

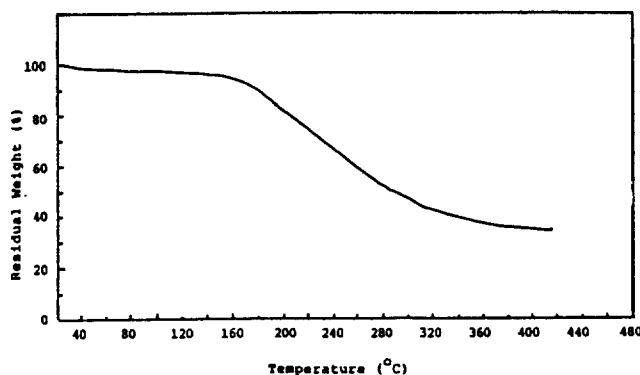


Figure 2. TGA thermogram of poly (POPI).

poly (POPI) in fair yields in DMF and Pyridine solvents. The relatively low polymer yields in the polymerization are thought to be due to the inhibition of polymerization by the poor solubility of the resulting polymers formed. The insolubility of the poly (POPI) were deduced to be due to some cross-linking of active allyl protons of poly (POPI), during polymerization, by catalyst moiety.

References

- (a) M. G. Chauser, Yu. M. Rodionov, V. M. Misin, and M. I. Cherkashin, *Russ. Chem. Rev.*, **45**, 348 (1976); (b) H. W. Gibson, "Substituted Polyacetylenes", Handbook of Conducting Polymers, Vol. I, Ed by Skotheim, Marcel Dekker Inc., New York and Basel, 1986, 405; (c) Y. S. Gal and S. K. Choi, *Polymer (Korea)*, **13**, 188 (1989).
- (a) L. A. Akopyan, *Vysokomol. Soedin., Ser. A.*, **17**, 2517 (1975); (b) L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Resuch, *J. Org. Chem.*, **26**, 5165 (1961); (c) M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 53 (1980); (d) W. C. Lee, M. W. Huh, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, **13**, 520 (1989); (e) W. C. Lee, Y. S. Gal, M. S. Ryoo, S. H. Han, and S. K. Choi, *Polymer (Korea)*, **15**, 283 (1991).
- L. A. Akopyan, S. G. Grigoryan, G. A. Zhamkochyan, and S. G. Mastoyan, *Polym. Sci. USSR*, **17**, 2896 (1976).
- S. Okamura and K. Hayshi, *Japan Pat.*, 7889 (1963). *Chem. Abst.*, **59**, P 7672a.
- A. Fulani, N. V. Russon, P. Carusi, S. Licocia, E. Leoni, and G. Valenti, *Gazz. Chim. Ital.*, **113**, 671 (1983).
- T. Masuda, Y. Kuwane, K. Yamamoto, and T. Higashimura, *Polymer*, **22**, 823 (1980).
- A. D. Pomogailo, S. Kiyashkina, A. I. Kuzaev, S. B. Yechmaev, I. N. Ivleva, and F. S. Dyachkovskii, *Vysokomol. Soedin.*, **17**, 707 (1985).
- (a) W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Bull. Korean Chem. Soc.*, **9**, 328 (1988); (b) W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, **12**, 720 (1988).
- Y. S. Gal and S. K. Choi, *J. Polym. Sci. Polym. Lett. Ed.*, **26**, 115 (1988).
- T. Masuda, K.-Q. Thieu, N. Sasaki, and T. Higashimura, *Macromolecules*, **9**, 661 (1976); (b) T. Higashimura, Y.-X. Deng, and T. Masuda, *Macromolecules*, **15**, 234 (1982).
- Y. S. Gal, H. N. Cho, and S. K. Choi, *Polymer (Korea)*, **9**, 361 (1985).
- T. Masuda, M. Kawai, and T. Higashimura, *Polymer*, **23**, 744 (1982).
- T. Yamagata, T. Masuda, and T. Higashimura, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2279 (1984).
- T. Masuda, M. Yamagata, and T. Higashimura, *Macromolecules*, **17**, 126 (1984).
- M. S. Ryoo, W. C. Lee, and S. K. Choi, *Macromolecules*, **23**, 3029 (1990).
- S. H. Han, U. Y. Kim, Y. S. Kang, and S. K. Choi, *Macromolecules*, **24**, 973 (1991).
- T. J. Katz, T. H. Ho, N. Y. Shih, Y. C. Ying, and V. I. W. Stuart, *J. Am. Chem. Soc.*, **106**, 2659 (1984).
- Y. S. Gal and S. K. Choi, *Polymer (Korea)*, **11**, 563 (1987).

Iridium(III) Insertion into an Aromatic C-H Bond and Si-H Bond

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The dihydrido iridium(III) complex $[\text{Ir}(\text{PPh}_3)_2\text{H}_2(\text{ac})_2]\text{BF}_4$ (ac=acetone) reacts with 2-phenylpyridine and 7,8-benzoquinoline to yield the C-H activated complexes $[\text{Ir}(\text{PPh}_3)_2\text{H}(\text{ac})(\text{L})]\text{BF}_4$ (L=phenylpyridine; 7,8-benzoquinoline). The dihydrido iridium(III) complex $[\text{Ir}(\text{PPh}_3)_2\text{H}_2(\text{ac})_2]\text{BF}_4$ also reacts with trialkylsilane via an oxidative addition reaction to yield the trihydrido iridium complexes $[\text{Ir}(\text{PPh}_3)_2\text{H}_3\text{SiR}_3]\text{BF}_4$ (R=Et and Ph). The structural configuration was studied by conventional spectroscopy.

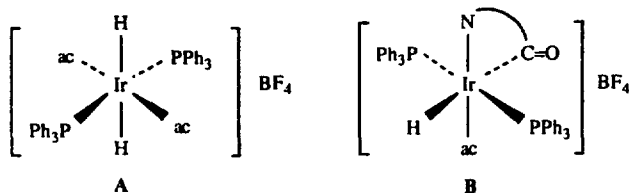
Introduction

The activation of carbon-hydrogen bonds by homogeneous

transition metal complexes is a topic that has received a great deal of attention¹. Interest in reactions of alkanes and arenes with metal complexes has led to the discovery of

many examples of intermolecular carbon-hydrogen bond activation². For an aromatic C-H activation, the stable M-H bonds are formed when ligands such as 2-phenylpyridine³, benzoquinoline⁴, or 8-alkyl quinolines⁵ are reacted with group 8-10 transition metals through chelate-assisted oxidative addition reaction.

Recently, we reported the PtPCy₃(C₂H₄)₂⁶ and Ir(PPh₃)₂(CO)OCIO₃⁷ mediated activation of aldehyde C-H bonds. We also reported the [Ir(PPh₃)₂H₂(ac)₂]⁺BF₄⁻(A)⁸ mediated activation of 8-quinolinecarboxaldehyde, which led to transition metal acyl hydride compound [Ir(PPh₃)₂(NC₉H₆CO)(H)(ac)]⁺BF₄⁻(B).



In an attempt to extend to the activation of aromatic C-H group, the low-valent iridium compound, A was selected as a candidate, because it has readily displaceable ligands, and provides a relatively nucleophilic metal center. Herein, we report on the activation of aromatic C-H bond that forms by reacting the iridium(III) cationic species A with 2-phenylpyridine and 7,8-benzoquinoline and substitution reaction of small molecules into the compound B.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ¹H NMR spectra were recorded on a Bruker WM-250 spectrometer in CDCl₃. Chemical shifts were referenced relative to an internal standard Me₄Si. IR spectra were measured on a Perkin-Elmer 1310 spectrometer by a KBr method. ³¹P-NMR spectra were recorded on a Bruker WM-250 spectrometer operating 81 MHz. The ³¹P chemical shifts are reported relative to 85% H₃PO₄. Conductivity measurement was conducted with an YSI Model 35 Conductance Meter. The molar conductivity was measured at a concentration of 3.6 × 10⁻⁴ M in acetone at 25°C. Elemental analyses were carried out at the Basic Science Research Center. Reagent grade tetrahydrofuran (THF) and benzene were distilled under argon from sodium-benzophenone ketyl. CH₂Cl₂⁹ was carefully purified and distilled under argon. The [Ir(PPh₃)₂H₂(ac)₂]⁺BF₄⁻(ac=acetone)¹⁰, [Ir(PPh₃)₂(NC₉H₆CO)(H)(ac)]⁺BF₄⁻, and 8-quinolinecarboxaldehyde¹¹ were prepared according to literature methods. The 2-phenylpyridine, benzoquinoline, phenylacetylene, HSiEt₃, and HSiPh₃ (Aldrich) reagents were used without further purification.

Synthesis of [Ir(PPh₃)₂(NC₁₁H₈)(H)(ac)]⁺BF₄⁻(1). [Ir(PPh₃)₂H₂(ac)₂]⁺BF₄⁻ (101 mg, 0.1 mmol) and 2-phenylpyridine (0.12 mmol) were dissolved in 14 ml of benzene. The solution was refluxed for 2 h. On cooling to room temperature, the hexane (25 ml) was added. The resulting pale yellow was recrystallized from CH₂Cl₂/Et₂O. The yield was 57%, mp. 215-220°C (dec.). Molar Conductivity: 109 ohm⁻¹cm²mmol⁻¹. ¹H-NMR (CDCl₃) δ (ppm) 8.85-5.80(m, 38H), 2.06(s, 6H, -CH₃),

-16.81(t, 1H, J_{H-P}=15.05 Hz, hydride). IR (on KBr pellet; cm⁻¹) 3042(m), 2078(s), 1594(m), 1578(m), 1422(w), 1305(w), 1257(s), 1182(w), 1170-990(vs, br), 858(w), 795(m), 745(s), 692(vs). Anal. Calcd for C₅₀IrH₄₅NOBF₄: C, 59.08; H, 4.43; N, 1.38. Found: C, 58.74; H, 4.36; N, 1.29.

Synthesis of [Ir(PPh₃)₂(NC₁₃H₉)(H)(ac)]⁺BF₄⁻(2). To a stirred dichloromethane (10 ml) solution of [Ir(PPh₃)₂H₂(ac)₂]⁺BF₄⁻ (100 mg, 0.10 mmol) was added 7,8-benzoquinoline (0.12 mmol) at room temperature and the volume was reduced to ca. 5 ml. The ether (15 ml) was added to the solution. The resulting pale yellow solid was filtered and washed with hexane (10 ml). The pale yellow solid was recrystallized from CH₂Cl₂/ether. The yield was 72%. mp. 154-160°C (dec.). Molar Conductivity: 118 ohm⁻¹cm²mol⁻¹. ¹H NMR (CDCl₃) δ (ppm) 7.72(d, 1H, J_{H-H}=4.32 Hz), 7.38(d, 1H, J_{H-H}=4.32 Hz), 7.30-6.62(m, 36H), 2.09(s, 6H, -CH₃), -16.23(t, 1H, J_{H-P}=14.96 Hz), IR (on KBr pellet; cm⁻¹) 3058(m), 2142(s), 1722(m), 1667(m), 1618(w), 1582(w), 1568(m), 1403(m), 1362(w), 1332(m), 1312(w), 1272(w), 1212(w), 1192(m), 1160-1005(vs, br), 1002(m), 935(w), 862(w), 837(m), 827(w), 745(m), 727(m), 689(s), 653(w), 622(w). Anal. Calcd. for C₅₂H₄₆IrNOBF₄: C, 59.96; H, 4.41; N, 1.34. Found: C, 59.12; H, 4.28; N, 1.30.

Synthesis of [Ir(PPh₃)₂(NC₉H₆CO)(F)(C₆H₁₀)]⁺BF₄⁻(3).

To a stirred dichloromethane (10 ml) solution of [Ir(PPh₃)₂(NC₉H₆CO)(H)(ac)]⁺BF₄⁻ (0.062 g, 0.06 mmol) was added cyclohexene (0.07 mmol) at room temperature. The reaction was continued for 4 hr. The volume was reduced to ca. 5 ml and ether (15 ml) was added to the solution. The pale yellow precipitate was filtered and washed with hexane. The yield was 76%. mp. 218-226°C (dec). Molar Conductivity: 104 ohm⁻¹cm²mol⁻¹. ¹H-NMR(CDCl₃) δ (ppm) 8.2-6.8(m, 36H), 4.32(m, 2H), 2.3-1.8(m, 8H), -14.72(t, 1H, J_{H-P}=15.08 Hz). IR(on KBr pellet; cm⁻¹) 3039(m), 2142(s), 1694(m), 1652(s), 1565(s), 1495(s), 1352(m), 1308(w), 1278(w), 1238(w), 1221(m), 1180(m), 1161(m), 1100-990(br, vs), 898(s), 832(br, s), 787(s), 745(s), 692(s), 670(m), 612(w). Anal. Calcd. for C₄₉BF₄H₄₇IrNOP₂: C, 58.46; H, 4.67. Found: C, 59.19; H, 4.81.

Synthesis of [Ir(PPh₃)₂(NC₉H₆CO)(H)(C₂H₄)]⁺BF₄⁻(4). Ethylene was bubbled into a dichloromethane (10 ml) solution of Ir(PPh₃)₂(NC₉H₆CO)(H)(ac)]⁺BF₄⁻ (0.072 g, 0.07 mmol) at room temperature for 2 hr. After the volume was reduced to ca. 5 ml, ether (15 ml) was added. The pale yellow precipitate was filtered and washed with hexane. The yield was 65%. mp. 154-160°C (dec). Molar Conductivity: 110 ohm⁻¹cm²mol⁻¹. ¹H-NMR (CDCl₃) δ (ppm) 7.9-6.9 (m, 36H), 3.67(s, 4H, CH₂), -14.72(t, 1H, J_{H-P}=15.21 Hz). IR (on KBr pellet; cm⁻¹) 3024(m), 2973(m), 2112(m), 1073(w), 1634(s), 1568(m), 1498(m), 1395(w), 1308(w), 1257(s), 1220(w), 1138(w), 1160-980(br, vs), 901(m), 798(s), 792(m), 704(m), 692(s), 672(w), 657(w), 612(w). Anal. Calcd. for C₄₈H₄₁IrNOP₂BF₄: C, 58.41; H, 4.14; N, 1.42. Found: C, 57.68; H, 3.94; N, 1.28.

Synthesis of [Ir(PPh₃)₂(NC₉H₆CO)(H)(CO)]⁺BF₄⁻(5).

Carbon monoxide was bubbled into a dichloromethane (10 ml) solution of [Ir(PPh₃)₂(NC₉H₆CO)(H)(ac)]⁺BF₄⁻ (0.124 g, 0.12 mmol) for 1 hr. The solvent was removed in vacuum. Dichloromethane (5 ml) was added to the pale yellow solid and then hexane was added. The pale yellow solid was filtered and dried in vacuum. The yield was 68%. mp. 147-151°C (dec). Molar Conductivity: 105 ohm⁻¹cm²mol⁻¹. ¹H NMR (CDCl₃) δ (ppm) 8.32(d, 1H, J_{H-H}=5.82 Hz) 7.68(dd, 1H, J_{H-H}=5.82 Hz) 7.54(d, 1H, J_{H-H}=5.82 Hz), 7.48-7.12(m, 32H), -15.16(t,

^1H , $J_{\text{H-P}} = 11.42$ Hz). IR (on KBr pellet; cm^{-1}) 3035 (m), 2246 (m), 2078(s), 1668(sh), 16442(s), 1586(s), 1515(m), 1410(m), 1327(m), 1295(w), 1276(w), 1253(w), 1239(m), 1217(w), 1200 (m), 1177(m), 1747(sh), 1110(m), 1096-1030(br, vs), 1012(s), 916(s), 870(m), 860(m), 817(w), 804(m), 772(s), 762(s), 723(s), 712(s), 700(sh), 632(w). Anal. Calcd. for $\text{C}_{47}\text{H}_{37}\text{IrNO}_2\text{P}_2\text{BF}_4$: C, 57.10; H, 3.74; N, 1.42. Found: C, 56.31; H, 3.61; N, 1.29.

Synthesis of $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{PhC}_2\text{H})]\text{BF}_4$ (6). Preparation of 6 followed the same procedure used for the synthesis of 3. The yield was 78%. m.p. 162-166°C. Molar Conductivity: 119 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.8-6.6(m, 41H), 3.48(s, 1H, CH), -19.70(t, 1H, $J_{\text{H-P}} = 13.89$ Hz). IR (on KBr pellet; cm^{-1}) 3030(m), 2937(m), 2104(w), 1703(w), 1658(s), 1578(m), 1558(sh), 1490(w), 1392 (m), 1303(w), 1249(s), 1232(w), 1229(w), 1208(w), 1178(w), 1154(m), 1108-960 (vs, br), 889(s), 825(m), 812(s), 798(s), 742 (s), 702(sh), 683(s), 672(m), 612(m), 608(w). Anal. Calcd. for $\text{C}_{54}\text{H}_{43}\text{IrNOP}_2\text{BF}_4$: C, 61.03; H, 4.04; N, 1.32. Found: C, 62.12; H, 4.32; N, 1.22.

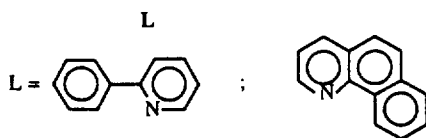
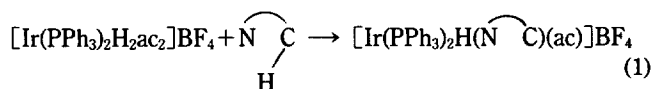
Synthesis of $[\text{Ir}(\text{PPh}_3)_2(\text{SiPh}_3)\text{H}_3]\text{BF}_4$ (7). Preparation of 7 followed the same procedure as described for the synthesis of 3. The yield was 67%. mp. 160-165°C. Molar Conductivity: 115 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.6-6.7(m, 45H), -11.62(ddt, $J_{\text{H-P(trans)}} = 132$ Hz, $J_{\text{H-H}} = 21$ Hz, $J_{\text{H-P(cis)}} = 6.32$ Hz, 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 28.54(d), δ 20.62(C, $J_{\text{P-P}} = 282.32$ Hz). IR (on KBr pellet; cm^{-1}) 3038(m), 2178(m), 2096(m), 1396(m), 1296(w), 1257(m), 1176-980(vs, br), 855(w), 817(m), 803(m), 742(s), 692(s). Anal. Calcd. for $\text{C}_{54}\text{H}_{48}\text{IrP}_2\text{SiBF}_4$: C, 60.86; H, 3.63. Found: C, 59.72; H, 3.51.

Synthesis of $[\text{Ir}(\text{PPh}_3)_2(\text{SiEt}_3)\text{H}_3]\text{BF}_4$ (8). Preparation of 8 followed the same procedure as described for the synthesis of 3. The yield was 54%. mp. 148-152°C. Molar Conductivity: 110 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.7-6.7(m, 30H), 3.41(q, $J_{\text{H-H}} = 5.32$ Hz, 6H), 1.14(t, $J_{\text{H-H}} = 5.32$ Hz, 9H). -11.72(ddt, $J_{\text{H-P(trans)}} = 147$ Hz, $J_{\text{H-H}} = 19$ Hz, $J_{\text{H-P(cis)}} = 6.22$ Hz, 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 27.87(d), δ 19.87(d, $J_{\text{P-P}} = 281$. 72 Hz). IR (on KBr pellet; cm^{-1}) 3022(m), 2148(m), 2094(m), 1582(w), 1568(w), 1253(m), 1182(m), 1122-978(vs, br), 798(m), 738(m), 718(w), 687(s). Anal. Calcd. for $\text{C}_{42}\text{H}_{48}\text{IrP}_2\text{SiBF}_4$: C, 54.74; H, 5.20. Found: C, 54.04; H, 5.12.

Results and Discussion

Aromatic C-H Activation

The iridium hydride complexes have been prepared according to Eq. (1).



The addition of equimolar quantity of $[\text{Ir}(\text{PPh}_3)_2\text{H}_2(\text{ac})_2]\text{BF}_4$ to a 2-phenylpyridine, followed by refluxing the solution, gave a pale yellow solution. The product, $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_{11}\text{H}_8)(\text{H})(\text{ac})]\text{BF}_4$ was isolated as air stable solid in 57% yield. The structure of compound 1 was deduced from its $^1\text{H-NMR}$ and IR spectra. The $^1\text{H-NMR}$ spectrum of 1 taken in CDCl_3

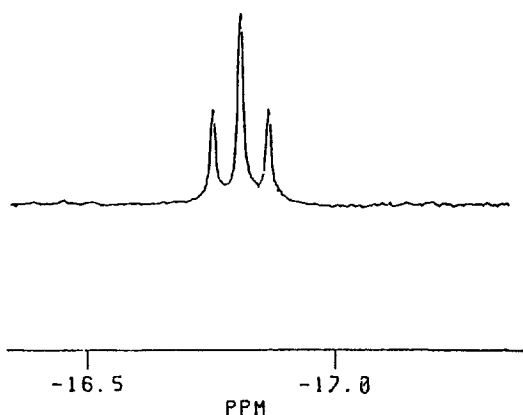
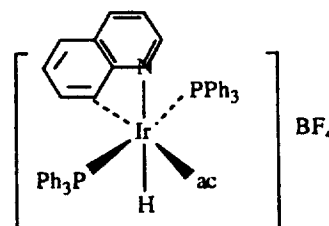


Figure 1. The $^1\text{H-NMR}$ spectrum of the complex $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_{11}\text{H}_8)(\text{H})(\text{ac})]\text{BF}_4$ in the hydride region.

at room temperature exhibits resonances of Ir-H centered at δ -16.81 ($J_{\text{H-P}} = 15.12$ Hz)(see Figure 1). Its pattern consists of a triplet due to the spin coupling between the hydride and two phosphines. The value is very close to that of the compounds $[\text{Ir}(\text{PPh}_3)_2(\text{benzoquinolinato})\text{H}(\text{H}_2\text{O})]\text{SbF}_6^{12}$ (δ -16.1) and $[\text{Ir}(\text{H})(\text{CO})(\text{bq})(\text{PPh}_3)_2]\text{PF}_6^{13}$ (δ -15.04). The spin system indicates that two phosphine ligands are chemically equivalent. The small coupling constant of 1 indicates that the hydride is *cis* to the phosphine and the Ir-H group is *trans* to a N-donor ligand, as shown below. In addition to that, there are two peaks at δ 8.85-5.80 and 2.06, assigned to aromatic hydrogens and acetone, respectively.



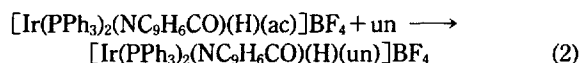
The infrared spectrum of 1 clearly indicates the presence of the Ir-H bond. The intense peak at 2078 cm^{-1} is assigned to the Ir-H stretching mode, which is expected to exhibit a bond with stretching frequency in the region $2300\text{-}1900\text{ cm}^{-1}$.¹⁴ It is interesting to note that the Ir-H stretching frequency of 1 is relatively low compared with that (2220 cm^{-1}) of the compound, $[\text{Ir}(\text{PPh}_3)_2(\text{H})(\text{CO})(\text{bq})]\text{PF}_6$, due probably to the absence of back bonding. The conductance measurement ($109\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) indicates that the complex is 1 : 1 electrolyte.

The complex $[\text{Ir}(\text{PPh}_3)_2(\text{bq})(\text{H})(\text{ac})]\text{BF}_4$ (bq = 7,8-benzoquinoline) was prepared through the refluxing of the solution of $[\text{Ir}(\text{PPh}_3)_2\text{H}_2(\text{ac})_2]\text{BF}_4$ and 7,8-benzoquinoline. The pale yellow iridium(III) hydride is relatively stable in the solid state. The infrared spectrum of 2 gave a relatively high value for the Ir-H stretching frequency (2142 cm^{-1}) compared with that of compound 1. The $^1\text{H-NMR}$ spectrum of 2 clearly shows the presence of the Ir-H. The Ir-H signal centered at δ -14.72 ($J_{\text{H-P}} = 15.08$ Hz) exhibits a pattern that is very similar to that of compound 1.

Substitution Reaction with Small Molecules

The substitution reaction of the compounds $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{-}$

$\text{H}_6\text{CO}(\text{H})(\text{ac})\text{BF}_4$ ($\text{NC}_9\text{H}_6\text{CO}$ = 8-quinolinecarboxaldehyde) with small molecules was achieved according to Eq. (2).



un = ethylene, phenylacetylene, carbon monoxide, cyclohexene

(a) Cyclohexene. The addition of an equimolar of cyclohexene to a stirred dichloromethane solution of $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{ac})]\text{BF}_4$ affords a pale yellow solution. The resulting pale yellow product, $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{C}_6\text{H}_{10})]\text{BF}_4$ was isolated as air stable solid in a relatively high yield. The structure of the compound was deduced from its ^1H -NMR and IR spectrum. The ^1H -NMR spectrum of the compound taken in CDCl_3 at room temperature exhibits resonances of Ir-H centered at δ -14.72 ($J_{\text{H-P}} = 15.04$ Hz). The small value of the coupling constant¹⁵ implies that the hydride is *cis* to the phosphine ligands. The value is very close to that of the compound $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{ac})]\text{PF}_6$. In addition to that, there are three broad peaks at δ 2.3-1.8, δ 4.32 and δ 8.2-6.8, assigned to CH_2 and CH of cyclohexene and aromatic hydrogens, respectively.

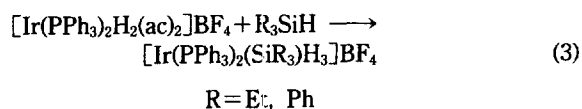
The infrared spectrum of the compound clearly indicates the presence of the Ir-H bond. The intense peak at 2142 cm^{-1} is assigned to the Ir-H stretching mode. The Ir-H stretching frequency of the complex is very close to that of the compound $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{ac})]\text{BF}_4$, which occurs at 2140 cm^{-1} .

(b) Carbon Monoxide. The carbonyl substitution product was prepared through the bubbling of CO to a CH_2Cl_2 solution of $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{ac})]\text{BF}_4$. The infrared spectrum of the compound gave a relatively high value for the Ir-H stretching frequency (2246 cm^{-1}) compared with that of the cyclohexene stretching mode. It may be attributable to the decrease of electron density on Ir site by substituting the strong π -acceptor carbonyl ligand for cyclohexene ligand. The peak at 2078 cm^{-1} is assigned to the carbonyl stretching frequency. The ^1H -NMR spectrum of the complex clearly shows a pattern that is very similar to that of $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{C}_6\text{H}_{10})]\text{BF}_4$.

(c) Ethylene and phenylacetylene. The ethylene substitution product was prepared through the bubbling of ethylene to a CH_2Cl_2 solution of $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{ac})]\text{BF}_4$. The ^1H -NMR spectrum of the complex exhibits a signal centered at δ -14.74 ($J_{\text{H-P}} = 15.21$ Hz) in the hydride region. The Ir-H stretching frequency (2112 cm^{-1}) is comparable to that of $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{H})(\text{C}_6\text{H}_{10})]\text{BF}_4$. The phenylacetylene substitution product $[\text{Ir}(\text{PPh}_3)_2(\text{NC}_9\text{H}_6\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{H})]\text{BF}_4$ was similarly assigned.

Oxidative Addition Reaction of R_3SiH ($\text{R} = \text{Ph}, \text{Et}$)

The iridium(III) dihydride complex $[\text{Ir}(\text{PPh}_3)_2(\text{H})_2(\text{ac})_2]\text{BF}_4$ reacts with trialkylsilane to give the formation of the stable iridium trihydride complex $[\text{Ir}(\text{PPh}_3)_2(\text{SiR}_3\text{H}_3)]\text{BF}_4$ according to Eq. (3).



The off-white products are air-stable and soluble in CH_2 -

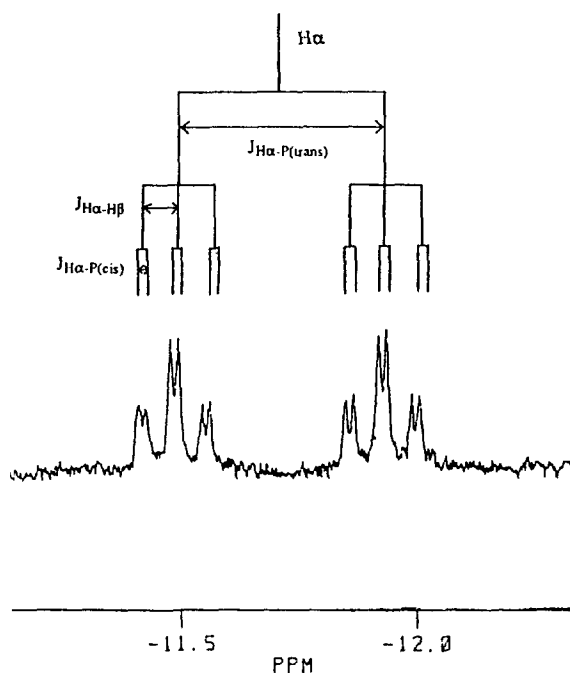
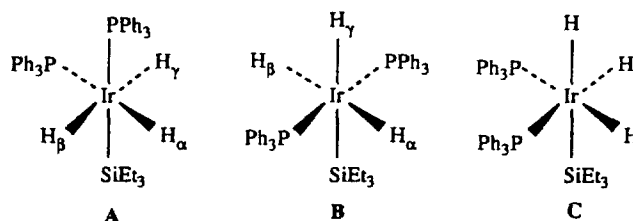


Figure 2. The ^1H -NMR spectrum of the complex $[\text{Ir}(\text{PPh}_3)_2(\text{SiEt}_3)\text{H}_3]\text{BF}_4$ in the hydride region.

Cl_2 , slightly soluble in CH_3CN . The ^1H -NMR spectrum of $[\text{Ir}(\text{PPh}_3)(\text{SiEt}_3)\text{H}_3]\text{BF}_4$ exhibits resonances centered at δ -11.72 (ddt, $J_{\text{H-P(trans)}} = 132$ Hz, $J_{\text{H-H}} = 21$ Hz, $J_{\text{H-P(cis)}} = 6.32$ Hz) in the hydride region (see Figure 2). Its pattern consists of doublets of doublets of triplets, due to the spin coupling between the phosphorus and hydride, corresponding to the AM_2PX_2 spin system. The spin system indicates that two phosphorus ligands or two hydride ligands are made equivalent by a molecular mirror plane of symmetry, as shown below (A, B, and C). These data are best explained by three possible octahedral structure A, B, and C. The next problem is to decide which of three possible structure A, B, and C is correct. The large coupling constant ($J_{\text{H-P}} = 132$ Hz) indicates that one hydride is *trans* to the phosphorus atom¹⁶. Therefore, the possibility of B will be eliminated. The triplet pattern arises from the coupling between the chemically equivalent two hydrogen atoms and H_α or the two phosphorus atoms and



hydrogen. Viewed from the ^1H -NMR spectrum, the structure of C will be eliminated. The small coupling constant of $J_{\text{H-P}}$ also indicates that the hydride is *cis* to the phosphorus atom. Accordingly, the correct structure of the complex appears to favor the structure A. These values are quite similar to those of the compounds $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{H}_3$ ¹⁷, $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{H}_2(\text{SiR}_3)$ ¹⁸, and analogous trihydrides¹⁹. The fact that intramolecular interchange could occur in the mer isomer, but not the fac isomer is likely due to the large *trans* effect of the

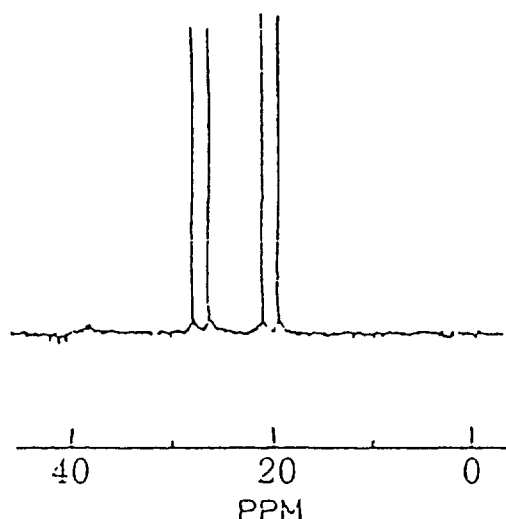


Figure 3. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex $[\text{Ir}(\text{PPh}_3)_2(\text{SiEt}_3)]\text{BF}_4$.

hydride ligand. The assignment was further evidenced by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **8** is shown in Figure 3. Its pattern consists of two doublet with almost equal intensity due to the spin coupling between the chemically inequivalent two phosphine ligands. Therefore, the possible structure of **B** will be clearly eliminated. The chemical shift and coupling constant of **8** are quite similar to those of compound $\text{Ir}(\text{Ph}_2\text{PC}_6\text{H}_4\text{CO})(\text{PPh}_3)(\text{CO})(\text{Cl})(\text{H})^{20}$. From the ^1H -NMR spectrum together with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the correct geometry of compounds **7** and **8** appears to favor the structure A.

In further studies, we are investigating the possibility of carbon-carbon bond cleavage under the same condition.

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References

- (a) P. L. Watson, *J. Am. Chem. Soc.*, **105**, 6491 (1983); (b) J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, **104**, 3723 (1982); (c) A. H. Janowicz, R. G. Bergman, *J. Am. Chem. Soc.*, **104**, 352 (1982); (d) M. J. Max, J. M. Stryker, J. M. Buchanan, C. A. Kovac, and R. G. Bergman, *J. Am. Chem. Soc.*, **106**, 1121 (1984); (e) A. G. Shilov and A. A. Shteinman, *Coord. Chem. Rev.*, **24**, 97 (1977); (f) D. Baudry, M. Ephritikhine, H. Felkin, *J. Chem. Soc. Chem. Commun.*, 1243 (1980); (g) R. H. Crabtree, P. C. Demou, D. Eden, J. M. Mihelcic, C. A. Parnell, J. M. Quirk, G. E. Morris, *J. Am. Chem. Soc.*, **104**, 6994 (1982).
- (a) A. E. Shilov, *Pure Appl. Chem.*, **50**, 725 (1978); (b) G. B. Shul'pin, G. V. Nizova, and A. E. Shilov, *J. Chem. Soc. Chem. Commun.*, 671 (1983); (c) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, **105**, 6243 (1983); (d) J. A. Smegal, B. C. Schardy, and C. L. Hall, *J. Am. Chem. Soc.*, **105**, 3515 (1983); (e) R. A. Periana and R. G. Bergman, *Organometallics*, **3**, 508 (1984); (f) M. Gomez, D. J. Robinson, and P. M. Maitlis, *J. Chem. Soc. Chem. Commun.*, 825 (1983); (g) C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, **101**, 1742 (1979).
- S. Sprose, K. A. King, P. J. Spellance, and R. J. Watte, *J. Am. Chem. Soc.*, **106**, 6647 (1984).
- J. Selbin and M. A. Gutierrez, *J. Organomet. Chem.*, **246**, 95 (1983).
- A. Albinati, C. G. Anklin, F. Ganazzoli, H. Rüegg, and P. S. Pregosin, *Inorg. Chem.*, **26**, 503 (1989).
- J. Ko, W. C. Hee, P. G. Williard, and W. M. Risen, *J. Organomet. Chem.*, **284**, 409 (1985).
- J. Ko, W. C. Joo, Y. K. Kong, *Bull. Kor. Chem. Soc.*, **7**, 338 (1986).
- J. Ko and W. C. Joo, *Bull. Kor. Chem. Soc.*, **8**, 372 (1987).
- D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, 3rd. Ed.
- R. H. Crabtree, E. M. Holt, M. Labin, and S. M. Morehouse, *Inorg. Chem.*, **24**, 1986 (1985).
- C. G. Anklin and P. S. Pregosin, *J. Organomet. Chem.*, **243**, 101 (1983).
- M. Lavin, E. M. Holt, and R. H. Crabtree, *Organometallics*, **8**, 99 (1989).
- F. Neve, M. Ghédini, A. Tiricchio, and F. Uguzzoli, *Inorg. Chem.*, **28**, 3084 (1989).
- (a) M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc. Chem. Commun.*, 671 (1976); (b) M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc. Dalton Trans.*, 801 (1978); (c) R. Ros, *J. Organomet. Chem.*, **118**, c53 (1976).
- R. H. Crabtree and R. J. Vriate, *Inorg. Chem.*, **22**, 4152 (1983).
- R. H. Crabtree, J. W. Faller, M. F. Mellea, and J. M. Quirk, *Organometallics*, **5**, 1361 (1982).
- J. F. Harrod, G. Hamer, and W. Yorke, *J. Am. Chem. Soc.*, **101**, 14, 3987 (1979).
- F. Gloeking, M. D. Wilbey, *J. Chem. Soc.(A)*, 1675 (1970).
- J. P. Jesson in *Transition Metal Hydrides*, E. L. Muetterties, Ed., Marcel Dekker, New York, p. 75, 1971.
- J. Wu, M. K. Reinking, P. E. Fanwick, and C. P. Kubiak, *Inorg. Chem.*, **26**, 247 (1987).