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Direct Observation of Reversible C(sp^3)−H Bond Activation. Characterization of the Structures of Both Ir Complexes before and after C−H Bond Activation by Using a Flexible P−N Heterochelate Hybrid Ligand

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Summary: Direct observation of reversible C−H bond activation of a C(sp^3)−H bond is shown for the Ir(I) complex ***2a****, which has a coordinatively flexible heterochelate hybrid PN$_{n=1}$ ligand (****1a****). Full characterization data for the Ir(I) and Ir(III) complexes, including their X-ray structures and estimation of the thermodynamic and kinetic parameters for the C−H bond activation, are provided.*

C−H bond activation is an intriguing subject of research in organometallic chemistry, and intensive efforts have been made to disclose the nature of C−H bond activation.[1] In the course of these studies, reversible C−H bond activation has been explored since the early 1980s;[2−4] however, examples of the isolation and structural characterization of the complexes just before and after C−H bond activation in the same system, showing reversible oxidative addition and reductive elimination of the C−H bond, are still extremely rare because there is considerable difference in stability between the two complexes.[2c,3,4l] Herein we describe direct observation of reversible C−H bond activation of an sp^3 C−H bond shown by iridium(I) complexes having a coordinatively flexible heterochelate hybrid PN$_{n=1}$ ligand (PN$_{n=1}$ = *o*-Ph$_2$PC$_6$H$_4$CH$_2$OCH$_2$C$_5$H$_4$N-2).[5] Furthermore, we clarify the structures of both iridium(I) and -(III) complexes obtained before and after the oxidative addition of a C−H bond under mild conditions.

Reaction of [IrCl(cod)]$_2$ with 2 equiv of the ligand PN$_{n=1}$ (**1a**; cod = cyclooctadiene) (Chart 1) in the presence of excess AgPF$_6$ in ethanol at room temperature for 16 h gave the Ir(I) cationic complex [Ir(cod)-(PN$_{n=1}$)]PF$_6$ (**2a**) as an orange powder in 88% yield (eq 1).[6] This complex was characterized by the usual

$$1/2\ [\mathrm{IrCl(cod)}]_2 \xrightarrow[\mathrm{EtOH}]{\mathrm{AgPF_6}} \xrightarrow{\mathrm{PN_n}} [\mathrm{Ir(cod)(PN_n)}][\mathrm{PF_6}] \qquad (1)$$

spectrometric methods as well as an X-ray analysis. Single crystals of **2a** suitable for an X-ray analysis were obtained directly from the reaction mixture.[7] An ORTEP view of **2a** is shown in Figure 1.[8,9] The diphenylphos-

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[1] Review: for example (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (c) Crabtree, R. H. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappaport, Z., Eds.; Wiley-Interscience: New York, 1992; pp 653−679. (d) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (e) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

[2] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121. (c) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

[3] (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620.

[4] For recent examples of reversible C−H bond activation, see: (a) Keyes, M. C.; Young, V. G., Jr.; Tolman, W. B. *Organometallics* **1996**, *15*, 4133. (b) Hascall, T.; Murphy, V. J.; Parkin, G. *Organometallics* **1996**, *15*, 3919. (c) Miller, R. L.; Lawler, K. A.; Bennett, J. L.; Wolczanski, P. T. *Inorg. Chem.* **1996**, *35*, 3242. (d) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696. (e) Chi, Y.; Chung, C.; Chou, Y.-C.; Su, P.-C.; Chiang, S.-J.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1997**, *16*, 1702. (f) Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974. (g) Chisholm, M. H.; Huang, J.-H.; Huffman, J. C.; Parkin, I. P. *Inorg. Chem.* **1997**, *36*, 1642. (h) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (i) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1998**, *17*, 2912. (j) Alias, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *J. Am. Chem. Soc.* **1998**, *120*, 5816. (k) Mobley, T. A.; Schade, C.; Bergman, R. G. *Organometallics* **1998**, *17*, 3574. (l) Dorta, R.; Togni, A. *Organometallics* **1998**, *17*, 3423.

[5] (a) Yabuta, M.; Nakamura, S.; Yamagata, T.; Tani, K. *Chem. Lett.* **1993**, 323. (b) Tani, K.; Yabuta, M.; Nakamura, S.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2781. (c) Tani, K.; Nakamura, S.; Yamagata, T.; Kataoka, Y. *Inorg. Chem.* **1993**, *32*, 5398. (d) Kataoka, Y.; Tsuji, Y.; Matsumoto, M.; Ohsashi, T.; Yamagata, T.; Tani, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2099.

[6] The neutral complex [IrCl(cod)(PN$_{n=1}$)]$_n$ could be isolated from [IrCl(cod)]$_2$ and 2 equiv of PN$_{n=1}$ in 94% yield. The initial attempts at synthesizing **2a** from the reaction of [IrCl(cod)(PN$_{n=1}$)]$_n$ with AgPF$_6$ in dichloromethane were foiled because the reaction gave only complex mixtures.

[7] Synthesis of **2a**: to an ethanol suspension (21 mL) of [IrCl(cod)]$_2$ (74 mg, 0.11 mmol) was added dropwise an ethanol solution (1 mL) of AgPF$_6$ (95 mg, 0.37 mmol). The reaction mixture was stirred for 30 min at room temperature. After removal of insoluble materials from the reaction mixture by filtration, the filtrate was added dropwise to an ethanol solution (2 mL) of PN$_{n=1}$ (**1a**; 89 mg, 0.37 mmol) at room temperature. The reaction mixture was stirred for 18 h at room temperature, resulting in a color change from orange to yellow. Removal of the solvent in vacuo gave **2a** as an orange powder in 88% yield (139 mg, 0.19 mmol). When single crystals of **2a** for an X-ray analysis were needed, after addition of an ethanol solution of **1a** the reaction mixture was stirred for a few minutes and then allowed to stand overnight (18 h) at room temperature, resulting in the formation of orange crystalline precipitates. The solvent was removed with a syringe, and the orange solid residue was washed with two portions of ethanol (2 × 3 mL) to give **2a**·C$_2$H$_5$OH as orange prisms in 71% yield (136 mg, 0.16 mmol); mp 142−144 °C. ^{1}H NMR (CDCl$_3$): δ 1.24 (t, J = 6.8 Hz, 3H, CH_3CH$_2$OH), 1.39−1.70 (br, 1H, CH$_3$CH$_2$OH), 3.72 (q, J = 6.8 Hz, 2H, CH$_3$CH_2OH), 1.70−1.94 (m, 4H, −CH_2− of cod), 2.27−2.56 (m, 4H, −CH_2− of cod), 3.76−3.88 (m, 2H, −CH= of cod), 4.08−4.22 (m, 2H, −CH= of cod), 4.73 (d, J = 13.2 Hz, 1H, OCH_2py), 4.95 (d, J = 15.6 Hz, 1H, ArCH_2O), 5.04 (d, J = 13.2 Hz, 1H, OCH_2-py), 5.28 (d, J = 15.1 Hz, 1H, ArCH_2O), 6.48 (dd, J = 7.8, 9.3 Hz, 1H, arom), 6.96−7.69 (m, 14H, arom), 7.82−7.96 (m, 2H, arom), 8.67 (d, J = 5.4 Hz, 1H, H^6 of py). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 7.8 (s). MS (FAB): *m*/*z* 684 (M$^+$ − PF$_6$). IR (Nujol): 3609, 1604, 1091, 1077, 844, 755, 701 cm^{-1}. Anal. Found: C, 47.79; H, 4.54; N, 1.60. Calcd for C$_{33}$H$_{34}$F$_6$-IrNOP$_2$·C$_2$H$_5$OH: C, 48.05; H, 4.61; N, 1.60.

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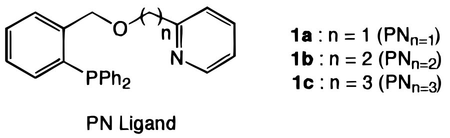
Chart 1



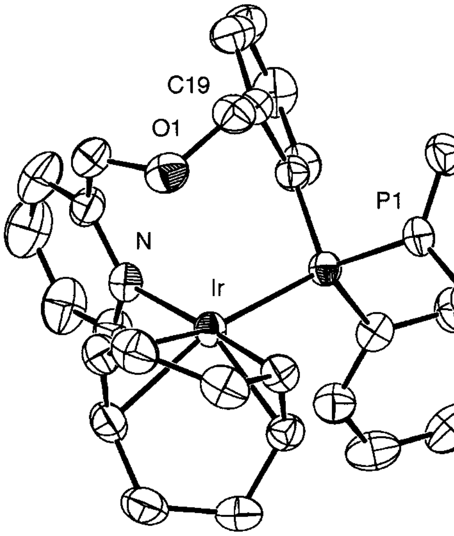
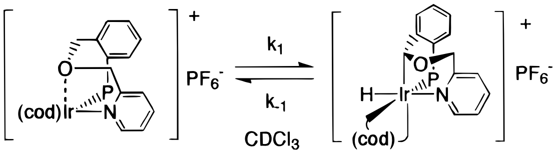


Figure 1. ORTEP drawing of the X-ray crystal structure of the cationic part of **2a**. Selected interatomic distances (Å) and angles (deg) are as follows: Ir−O1 = 2.650(3), Ir−P1 = 2.3348(10), Ir−N = 2.162(3), Ir···Cl9 = 3.487(4); N−Ir−P1 = 89.93(9), N−Ir−O1 = 69.79(11), P1−Ir−O1 = 83.78(7).

phino group and the 2-pyridyl group of the PN ligand coordinate to the square-planar iridium−cyclooctadiene fragment in a *cis* configuration. The ethereal oxygen atom in the PN ligand is placed at the apical position. The distance between the iridium and the oxygen atom (2.650 (3) Å) is shorter than the sum of the van der Waals radii[10] of an iridium (1.26 Å, covalent radius) and an oxygen atom (1.40 Å, van der Waals radius), indicating that there should be a certain interaction between them. The existence of the interaction in solution was also indicated by ^{1}H NMR. The inequivalence of the two benzylic protons (δ 4.95 and 5.28) and the two α-methylene protons of the 2-pyridyl group (δ 4.73 and 5.04) shows that free rotation of the chelate chain in the PN ligand is restricted by the weak coordination of the oxygen atom to the iridium metal. A similar binding mode of the PN ligand (P−O−N tridentate coordination) in a d^8 square-planar complex was previously observed in *cis*-$PdCl_2(PN_{n=1})$.[5,11] The interaction became weaker at higher temperature. The ^{1}H NMR spectra of the benzylic protons and the α-methylene protons of the 2-pyridyl group at 60 °C show broadening, while the other peaks of **2a** remain sharp.

The complex **2a** was stable in the solid state, but when it was dissolved in $CDCl_3$, the color of the solution gradually changed from orange to pale orange and intramolecular C−H bond activation at the benzylic position of the PN ligand easily occurred even at 30 °C to give an equilibrium mixture of **2a** and Ir(III) hydrido alkyl complex **3a** (after 90 h, **2a**:**3a** = 18.4:81.6) (eq 2).



(2)

2a **3a**

The crude hydrido alkyl iridium complex **3a** was obtained as air-stable pale yellow crystals along with orange crystals **2a** by recrystallization of the equilibrium mixture from a dichloromethane−hexanes solution, from which the pure complex **3a** could be separated as well-developed crystals.[12] The complex **3a** was also fully characterized, including an X-ray analysis.[9,13] An ORTEP view (Figure 2) displays a distorted-octahedral geometry around the Ir(III) center. The PN ligand functions as a facial P−C−N ligand coordinated by phosphorus, benzylic carbon, and nitrogen atoms. The ^{1}H NMR also reveals the oxidative addition of the benzylic position. Appearance of the singlet signal at δ 6.58 (1H) shows the presence of the proton attached to the metal-bound benzylic carbon atom, and that of a doublet signal at δ −18.43 (d, J_{P-H} = 14.3 Hz, 1H) shows the presence of the metal hydride at the *cis* position of the phosphorus atom, though it could not be detected by the X-ray analysis.

Reductive elimination from **3a** also easily took place in $CDCl_3$ even at 30 °C to give again an equilibrium mixture of **2a** and **3a** (after 90 h, **2a**:**3a** = 18.4:81.6), though **3a** was stable in the solid state. From the equilibrium constant (K = 4.30(9) in $CDCl_3$ at 30 °C)

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[8] Crystal data for **2a**: $C_{35}H_{40}F_6IrNO_2P_2$, (M_r = 874.82), triclinic, space group $P\bar{1}$ (No. 2), a = 11.2997(11) Å, b = 14.1186(12) Å, c = 11.2743(14) Å, α = 90.057(9)°, β = 109.243(8)°, γ = 95.232(8)°, V = 1690.2(3) Å^3, Z = 2, D_{calcd} = 1.719 g/cm^3, μ = 4.111 mm^{-1}, R_{int} = 0.0205, R1(all) = 0.0387, R1(obsd) = 0.0292 (>2.0$\sigma(I)$), wR2(all) = 0.0345, wR2(obsd) = 0.0707 (>2.0$\sigma(I)$).

[9] Selected bond lengths, bond angles, and crystal and data collection parameters are given in the Supporting Information.

[10] Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; pp 258−259.

[11] The analogous rhodium(I) complex $[Rh(cod)PN_{n=1}]PF_6$ was also prepared from $[Rh(cod)Cl_2]$ and $PN_{n=1}$ in the presence of $AgPF_6$ in ethyl alcohol. The $PN_{n=1}$ ligand was also coordinated as a P−O−N tridentate ligand. The rhodium complex, however, did not show any indication of similar C−H bond activation at ambient temperature. Preparation and properties of the rhodium complex will be reported separately.

[12] Synthesis of **3a**: **2a** (101 mg, 0.12 mmol) was dissolved in 2.0 mL of dichloromethane, and the obtained orange solution was stirred for 24 h at room temperature. After removal of the solvent, careful recrystallization of the resulting orange solid residue from dichloromethane−hexane gave a mixture of well-developed pale yellow crystals of **3a** together with orange crystals of **2a**, from which pale yellow crystals of pure **3a** could be collected in 73% yield (73 mg, 0.088 mmol) with tweezers; mp 149 °C dec. ^{1}H NMR ($CDCl_3$): δ −18.43 (d, J = 14.3 Hz, 1H, Ir−H), 1.89−1.96 (m, 1H, −CH_2− of cod), 1.97−2.16 (m, 2H, −CH_2− of cod), 2.43−2.59 (m, 1H, −CH_2− of cod), 2.57−2.77 (m, 2H, −CH_2− of cod), 2.78−2.92 (m, 1H, −CH_2− of cod), 3.21−3.33 (m, 1H, −CH_2− of cod), 4.79−4.90 (m, 1H, −CH= of cod), 4.96−5.06 (m, 1H, −CH= of cod), 5.06−5.16 (m, 1H, −CH= of cod), 5.59−5.71 (m, 1H, −CH= of cod), 4.13 (d, J = 17.0 Hz, 1H, OCH_2py), 4.45 (d, J = 17.0 Hz, 1H, OCH_2py), 6.58 (s, 1H, Ir−CH(O)Ar), 6.74 (d, J = 7.6 Hz, 1H, arom), 6.85−6.94 (m, 2H, arom), 7.06−7.15 (m, 2H, arom), 7.23−7.35 (m, 4H, arom), 7.44−7.65 (m, 7H, arom), 7.71−7.78 (m, 1H, arom), 8.52 (d, J = 6.0 Hz, 1H, H^6 of py). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.4 (s, methylene of cod), 28.0 (s, methylene of cod), 31.8 (s, methylene of cod), 39.1 (s, methylene of cod), 93.4 (s, olefin of cod), 97.1 (d, J = 11.9 Hz, olefin of cod), 99.0 (d, J = 11.1 Hz, olefin of cod), 99.9 (s, olefin of cod), 65.9 (s, OCH$_2$py), 70.5 (d, J = 3.5 Hz, Ir−CH(O)Ar), 157.9 (s, C^6 of py). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.5 (s). MS (FAB): m/z 684 ($M^+ - PF_6$). IR (Nujol): 2249, 1605, 1088, 839 cm^{-1}. Anal. Found: C, 47.66; H, 4.14; N, 1.65. Calcd for $C_{33}H_{34}F_6IrNOP_2$: C, 47.82; H, 4.13; N, 1.69.

[13] Crystal data for **3a**: $C_{33}H_{34}F_6IrNO_2P_2$, (M_r = 830.77), monoclinic, space group $P2_1/n$, a = 15.760(3) Å, b = 12.202(5) Å, c = 17.202 Å, β = 109.754(12)°, V = 3103.8(14) Å^3, Z = 4, D_{calcd} = 1.778 g/cm^3, μ = 4.470 mm^{-1}, R_{int} = 0.0205, R1(all) = 0.0548, R1(obsd) = 0.0335 (>2.0$\sigma(I)$), wR2(all) = 0.0956, wR2(obsd) = 0.0807 (>2.0$\sigma(I)$).

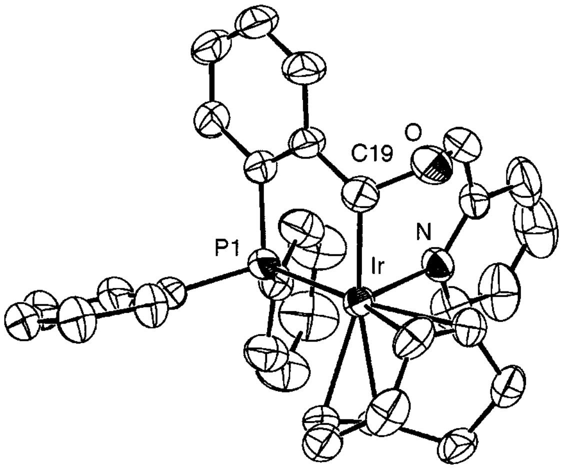

Figure 2. ORTEP drawing of the X-ray crystal structure of the cationic part of **3a**. Selected interatomic distances (Å) and angles (deg) are as follows: Ir−O19 = 2.092(5), Ir−P1 = 2.2677(14), Ir−N = 2.258(4); N−Ir−P1 = 89.04(11), P1−Ir−Cl9 = 84.85(16), Cl9−Ir−N = 86.2(2), P1−Ir−H0 = 86.9(19), Cl9−Ir−H0 = 82.9(18), N−Ir−H0 = 168.6(18).

and the kinetic studies using ^{1}H NMR, the thermodynamic and kinetic parameters for the oxidative addition of eq 2 were determined; at 30 °C $\Delta G = -0.878(13)$ kcal/mol, $\Delta G_1^{\ddagger} = 24.53(8)$ kcal/mol, $\Delta H_1^{\ddagger} = 21.4(5)$ kcal/mol, and $\Delta S_1^{\ddagger} = -10.0(34)$ cal/Kmol.[14]

To our knowledge, this is the first example of a determination of the molecular structures of both complexes, which show equilibration before and after intramolecular C−H bond activation.[16] The reason we can isolate both complexes is explained by the following two findings. (i) The obtained iridium(I) complex **2a** is precipitated as crystals immediately from the reaction mixture before C−H bond activation occurs, due to its poor solubility in ethanol. (ii) Although there is no evidence for agostic interaction between the benzylic proton and the iridium from the X-ray analysis of complex **2a** (Ir−C$_{\text{benzyl}}$ distance is 3.487(4) Å),[18] appropriate interaction between the oxygen atom and the iridium metal would regulate the oxidative addition as well as the reductive elimination; the formation of the [6,5]-fused bimetallacycle in **2a** and the energetically similar [5,6]-fused bimetallacycle in **3a** prepared by the reconstruction of the chelate coordination of the coordinatively flexible PN$_{n=1}$ ligand brought about the isolation of both complexes.

Analogous cationic complexes [Ir(cod)(PN$_n$)]PF$_6$ (**2b**, $n = 2$; **2c**, $n = 3$) were prepared by methods similar to the synthesis of **2a**. As can be seen from their spectrometric data and an X-ray analysis (for **2b**),[19] their structures bear a resemblance to that of **2a**. The X-ray analysis of **2b** shows that the distance between the oxygen atom and the iridium center (2.867 (4) Å) is longer than the sum of the van der Waals radii (vide supra).[10] The ^{1}H NMR spectra of the benzylic protons in **2b** and **2c**, respectively, at 30 °C show two broad doublet signals, different from the sharp doublet signal for **2a**. These observations suggest that the interactions between the oxygen atom and the iridium atom in **2b** and **2c** are weaker compared to that in **2a**, both in the solid state and in solution, and actually their C−H bond activation occurred only very slowly or not at all.[20] One reason could be that complexes **2b** and **2c** would form energetically unfavorable [5,7]- and [5,8]-fused bimetallacycles, respectively, by oxidative addition of the benzylic C−H bonds.

In summary, we have demonstrated reversible C−H bond activation and clarified the structures of Ir(I) and Ir(III) complexes before and after the C−H bond activation. The flexibility of the PN ligand in its coordination to the central metal is an important factor for the isolation of both Ir complexes.

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Supporting Information Available: Text giving synthetic procedures and spectroscopic and analytical data for **2a**, **2b**, **2c**, **3a**, and IrCl(cod)(PN$_{n=1}$) and text and tables giving X-ray structural information on **2a**, **2b**, and **3a**. The material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Normally CHCl$_3$ reacts with metal hydride complexes to afford the corresponding metal chlorides and CH$_2$Cl$_2$.[15] In fact, we observed the slow decomposition of **3a** generating a trace of unknown products after 90 h at 30 °C only when **3a** was dissolved in CDCl$_3$; however, the effect of the decomposition was negligible for the estimation of the kinetic parameters.

(15) Schunn, R. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 244−246.

(16) Although a system in which an Ir(I) complex and its C−H bond activation product Ir(III) complex are in equilibrium has been reported by Eisenberg,[17] the reverse process from the Ir(III) complex to the Ir(I) complex is not clear.

(17) Cleary, B. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1995**, *117*, 3510.

(18) The observed kinetic isotope effect of 2.8 (50 °C) in the oxidative addition indicates that an alkane complex is not a key intermediate in this reversible C−H bond activation.

(19) An ORTEP drawing and crystal data for **2b** are provided in the Supporting Information.

(20) Thermolysis of **2b** in CDCl$_3$ at 30 °C for 7 days did not show any evidence of C−H bond activation. In the sample obtained after thermolysis of **2c** in CDCl$_3$ at 30 °C for 7 days, a small amount of hydride species (<5%) was observed, but it could not be characterized.