3\text{C}_6\text{H}_4$  (4); P =  $\text{P}(\text{OEt})_3$  (a),  $\text{PPh}(\text{OEt})_2$  (b)].** An equimolar amount of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.12 mmol, 17  $\mu\text{L}$  of a 54% solution in diethyl ether) was added to a solution of hydride  $\text{IrHCl}_2\text{P}_3$  (0.12 mmol) in 8 mL of dichloromethane cooled to  $-196\text{ }^\circ\text{C}$ . The reaction mixture was left to reach room temperature and stirred for 1 h, and then an

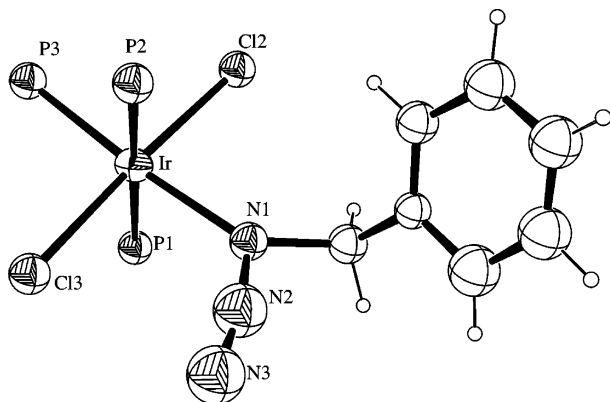
- (7) (a) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Busatto, F.; Pelizzi, G. *Inorg. Chem.* **1997**, *36*, 1296–1305. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergamo, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479–489. (c) Albertin, G.; Antoniutti, S.; Bacchi, A.; Barbera, D.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1998**, *37*, 5602–5610. (d) Albertin, G.; Antoniutti, S.; Bordignon, E.; Menegazzo, F. *J. Chem. Soc., Dalton Trans.* **2000**, 1181–1189. (e) Albertin, G.; Antoniutti, S.; Bacchi, A.; Ballico, G. B.; Bordignon, E.; Pelizzi, G.; Ranieri, M.; Ugo, P. *Inorg. Chem.* **2000**, *39*, 3265–3279. (f) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Miani, F.; Pelizzi, G. *Inorg. Chem.* **2000**, *39*, 3283–3293. (g) Albertin, G.; Antoniutti, S.; Bortoluzzi, M.; Castro-Fojo, J.; Garcia-Fontán, S. *Inorg. Chem.* **2004**, *43*, 4511–4522. (h) Albertin, G.; Antoniutti, S.; Bedin, M.; Castro, J.; Garcia-Fontán, S. *Inorg. Chem.* **2006**, *45*, 3816–3825.
- (8) (a) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Giorgi, M. T.; Pelizzi, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2192–2194. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; De Marchi, F.; Pelizzi, G. *Inorg. Chem.* **2005**, *44*, 8947–8954. (c) Albertin, G.; Antoniutti, S.; Bordignon, E.; Carrera, B. *Inorg. Chem.* **2000**, *39*, 4646–4650. (d) Albertin, G.; Antoniutti, S.; Bacchi, A.; Boato, M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **2002**, 3313–3320. (e) Albertin, G.; Antoniutti, S.; Giorgi, M. T. *Eur. J. Inorg. Chem.* **2003**, 2855–2866.
- (9) Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623–4626.

(10) Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413–414.

(11) Lindsay, R. O.; Allen, C. F. H. *Org. Synth.* **1955**, *3*, 710–711.

(12) Balacco, G. <http://www.inmr.net/>.

(13) Simpson, R. D.; Marshall, W. J.; Farischon, A. A.; Roe, D. C.; Grushin, V. V. *Inorg. Chem.* **1999**, *38*, 4171–4173.



**Figure 1.** Perspective view of the cation  $[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{C}_6\text{H}_5)\text{-}\{\text{P}(\text{OEt})_3\}_3]^+$  (**3a**<sup>+</sup>). Thermal ellipsoids are at 20% probability level. Ethoxy groups of phosphite ligands are omitted.

excess of the appropriate azide  $\text{RN}_3$  (0.36 mmol) was added. The solution was stirred for 3 h and the solvent removed under reduced pressure. The resulting oil was triturated with ethanol (3 mL) containing an excess of  $\text{NaBPh}_4$  (0.24 mmol, 82 mg). Cooling the solution to  $-25^\circ\text{C}$  gave a pale yellow solid, which was filtered out and crystallized from  $\text{CH}_2\text{Cl}_2$  and ethanol; yield  $\geq 75\%$ .

Anal. Calcd for  $\text{C}_{49}\text{H}_{72}\text{BCl}_2\text{IrN}_3\text{O}_9\text{P}_3$  (**3a**): C, 48.48; H, 5.98; Cl, 5.84; N, 3.46. Found: C, 48.31; H, 6.06; Cl, 5.70; N, 3.59.  $\Lambda_{\text{M}} = 52.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 7.46–6.86 (m, 25 H, Ph), 4.69 (s, 2 H,  $\text{CH}_2$  benzyl), 4.32 (qnt), 4.23 (m) (18 H,  $\text{CH}_2$  phos), 1.37, 1.33 (t, 27 H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{B}$  spin syst,  $\delta_{\text{A}}$  53.1,  $\delta_{\text{B}}$  25.7,  $J_{\text{AB}} = 37.5$  Hz. IR (KBr):  $\nu_{\text{N}_3}$  2143 (m),  $\nu_{\text{IrCl}}$  348 (m)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{61}\text{H}_{72}\text{BCl}_2\text{IrN}_3\text{O}_6\text{P}_3$  (**3b**): C, 55.92; H, 5.54; Cl, 5.41; N, 3.21. Found: C, 55.76; H, 5.63; Cl, 5.28; N, 3.12.  $\Lambda_{\text{M}} = 50.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 7.74–6.86 (m, 40 H, Ph), 4.32 (s, 2 H,  $\text{CH}_2$  benzyl), 4.24–3.85 (m, 12 H,  $\text{CH}_2$  phos), 1.34, 1.29, 1.21 (t, 18 H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{B}$  spin syst,  $\delta_{\text{A}}$  80.4,  $\delta_{\text{B}}$  59.3,  $J_{\text{AB}} = 25.1$  Hz. IR (KBr):  $\nu_{\text{N}_3}$  2148 (m),  $\nu_{\text{IrCl}}$  337 (m)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{50}\text{H}_{74}\text{BCl}_2\text{IrN}_3\text{O}_9\text{P}_3$  (**4a**): C, 48.90; H, 6.07; Cl, 5.77; N, 3.42. Found: C, 48.75; H, 6.00; Cl, 5.91; N, 3.34.  $\Lambda_{\text{M}} = 54.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 7.35–6.88 (m, 24 H, Ph), 4.67 (s, 2 H,  $\text{CH}_2$  benzyl), 4.35 (qnt), 4.25 (m) (18 H,  $\text{CH}_2$  phos), 2.41 (s, 3 H,  $\text{CH}_3$  *p*-tolyl), 1.38, 1.35, 1.32 (t, 27 H,  $\text{CH}_3$  phos).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{B}$  spin syst,  $\delta_{\text{A}}$  53.1,  $\delta_{\text{B}}$  25.8,  $J_{\text{AB}} = 37.0$  Hz. IR (KBr):  $\nu_{\text{N}_3}$  2150 (m),  $\nu_{\text{IrCl}}$  346 (m)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{62}\text{H}_{74}\text{BCl}_2\text{IrN}_3\text{O}_6\text{P}_3$  (**4b**): C, 56.24; H, 5.63; Cl, 5.35; N, 3.17. Found: C, 56.37; H, 5.51; Cl, 5.49; N, 3.03.  $\Lambda_{\text{M}} = 51.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 7.71–6.85 (m, 39 H, Ph), 4.27 (s, 2 H,  $\text{CH}_2$  benzyl), 4.25–3.80 (m, 12 H,  $\text{CH}_2$  phos), 2.38 (s, 3 H,  $\text{CH}_3$  *p*-tolyl), 1.33, 1.28, 1.26 (t, 18 H,  $\text{CH}_3$  phos).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{B}$  spin syst,  $\delta_{\text{A}}$  80.4,  $\delta_{\text{B}}$  59.5,  $J_{\text{AB}} = 24.9$  Hz. IR (KBr):  $\nu_{\text{N}_3}$  2147 (m)  $\text{cm}^{-1}$ .

**$[\text{IrCl}_2(\eta^1\text{-}^{15}\text{N}_3\text{CH}_2\text{C}_6\text{H}_5)\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$  (**3b**<sub>1</sub>).** This complex was prepared exactly like the related unlabeled compound **3b**, using  $\text{C}_6\text{H}_5\text{CH}_2\text{N}_3$  as a reagent; yield  $\geq 70\%$ .

$^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 7.75–6.87 (m, 40 H, Ph), 4.33 (s, 2 H,  $\text{CH}_2$  benzyl), 4.25–3.80 (m, 12 H,  $\text{CH}_2$  phos), 1.34, 1.28, 1.21 (t, 18 H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{BX}$  spin syst ( $\text{X} = ^{15}\text{N}$ ),  $\delta_{\text{A}}$  80.4,  $\delta_{\text{B}}$  59.4,  $J_{\text{AB}} = 25.1$ ,  $J_{\text{AX}} = 3.0$ ,  $J_{\text{BX}} = 54.5$  Hz.  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $-139.6$  (s,  $^{15}\text{N}\alpha$ ),  $-333.2$  (d,  $^{15}\text{N}\gamma$ ),  $J_{^{15}\text{N}^{31}\text{P}} < 1$ ,  $J_{^{15}\text{N}^{31}\text{P}} = 55.0$  Hz. IR (KBr):  $\nu_{^{15}\text{N}_3}$  2126 (m)  $\text{cm}^{-1}$ .

**$[\text{IrCl}_2\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_5\}_3]\text{BPh}_4$  (**5**)** [**P** = **P**(**OEt**)<sub>3</sub> (**a**), **PPh**(**OEt**)<sub>2</sub> (**b**)]. A solution of compound  $[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{C}_6\text{H}_5)\text{P}_3]\text{BPh}_4$  (**3**) (0.1 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$  was stirred at room temperature in the presence of daylight for about 48 h. The solvent was removed under reduced pressure, to give an oil which was triturated with ethanol (3 mL). A white solid slowly separated out from the resulting solution, which was filtered out and crystallized from ethanol; yield  $\geq 55\%$ .

Anal. Calcd for  $\text{C}_{49}\text{H}_{72}\text{BCl}_2\text{IrNO}_9\text{P}_3$  (**5a**): C, 49.63; H, 6.12; Cl, 5.98; N, 1.18. Found: C, 49.49; H, 6.18; Cl, 5.87; N, 1.12.  $\Lambda_{\text{M}} = 52.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 9.8 (d, br,  $J_{\text{HH}} = 21.8$  Hz, 1 H, NH), 8.83 (dd,  $J_{\text{HH}} = 21.8$ ,  $J_{\text{HPA}} < 1$ ,  $J_{\text{HPB}} = 6.8$  Hz, 1 H, =CH), 7.72–6.87 (m, 25 H, Ph), 4.32 (qnt), 4.21 (m) (18 H,  $\text{CH}_2$ ), 1.31, 1.24 (t, 27 H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{B}$  spin syst,  $\delta_{\text{A}}$  50.3,  $\delta_{\text{B}}$  41.0,  $J_{\text{AB}} = 37.7$  Hz.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 171.4 (s, =CH), 165–122 (m, Ph), 66.0 (d), 64.9 (m) ( $\text{CH}_2$ ), 16.1 (m,  $\text{CH}_3$ ). IR (KBr):  $\nu_{\text{NH}}$  3260 (w)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{61}\text{H}_{72}\text{BCl}_2\text{IrNO}_9\text{P}_3$  (**5b**): C, 57.15; H, 5.66; Cl, 5.53; N, 1.09. Found: C, 56.97; H, 5.74; Cl, 5.70; N, 1.03.  $\Lambda_{\text{M}} = 53.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 9.0 (d, br,  $J_{\text{HH}} = 21.6$  Hz, 1 H, NH), 8.05 (ddm,  $J_{\text{HH}} = 21.6$ ,  $J_{\text{HPA}} = 1.6$ ,  $J_{\text{HPB}} = 5.5$  Hz, 1 H, =CH), 7.80–6.86 (m, 40 H, Ph), 4.20–3.80 (m, 12 H,  $\text{CH}_2$ ), 1.32, 1.28, 1.27 (t, 18 H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{B}$  spin syst,  $\delta_{\text{A}}$  78.9,  $\delta_{\text{B}}$  70.8,  $J_{\text{AB}} = 26.9$  Hz.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 170.6 (s, =CH), 164–122 (m, Ph), 65.5 (m,  $\text{CH}_2$ ), 16.3 (m,  $\text{CH}_3$ ). IR (KBr):  $\nu_{\text{NH}}$  3255 (w),  $\nu_{\text{IrCl}}$  318 (m)  $\text{cm}^{-1}$ .

**$[\text{IrCl}_2\{\eta^1\text{-}^{15}\text{NH}=\text{C}(\text{H})\text{C}_6\text{H}_5\}_3]\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$  (**5b**<sub>1</sub>).** This complex was prepared exactly like the related unlabeled compound **5b**, starting from the precursor  $[\text{IrCl}_2(\text{C}_6\text{H}_5\text{CH}_2\text{N}_3)\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$  (**3b**<sub>1</sub>); yield  $\geq 55\%$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ): 9.00 (ddm,  $J_{^{15}\text{N}\text{H}} = 73.5$ ,  $J_{\text{HH}} = 21.6$  Hz, 1 H, NH), 8.05 (ddm,  $J_{\text{HH}} = 21.6$ ,  $J_{\text{HPA}} = 1.6$ ,  $J_{\text{HPB}} = 5.5$  Hz, 1 H, =CH), 7.82–6.86 (m, 40 H, Ph), 4.20–3.82 (m, 12 H,  $\text{CH}_2$ ), 1.32, 1.29, 1.27 (t, 18 H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{BX}$  spin syst ( $\text{X} = ^{15}\text{N}$ ),  $\delta_{\text{A}}$  79.0,  $\delta_{\text{B}}$  70.9,  $J_{\text{AB}} = 26.9$ ,  $J_{\text{AX}} = 1.5$ ,  $J_{\text{BX}} = 61.7$  Hz.  $^{15}\text{N NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) ( $\delta$ ):  $\text{A}_2\text{BXY}$  spin syst ( $\text{X} = ^{15}\text{N}$ ,  $\text{Y} = ^1\text{H}$ ),  $\delta_{\text{X}} = -179.6$ ,  $J_{\text{AX}} = 1.5$ ,  $J_{\text{BX}} = 61.7$ ,  $J_{\text{AY}} = 1.0$ ,  $J_{\text{BY}} = 0.1$ ,  $J_{\text{XY}} = 73.5$  Hz. IR (KBr):  $\nu_{\text{NH}}$  3243 (w)  $\text{cm}^{-1}$ .

**X-ray Crystal Structure Determination for  $[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{C}_6\text{H}_5)\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$  (**3a**) and  $[\text{IrCl}_2\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_5\}_3]\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$  (**5a**).** Data were collected on a Siemens Smart CCD area-detector diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation. Absorption correction was made using SADABS.<sup>14</sup>

Crystallographic calculations were performed with the Oscale program.<sup>15</sup> Structures were solved by Patterson methods and refined by a full-matrix least-squares method on the basis of  $F^2$ .<sup>16</sup>

For **3a**, due the poor quality of the crystal data [ $R(\sigma) > 45\%$ ], non-hydrogen atoms were refined with isotropic displacement parameters, and only the iridium atom was refined with anisotropical parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters (except those of a very disordered ethyl, which were not included in the model).

For **5a**, non-hydrogen atoms were refined with anisotropical parameters. Hydrogen atoms were included in idealized positions

(14) Sheldrick, G. M. *SADABS. An empirical absorption correction program for area detector data*; University of Göttingen: Göttingen, Germany, 1996.

(15) McArdle, P. J. *Appl. Crystallogr.* **1995**, *28*, 65.

(16) Sheldrick, G. M. *SHELX-97. Program for the solution and refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.



**Table 1.** Crystal and Structure Refinement Data for  $[\text{IrCl}_2(\eta^1\text{-N}_3\text{CH}_2\text{C}_6\text{H}_5)\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$  (**3a**)

empirical formula	$\text{C}_{49}\text{H}_{67}\text{BCl}_2\text{IrN}_3\text{O}_9\text{P}_3$
fw	1208.88
temp	293(2) K
wavelength	0.710 73 Å
cryst system, space group	monoclinic, $C2/c$
unit cell dimens	$a = 37.896(7)$ Å $b = 12.615(2)$ Å $c = 26.290(5)$ Å $\beta = 111.960(3)^\circ$
$V$	$11656(4)$ Å <sup>3</sup>
$Z$	8
$D(\text{calcd})$	$1.378$ Mg/m <sup>3</sup>
abs coeff	$2.515$ mm <sup>-1</sup>
$F(000)$	4920
cryst size	$0.29 \times 0.28 \times 0.12$ mm
$\theta$ range for data collcn	$1.64\text{--}28.17^\circ$
index ranges	$-50 \leq h \leq 47$ ; $-16 \leq k \leq 16$ ; $-20 \leq l \leq 34$
reflcs collcd	27 602
indpdnt reflns	12 376 [R(int) = 0.1648]
reflcs obsd ( $>2\sigma$ )	2918
data completeness	0.864
abs corr	semiempirical from equivalents
max and min transm	1.000 and 0.409
refinement method	full-matrix least squares on $F^2$
data/restraints/params	12 376/24/242
goodness-of-fit on $F^2$	0.808
final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0875$ , $wR_2 = 0.1784$
R indices (all data)	$R_1 = 0.3238$ , $wR_2 = 0.2307$
largest diff peak and hole	$1.218$ and $-0.704$ e Å <sup>-3</sup>

and refined with isotropic displacement parameters (except those bonded to the nitrogen and carbon of the imine moiety, which were found on the density map and refined with isotropical parameters).

Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref 17. Details of crystal data and structural refinement are given in Tables 1 (**3a**) and 2 (**5a**).

## Results and Discussion

**Preparation of Hydride Precursors.** Phosphite-containing Ir(III) hydride complexes of types  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  (**1**) and  $\text{IrHCl}_2\text{P}_3$  (**2**) were prepared by reacting  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  species with phosphites (P), as shown in Scheme 1.

Treatment of  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  with  $\text{P}(\text{OEt})_3$  or  $\text{PPh}(\text{OEt})_2$  in refluxing benzene gave the mixed-ligand  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  (**1**) hydride complexes, which further reacted with phosphites in toluene, yielding  $\text{IrHCl}_2\text{P}_3$  (**2**) as final product. Tris-(phosphite) complexes **2** could also be obtained in good yields by reacting the  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  precursor with  $\text{P}(\text{OEt})_3$  or  $\text{PPh}(\text{OEt})_2$  in refluxing toluene. Although iridium forms a large number of hydride complexes, those with phosphites are rare,<sup>18</sup> and none has been reported with the  $\text{P}(\text{OEt})_3$  ligand.<sup>19</sup>

New hydrides **1** and **2** are yellow solids stable in air and in solution of common organic solvents, where they behave as nonelectrolytes. Analytical and spectroscopic (IR, NMR) data support the proposed formulation.

**Table 2.** Crystal and Structure Refinement Data for  $[\text{IrCl}_2\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_5\}\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$  (**5a**)

empirical formula	$\text{C}_{49}\text{H}_{72}\text{BCl}_2\text{IrNO}_9\text{P}_3$
fw	1185.90
temp	173(2) K
wavelength	0.710 73 Å
cryst system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 13.3658(16)$ Å $b = 14.0824(17)$ Å $c = 14.7739(18)$ Å $\alpha = 86.169(2)^\circ$ $\beta = 81.073(2)^\circ$ $\gamma = 87.926(2)^\circ$
$V$	$2740.0(6)$ Å <sup>3</sup>
$Z$	2
$D(\text{calcd})$	$1.437$ Mg/m <sup>3</sup>
abs coeff	$2.672$ mm <sup>-1</sup>
$F(000)$	1212
cryst size	$0.37 \times 0.35 \times 0.12$ mm
$\theta$ range for data collcn	$1.45\text{--}27.96^\circ$
index ranges	$-17 \leq h \leq 17$ ; $-11 \leq k \leq 18$ ; $-17 \leq l \leq 19$
reflcs collcd	17 842
indpdnt reflns	12 462 [R(int) = 0.0365]
reflcs obsd ( $>2\sigma$ )	9727
data completeness	0.945
abs corr	semiempirical from equivalents
max and min transm	1.000 and 0.696
refinement method	full-matrix least squares on $F^2$
data/restraints/params	12 462/0/612
goodness-of-fit on $F^2$	1.012
final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0442$ , $wR_2 = 0.1035$
R indices (all data)	$R_1 = 0.0647$ , $wR_2 = 0.1147$
largest diff peak and hole	$2.032$ and $-1.668$ e Å <sup>-3</sup>

The IR spectra of **1** and **2** show one medium-intensity band at  $2126\text{--}2051$  cm<sup>-1</sup>, attributed to the  $\nu_{\text{IrH}}$  of the hydride ligand; in the far IR region, only one  $\nu_{\text{IrCl}}$  absorption at  $323\text{--}318$  cm<sup>-1</sup> was observed, indicating the mutually trans position of the two chloride ligands. The <sup>1</sup>H NMR spectra confirmed the presence of the hydride showing a rather complicated multiplet between  $-11.67$  and  $-12.41$  ppm. As the <sup>31</sup>P{<sup>1</sup>H} NMR spectra were either ABC multiplets, for complexes  $\text{IrHCl}_2(\text{P}^i\text{Pr}_3)_2$  (**1**), or AB<sub>2</sub> ones, for  $\text{IrHCl}_2\text{P}_3$  (**2**), the hydride pattern was simulated with an ABCX or an AB<sub>2</sub>X (X = <sup>1</sup>H) model, respectively, with the parameters reported in the Experimental Section. On the basis of these data, a mer-trans geometry of types **I** and **II** (Scheme 1) is proposed for Ir(III) hydride derivatives **1** and **2**.

Protonation of new hydrides **1** and **2** with Brønsted acid at low temperature ( $-80$  °C) proceeded with the evolution of H<sub>2</sub> and the formation of either pentacoordinate  $[\text{IrCl}_2(\text{P}^i\text{Pr}_3)_2]^+$  and  $[\text{IrCl}_2\text{P}_3]^+$  cations or neutral  $\text{Ir}(\text{Y})\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$  and  $\text{Ir}(\text{Y})\text{Cl}_2\text{P}_3$  compounds (Scheme 2), which were stable in solution but which decomposed on attempts at separating them in the solid state.

The addition at  $-80$  °C of an equimolar amount of Brønsted acid HY to a solution of complexes **1** and **2** in an NMR tube caused the disappearance of the hydride resonance near  $-12$  ppm and the appearance of a slightly broad signal at 4.6 ppm, which decreased on shaking and was attributed<sup>20</sup> to free H<sub>2</sub>. No new signals attributable to a  $\eta^2\text{-H}_2$  complex<sup>21</sup>

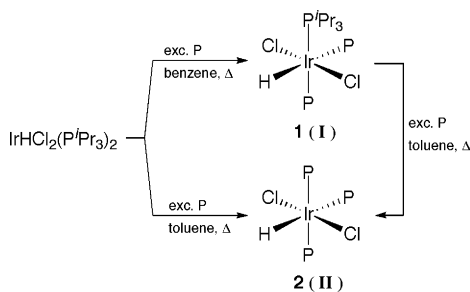
(17) *International Tables for X-ray Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol C.

(18) Couch, D. A.; Robinson, S. D.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1974**, 1309–1313.

(19) For hydride complexes, see: Muetterties, E. L. *Transition Metal Hydrides*; M. Dekker: New York, 1971. Dedieu, A. *Transition Metal Hydrides*; Wiley-VCH: New York, 1992. Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077–2091. Peruzzini, M.; Poli, R. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001.

(20) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037.

(21) Kubas, G. J. *Metal Dihydrogen and  $\sigma$ -Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001.

Scheme 1<sup>a</sup>

<sup>a</sup> Key: P = P(OEt)<sub>3</sub> (a), PPh(OEt)<sub>2</sub> (b).

formed by protonation were observed in the spectra, according to the reaction shown in Scheme 2.

**Benzyl Azide Complexes.** The unsaturated complexes formed by protonation of hydrides IrHCl<sub>2</sub>P<sub>3</sub> (2) with HBF<sub>4</sub>·Et<sub>2</sub>O react with ArCH<sub>2</sub>N<sub>3</sub> to give azide cations [IrCl<sub>2</sub>(η<sup>1</sup>-N<sub>3</sub>CH<sub>2</sub>Ar)P<sub>3</sub>]<sup>+</sup> (3, 4), which were separated as BPh<sub>4</sub> salts and characterized (Scheme 3).

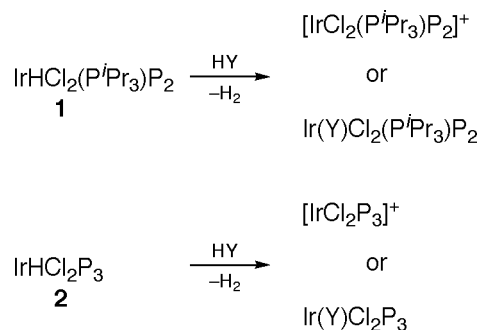
Instead, the mixed-ligand hydrides IrHCl<sub>2</sub>(P'Pr<sub>3</sub>)<sub>2</sub> (1) did not give the related azide complexes after treatment with HBF<sub>4</sub>·Et<sub>2</sub>O and excess of organic azide. Similarly, other hydrides, such as IrHCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>22</sup> and IrHCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>P<sup>7d</sup> also prevented synthesis of azide complexes, and it seems that only the IrCl<sub>2</sub>P<sub>3</sub> fragment containing exclusively phosphite ligands is able to stabilize [Ir]-η<sup>1</sup>-N<sub>3</sub>CH<sub>2</sub>Ar species. However, isolable azide complexes were obtained only with aliphatic azides ArCH<sub>2</sub>N<sub>3</sub>, as C<sub>6</sub>H<sub>5</sub>N<sub>3</sub> does not give any complexes with the IrCl<sub>2</sub>P<sub>3</sub> fragment.

Azide complexes [IrCl<sub>2</sub>(η<sup>1</sup>-N<sub>3</sub>CH<sub>2</sub>Ar)P<sub>3</sub>]BPh<sub>4</sub> (3, 4) are white solids, very stable in air but slightly unstable in solution of polar organic solvents, where they behave as 1:1 electrolytes.<sup>23</sup> Analytical and spectroscopic data (IR, <sup>1</sup>H, <sup>31</sup>P, <sup>15</sup>N NMR) support the proposed formulation, and the coordination of the azide was proven by the X-ray structure determination of [IrCl<sub>2</sub>(η<sup>1</sup>-N<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>){P(OEt)<sub>3</sub>}<sub>3</sub>]BPh<sub>4</sub> (3a) (Figure 1).

The X-ray study was carried out with the best crystal obtained after several attempts. Unfortunately, as its quality did not allow good refinement, the resulting geometric parameters were imprecise. However, the connectivity of the atoms demonstrated the η<sup>1</sup>-coordination mode of the azide. The asymmetric unit contains both an anion BPh<sub>4</sub><sup>-</sup> and a cation complex, in which the iridium(III) atom is coordinated by the γ-nitrogen atom of the azide, two trans chloride atoms, and three mer phosphorus atoms of three triethoxyphosphite ligands. In view of the inexactness of the data, the values obtained for bond distances and angles are within expected values for octahedral Ir(III) complexes, and the Ir-P bond lengths also show the different trans influence of the azide ligand. The latter shows N-N bond lengths short enough to fit the η<sup>1</sup>-diazoamino coordination mode [B] (Chart 1) and the N-N-N angle is essentially linear.

(22) (a) Park, S.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 3001. (b) Albertin, G.; Antoniutti, S.; Bordignon, E.; Menegazzo, F. *J. Chem. Soc., Dalton Trans.* **2000**, 1181–1189.

(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

Scheme 2<sup>a</sup>

<sup>a</sup> Key: P = P(OEt)<sub>3</sub> or PPh(OEt)<sub>2</sub>; HY = HBF<sub>4</sub> or CF<sub>3</sub>SO<sub>3</sub>H.

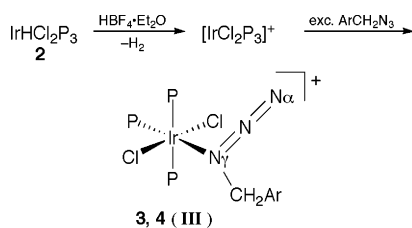
The bonding mode [B] for the azide in 3 and 4 is unexpected, as many of the known examples of azide complexes show a diazenylimido coordination mode [A]<sup>4–6</sup> or a terminal Nα azide ligand [C]<sup>5b</sup> (Chart 1). Only one example of Nγ coordination [B] has been reported, in the silver HB[3,5-(CF<sub>3</sub>)<sub>2</sub>Pz]<sub>3</sub>AgN(1-Ad)NN (Pz = pyrazolyl; 1-Ad = adamantyl) derivative,<sup>5b</sup> the Nγ coordination observed in chelate Pd and Cu complexes<sup>5a</sup> is most probably influenced by the formation of a six-membered metallacycle. Instead, the coordination through the substituted Nγ is favored by the greater basicity of this site<sup>24</sup> and should be the more common type of azide complexes, with linear “NNN” geometry. The terminal Nα coordination observed in the HB[3,5-(CF<sub>3</sub>)<sub>2</sub>Pz]<sub>3</sub>CuNNN(1-Ad) complex was attributed, by theoretical calculations,<sup>5b</sup> to Cu(I), which exhibits “enough π-donating ability to favor binding through the terminal nitrogen”. Conversely, the bent “NNN” coordination mode [A] observed in Ta, V, and W complexes involves rearrangement of the RN<sub>3</sub> group and cannot be considered an azide adduct but rather a diazenylimido ligand of a metal complex in a higher oxidation state. This coordination mode probably occurs in a metal complex able to undergo 2 e<sup>-</sup> oxidation, whereas in the other cases a η<sup>1</sup>-diazoamino species [B] is favored. It is worth noting that organic azide complexes are probably involved as intermediates in the metal-catalyzed cycloaddition of alkyne and organic azides yielding triazoles,<sup>25</sup> and information on the coordination chemistry of RN<sub>3</sub> can help to understand the mechanism of the reaction and to find new catalysts.

The IR spectra of azide complexes 3 and 4 show a medium-intensity band at 2143–2148 cm<sup>-1</sup>, attributed to the ν<sub>N<sub>3</sub></sub> of the coordinated azide ligand. Support for this attribution came from the spectra of the labeled compound [IrCl<sub>2</sub>(η<sup>1</sup>-<sup>15</sup>N<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>){PPh(OEt)<sub>2</sub>}<sub>3</sub>]BPh<sub>4</sub> (3b<sub>1</sub>), which shows ν<sup>15</sup>N<sub>3</sub> (2126 cm<sup>-1</sup>) shifted to a lower wavenumber<sup>26</sup> by 22 cm<sup>-1</sup>. The high values of ν<sub>N<sub>3</sub></sub> of our complexes fit the η<sup>1</sup>-diazoamino coordination mode [B] of the azide ligand.

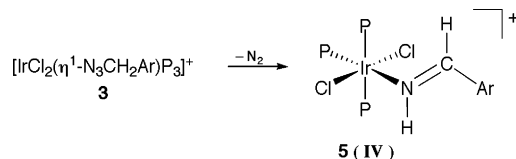
(24) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926. (b) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221–7230.

(25) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599. (b) Zhang, L.; Chen, X.; Xue, P.; Sun, H. H. Y.; Williams, I. D.; Sharpless, K. B.; Fokin, V. V.; Jia, G. *J. Am. Chem. Soc.* **2005**, *127*, 15998–15999.

(26) For the labeled complex [IrCl<sub>2</sub>(η<sup>1</sup>-<sup>15</sup>N<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>){PPh(OEt)<sub>2</sub>}<sub>3</sub>]BPh<sub>4</sub> (3b<sub>1</sub>), a value of 2112 cm<sup>-1</sup> was calculated for ν<sup>15</sup>N<sub>3</sub>.

Scheme 3<sup>a</sup>

<sup>a</sup> Key: Ar = C<sub>6</sub>H<sub>5</sub> (3), 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (4); P = P(OEt)<sub>3</sub> (a), PPh(OEt)<sub>2</sub> (b).

Scheme 4<sup>a</sup>

<sup>a</sup> Key: Ar = C<sub>6</sub>H<sub>5</sub>; P = P(OEt)<sub>3</sub> (a), PPh(OEt)<sub>2</sub> (b).

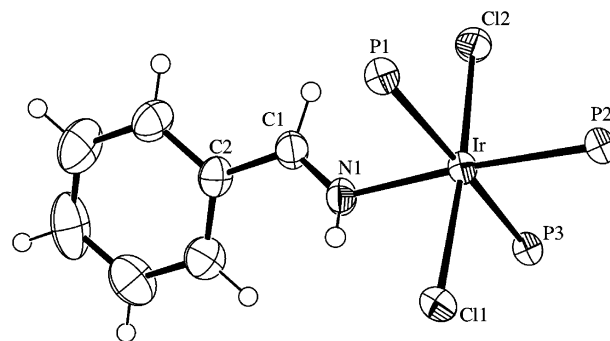
In the far IR region, the spectra of **3** and **4** show only one  $\nu_{\text{IrCl}}$  band, at 337–348 cm<sup>-1</sup>, fitting the mutually trans position of the two chloride ligands. In the temperature range between +20 and -80 °C, the <sup>31</sup>P NMR spectra of **3** and **4** are A<sub>2</sub>B multiplets, indicating that two phosphites are magnetically equivalent and different from the third. A mer-trans geometry (III), like that observed in the solid state, may therefore be proposed for azide complexes **3** and **4**.

The <sup>15</sup>N NMR spectrum of the labeled complex [IrCl<sub>2</sub>(η<sup>1-15</sup>N<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>){PPh(OEt)<sub>2</sub>]<sub>3</sub>BPh<sub>4</sub> (**3b**<sub>1</sub>) may be used as a diagnostic tool for the coordinate azide molecule. A singlet at -139.6 ppm and a doublet<sup>27</sup> at -333.2 ppm, with *J*<sup>15N<sup>31</sup>P</sup> of 55.0 Hz, were observed in the spectrum and attributed to the N<sub>α</sub> and N<sub>γ</sub> nuclei, respectively, of the coordinated C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub><sup>15</sup>N<sub>3</sub> group.

Complexes [IrCl<sub>2</sub>(η<sup>1</sup>-N<sub>3</sub>CH<sub>2</sub>Ar)P<sub>3</sub>]BPh<sub>4</sub> (**3**, **4**) are stable as solids but react slowly in solution to give a new species, characterized as the imine complex [IrCl<sub>2</sub>{η<sup>1</sup>-NH=C(H)-C<sub>6</sub>H<sub>5</sub>}P<sub>3</sub>]BPh<sub>4</sub> (**5**) (Scheme 4). Extrusion of N<sub>2</sub> in coordinate azide **3**, followed by a 1,2-shift of one hydrogen atom, may lead to the formation of imine derivatives **5**.

This reaction is important because it allows the synthesis of the first example, to the best of our knowledge, of N-protio imine complexes of iridium.<sup>28</sup>

Good analytical data were obtained for imine complexes **5**, which are white solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.<sup>23</sup> The IR spectra of **5** show a weak-intensity band at 3255–3260 cm<sup>-1</sup>, due to the  $\nu_{\text{NH}}$  of the imine, and one  $\nu_{\text{IrCl}}$



**Figure 2.** Perspective view of the cation [IrCl<sub>2</sub>{η<sup>1</sup>-NH=C(H)C<sub>6</sub>H<sub>5</sub>}-{P(OEt)<sub>3</sub>}]<sup>+</sup> (**5a**<sup>+</sup>). Thermal ellipsoids are at 30% probability level. Ethoxy groups of phosphite ligands are omitted.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **5a**

Ir–N(1)	2.130(4)	Ir–P(2)	2.2598(12)
Ir–P(3)	2.3377(14)	Ir–P(1)	2.3390(14)
Ir–Cl(1)	2.3613(12)	Ir–Cl(2)	2.3731(12)
N(1)–C(1)	1.260(6)		
N(1)–Ir–P(2)	175.26(13)	N(1)–Ir–P(3)	87.63(13)
P(2)–Ir–P(3)	92.04(5)	N(1)–Ir–P(1)	89.30(13)
P(2)–Ir–P(1)	91.13(5)	P(3)–Ir–P(1)	176.66(4)
N(1)–Ir–Cl(1)	86.59(13)	P(2)–Ir–Cl(1)	88.68(4)
P(3)–Ir–Cl(1)	90.57(4)	P(1)–Ir–Cl(1)	90.58(4)
N(1)–Ir–Cl(2)	88.72(13)	P(2)–Ir–Cl(2)	96.00(4)
P(3)–Ir–Cl(2)	89.47(4)	P(1)–Ir–Cl(2)	89.14(5)
Cl(1)–Ir–Cl(2)	175.31(4)	N(1)–C(1)–C(2)	126.1(5)

absorption at 318 cm<sup>-1</sup> (**5b**) of two chloride ligands in a mutually trans position. Diagnostic for the presence of the imine ligand are the <sup>1</sup>H and <sup>15</sup>N NMR spectra. In the proton spectra, a slightly broad doublet was observed at 9.0–9.8 ppm (*J*<sub>HH</sub> = 21.6–21.8 Hz) and attributed to the NH imine resonance.<sup>29</sup> In the spectrum of labeled complex **5b**<sub>1</sub>, this doublet is split into a doublet of doublets, with *J*<sup>15NH</sup> of 73.5 Hz, fitting the proposed attribution. In addition, the proton-coupled <sup>15</sup>N NMR spectrum appears as a complicated pattern at -179.6 ppm. As the <sup>31</sup>P spectrum is an A<sub>2</sub>BX multiplet, the <sup>15</sup>N NMR spectrum may be simulated with an A<sub>2</sub>BXY model (X = <sup>15</sup>N; Y = <sup>1</sup>H), in agreement with the presence of the imine ligand in a type IV geometry.

Conclusive support for the formulation of **5** came from the X-ray crystal structure determination of [IrCl<sub>2</sub>{η<sup>1</sup>-NH=C(H)C<sub>6</sub>H<sub>5</sub>}-{P(OEt)<sub>3</sub>}]<sub>3</sub>BPh<sub>4</sub> (**5a**), whose ORTEP is shown in Figure 2.

The asymmetric unit contains both an anion BPh<sub>4</sub><sup>-</sup> and a cation complex, in which the iridium(III) atom is coordinated by the nitrogen atom of a benzylideneamidate ligand, two trans chloride atoms, and three mer phosphorus atoms of three triethoxyphosphite ligands. The environment of the iridium atom is a slightly distorted octahedron, with cis angles ranging from 86.6(1) to 96.0(1)° (Table 3). Ir–Cl bond distances of average 2.367(1) Å and Ir–P bond distances of average 2.338(1) Å, for those mutually trans, and 2.259(1) Å, for that trans to the nitrogen atom of the benzylideneamidate ligand, were expected, due to the well-known trans influence of these ligands.

(29) These signals, at 9.0 and 9.8 ppm, were correlated in a COSY experiment with the signals at 8.05 and 8.83 ppm, attributed to the =CH methyne proton of the NH=C(H)Ar imine ligand.

(27) As the <sup>31</sup>P NMR spectrum of **3b**<sub>1</sub> is an A<sub>2</sub>BX multiplet (X = <sup>15</sup>N), the <sup>15</sup>N NMR spectrum should appear as a doublet of triplets (A<sub>2</sub>BX spin system), but the low value of one of the two *J*<sup>15N<sup>31</sup>P</sup> gives an apparent doublet for <sup>15</sup>N<sub>γ</sub> signals.

(28) For imine complexes, see: (a) Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261. (b) McGilligan, B. S.; Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 1737. (c) Michelin, R. A.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Angelici, R. *Organometallics* **1991**, *10*, 1751. (d) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 1295. (e) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (f) Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 2496. (g) Bustelo, F.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1999**, 2399 and ref 8a.

The Ir–N bond distance, 2.130(4) Å, is shorter than that found in an aminoiridium(III) complex.<sup>30</sup> The C=N bond distance, 1.260(7) Å, is also shorter than that found in an imine–tungsten complex.<sup>31</sup> For the time being, to the best of our knowledge, this tungsten complex is the only transition metal  $\eta^1$ -benzylideneamidate complex described in the literature, although some chelating salicylaldiminato or substituted benzylideneamidate complexes are known.<sup>32</sup> The C(1)–N(1)–Ir angle, 131.7(4)°, and N(1)–C(1)–C(2) angle, 126.1(5)°, are surprisingly large for an sp<sup>2</sup>-hybridized N atom, but similar values have been found for the above-mentioned tungsten complex.<sup>31</sup> This distortion is also confirmed in the lack of planarity of the benzylideneamidate ligand, where the nitrogen atom is 0.612(7) Å out of the benzyl plane (rms = 0.0419). As in the azide complex, the ethoxy groups of the mutually trans phosphite ligands are eclipsed but with lesser regularity than that shown in the azide complex. The average O–P–P–O torsion angle is

(30) Deeming, A. J.; Doherty, S.; Marshall, J. E.; Powell, J. L.; Senior, A. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1093–1100.

(31) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6916–6923.

(32) See, for example: (a) Albert, J.; Cadena, J. M.; Gonzalez, A.; Granell, J.; Solans, X.; Font-Bardia, M. *Chem.–Eur. J.* **2006**, *12*, 887–894. (b) Muller, B.; Vahrenkamp, H. *Inorg. Chim. Acta* **2000**, *300–302*, 181–185. (c) Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *306*, 113–116.

much greater, 22.5(2)°. One of the ethoxy groups is directed in the same direction as the chloride ligand labeled Cl(1) and shows an O–P–Ir–Cl torsion angle of 3.2(2)°, but in the trans phosphite ligand the lower torsion angle is that between the ethoxy group and the nitrogen atom, with a torsion angle of 11.0(2)°. Similarly, in the axis P–Ir–N, one of the ethoxy groups is directed toward the nitrogen atom, but the torsion angle has a value of 11.3(2)°. The trans angles, consequently, are more regular (average 175.7(1)°).

Studies are in progress to prepare other azide complexes and to examine the reactivity of coordinated azides.

## Conclusions

In this paper we report details of the first organic azide complexes of iridium [IrCl<sub>2</sub>( $\eta^1$ -N<sub>3</sub>CH<sub>2</sub>Ar)P<sub>3</sub>]BPh<sub>4</sub>, prepared using phosphite-containing hydride species IrHCl<sub>2</sub>P<sub>3</sub> as precursors. Spectroscopic and crystallographic data indicated the  $\eta^1$ -diazoamino coordination mode of the azide ligand. The unprecedented N-protio imine complex of iridium(III) [IrCl<sub>2</sub>{ $\eta^1$ -NH=C(H)C<sub>6</sub>H<sub>5</sub>}P<sub>3</sub>]BPh<sub>4</sub> was also obtained from the azide derivatives.

**Supporting Information Available:** Crystallographic data for compounds **3a** and **5a** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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