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Oxidative Addition of N-H Bonds to Iridium: Synthesis and Structure of (Heterocyclic amine)iridium Hydride Complexes

While the area of C-H activation chemistry has attracted a great deal of activity over the past several years,[1] there has been much less effort devoted to examining N-H bond activation in spite of the possibilities for developing systems for the catalytic functionalization of ammonia and other amines. Examples in the literature of oxidative-addition reactions of N-H bonds with transition-metal complexes are rare,[2] many dealing with chelate-assisted N-H bond addition. Recently, the addition of amide N-H bonds to low-valent Fe and Ru compounds was reported,[3] but the most intriguing reports to date have come from Du Pont Central Research, where oxidative-addition of NH_3 and aniline was demonstrated, the latter as part of a catalyst system capable of adding aniline to norbornene.[4] Recently we have reported the oxidative addition of aromatic C-H bonds to Ir using $[Ir(COD)PMe_3)_3]Cl$ (COD = cyclooctadiene) and the further reactions of the resulting iridium hydride complexes with alkynes.[5] We believed that this iridium system would provide us with an ideal opportunity to examine the general reactions of a series of E-H compounds with iridium (E = C, B, H, Al, Si) and the reactivity of the resulting hydrides. In a separate paper we have reported some results with B-H compounds,[6] and in this paper we discuss our initial results with N-H compounds.

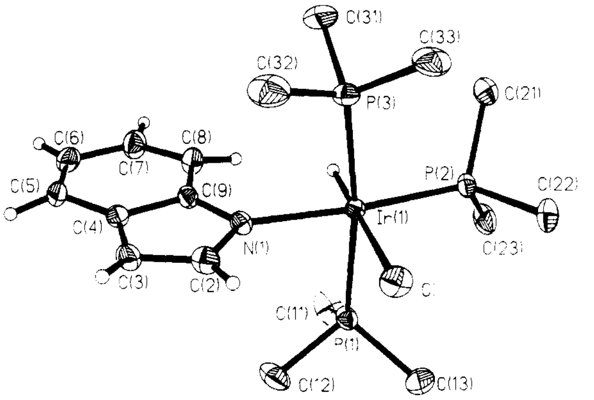

Figure 1. ORTEP plot of **1b** (PMe_3 hydrogen atoms omitted for clarity). Important bond distances (Å): Ir(1)-Cl, 2.491 (2); Ir(1)-P(1), 2.326 (2); Ir(1)-P(2), 2.271 (2); Ir(1)-P(3), 2.335 (2); Ir(1)-N(1), 2.131 (4); Ir(1)-H(1), 1.489 (49). Important bond angles (deg): Cl-Ir(1)-P(1), 89.1 (1); Cl-Ir(1)-P(2), 96.0 (1); P(1)-Ir(1)-P(2), 95.0 (1); Cl-Ir(1)-P(3), 88.7 (1); P(1)-Ir(1)-P(3), 170.6 (1); P(2)-Ir(1)-P(3), 94.4 (1); Cl-Ir(1)-N(1), 91.6 (1); P(1)-Ir(1)-N(1), 85.7 (1); P(2)-Ir(1)-N(1), 172.3 (1); P(3)-Ir(1)-N(1), 85.2 (1); Cl-Ir(1)-H(1), 179.0 (19); P(1)-Ir(1)-H(1), 91.6 (20); P(2)-Ir(1)-H(1), 84.6 (18); P(3)-Ir(1)-H(1), 90.5 (20); N(1)-Ir(1)-H(1), 87.7 (18).

Heating $[Ir(COD)(PMe_3)_3]Cl$[7] with the heterocyclic amines pyrrole,[8] indole,[9] 3-methylindole,[10] and 7-azaindole[11] leads to the

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(1) Some important references: (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Hingham, MA, 1984 (also references therein). (b) Bergman, R. G. *Science* **1984**, *223*, 902. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (d) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. M.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (f) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (g) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (h) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(2) (a) Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254. (b) Nelson, J. H.; Schmidt, D. L.; Henry, R. A.; Moore, D. W.; Jonassen, H. B. *Inorg. Chem.* **1970**, *9*, 2678. (c) Sappa, E.; Milone, L. *J. Organomet. Chem.* **1973**, *61*, 383. (d) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098. (e) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328. (f) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (g) Suss-Fink, G. *Z. Naturforsch. B* **1980**, *35B*, 454. (h) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56. (i) Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* **1982**, 907. (j) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014. (k) Lin, Y.-C.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1984**, *272*, 207. (l) Park, S.; Johnson, M. P.; Roundhill, D. M. *Organometallics* **1989**, *8*, 1700.

(3) Schaad, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 1628.

(4) (a) Casalnuova, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.

(5) Merola, J. S. *Organometallics* **1989**, *8*, 2975.

(6) Knorr, J. R.; Merola, J. S. *Organometallics*, in press.

(7) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

(8) A 0.42-g (0.75-mmol) quantity of $[Ir(COD)(PMe_3)_3]Cl$ was dissolved in 2.0 mL of dry pyrrole, and the mixture was refluxed under N_2 for 16 h. A small amount of solid was filtered out, and the pyrrole was removed under reduced pressure to yield a brown oil. The oil was dissolved in 5 mL of dry THF, and the mixture was then concentrated to 0.5 mL and treated with 2 mL of dry pentane to crystallize pale yellow solids. The solids were collected and dried to yield 0.36 g (0.69 mmol, 93%) of $Ir(PMe_3)_3(Cl)(H)(NC_4H_4)$ (**1a**), identified on the basis of the following information. ^1H NMR (270 MHz at 20 °C in $CDCl_3$): δ -22.12 (dt, J_{P-H} = 17, 15 Hz, 1 H, Ir-H), 1.28 (t, J_{P-H} = 3.6 Hz, 18 H, trans PMe_3), 1.65 (d, J_{P-H} = 9.4 Hz, cis PMe_3), 5.98-5.99 (m, 2 H, H(3) and H(4), NC_4H_4), 6.39 (m, 1 H, H(5), NC_4H_4), 7.18 ppm (m, 1 H, H(2), NC_4H_4). $^{31}P\{^1H\}$ NMR (81 MHz at 20 °C in $CDCl_3$): δ -50.85 (vbr, 1 P, cis PMe_3), -34.02 ppm (d, J_{P-P} = 42 Hz, 2 P, trans PMe_3). ^{13}C NMR (50 MHz at 20 °C in $CDCl_3$): δ 15.88 (t, J_{P-C} = 18.3 Hz, trans PMe_3), 20.48 (d, J_{P-C} = 37 Hz, cis PMe_3), 104.2, 106.9, 128.6, 135.1 ppm (all s, NC_4H_4). Anal. Calcd (found): C, 29.86 (29.92); H, 6.17 (6.19). IR (CH_2Cl_2) ν_{Ir-H} = 2168 cm^{-1}.

(9) A suspension of 1.0 g (1.78 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ and 0.208 (1.78 mmol) of indole was refluxed under N_2 in 4 mL of dry mesitylene for 18 h. After 18 h, the mixture was a pale pink solution with off-white solids suspended. The precipitate was filtered out, washed with pentane, and dried to yield 0.70 g (1.21 mmol, 68%) of $Ir(PMe_3)_3(H)(Cl)(NC_8H_6)$ (**1b**), identified on the basis of the following information. ^1H NMR (270 MHz at 20 °C in acetone-d_6): δ -20.86 (dt, J_{P-H} = 16, 14 Hz, 1 H, Ir-H), 1.15 (t, J_{P-H} = 3.6 Hz, 18 H, trans PMe_3), 1.79 (d, J_{P-H} = 9.8 Hz, cis PMe_3), 6.24 (d, J = 1.2 Hz, 1 H, H(3), NC_8H_6), 6.67 (dt, J = 7.7, 0.9 Hz, 1 H, H(5), NC_8H_6), 6.78-6.84 (m, 1 H, H(6), NC_8H_6), 7.34 (dd, J = 7.7, 0.6 Hz, 1 H, H(7), NC_8H_6), 7.43 (dd, J = 8.3, 0.6 Hz, 1 H, H(4), NC_8H_6), 8.04-8.03 ppm (m, 1 H, H(2), NC_8H_6). $^{31}P\{^1H\}$ NMR (81 MHz at 20 °C in $CDCl_3$): δ -49.44 (br t, J_{P-P} = 22 Hz, 1 P, cis PMe_3), -33.70 ppm (d, J_{P-P} = 21 Hz, 2 P, trans PMe_3). Anal. Calcd (found): C, 35.63 (35.36); H, 5.98 (5.85). IR (CH_2Cl_2): ν_{Ir-H} = 2221 cm^{-1}.

(10) A suspension of 0.25 g (0.44 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ and 0.064 g (0.49 mmol) of 3-methylindole was refluxed under N_2 in 3 mL of mesitylene for 15 h. After 15 h, the reaction mixture was a brown solution with a white precipitate. The precipitate was collected and washed with pentane to yield 0.16 g (0.27 mmol, 62%) of $Ir(PMe_3)_3(H)(Cl)(NC_9H_8)$ (**1c**), identified on the basis of the following information. ^1H NMR (270 MHz at 20 °C in acetone-d_6): δ -20.92 (q, J_{P-H} = 16 Hz, 1 H, Ir-H), 1.14 (t, J_{P-H} = 3.6 Hz, 18 H, trans PMe_3), 1.78 (d, J_{P-H} = 9.8 Hz, cis PMe_3), 2.31 (s, 3 H, 3-methyl), 6.63-6.84 (m, 2 H, H(5) and H(6), NC_9H_8), 7.25-7.35 (m, 2 H, H(4) and H(7), NC_9H_8), 7.81 ppm (s, 1 H, H(2), NC_9H_8). $^{31}P\{^1H\}$ NMR (81 MHz at 20 °C in $CDCl_3$): δ -49.00 (br t, J_{P-P} = 22 Hz, 1 P, cis PMe_3), -33.42 ppm (d, J_{P-P} = 21 Hz, 2 P, trans PMe_3). Anal. Calcd (found): C, 36.83 (36.86); H, 6.18 (6.22). IR (CH_2Cl_2): ν_{Ir-H} = 2180 cm^{-1}.

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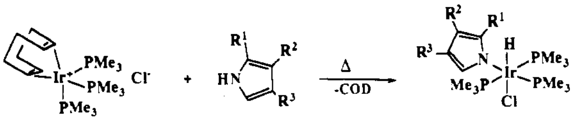
production of amidoiridium hydride compounds (eq 1) through oxidative addition of the N–H bond.



(1)

1a:  = pyrrole

1b: " " = indole

1c: " " = 3-methylindole

1d: " " = 7-azaindole

We had already have seen that [Ir(COD)(PMe$_3$)$_3$]Cl would react with aromatic C–H bonds,[5] so the site of oxidative addition in these compounds (C–H or N–H) was of some concern. That the iridium is attached to the rings in these compounds via an Ir–N bond was established as follows: First, both the ^{1}H and ^{31}P NMR spectra clearly indicate that the three PMe$_3$ ligands are arranged in meridional fashion around the iridium. The ^{31}P NMR spectra of the central PMe$_3$ in all compounds is extremely broad, an indication of coupling to a trans N. Second, in the ^{13}C NMR spectra there is no resonance attributable to a carbon atom directly bound to iridium. (Such a carbon would appear as a doublet of triplets due to P–C coupling.) This is most clearly seen is the case of the pyrrole compound, where the four ring carbons all appear as singlets in the ^{13}C{^{1}H} NMR spectrum. Third, there is no N–H stretch in the IR spectra of any of the compounds **1a–d**.

The X-ray structure of the indole compound, **1b**, was obtained, and the resulting ORTEP plot is shown in Figure 1.[12] The solid-state structure of **1b** confirmed the structure assigned by spectroscopy: an octahedral arrangement of ligands about the iridium with the three PMe$_3$ groups in a meridional arrangement and the indole group trans to PMe$_3$. The Ir–N distance of 2.131 (4) Å seems to be in line with those found in other crystallography characterized Ir–N compounds with similar trans ligands.[4] The relatively short Ir–P distance for the PMe$_3$ trans to the indole (2.271 (2) Å) compared to those for the mutually trans PMe$_3$ ligands (2.326 (2) and 2.335 (2) Å) shows that indole (unlike phenyl where the same values are 2.339 (2) Å vs 2.307 (2) and 2.306 (2) Å[13]) does not exert as strong a trans influence as phenyl and is weaker than PMe$_3$. The hydride in this compound was located and refined. The Ir–Cl distance of 2.491 (2) Å is quite long, presumably due to the strong trans influence of the hydride.

The NMR spectra of compounds **1a–d** show evidence for hindered rotation about the Ir–N bond in solution. This is most clearly seen in the case of the pyrrole compound, **1a**, where signals of the four pyrrole protons in the ^{1}H NMR spectrum and the four pyrrole carbons in the ^{13}C NMR spectrum are all inequivalent. Molecular modeling[14] of these compounds suggests that a large barrier to rotation about the Ir–N bond can be accounted for on the basis of steric factors alone, with rotation being blocked by the cis PMe$_3$ ligands. Moreover, for the indole compounds there are two different conformations possible: with the C$_6$ ring on the same side of the Ir as the hydride ligand and with the C$_6$ ring on the same side of the iridium as the chloride ligand. The solid-state structure for the indole compound **1b** is that with the C$_6$ ring on the same side as hydride. The solution structure as seen in the ^{1}H and ^{13}C NMR spectra would indicate that there is only one conformation in solution. We presume that the solid-state structure persists in solution due to the hindered rotation about the Ir–N bond, and it is this conformation with the C$_6$ ring on the same side of the iridium as hydride that minimizes unfavorable interactions between Cl and the hydrogens on the C$_6$ ring.

Initial experiments to explore the reactivity of compounds **1a–d** show that they are less reactive than the hydrido compounds obtained from C–H or B–H addition. For example, the phenyliridium hydride compound previously reported will undergo reactions with alkynes[5] upon removal of the chlorine as Cl$^-$ with Tl$^+$, but compounds **1a–d** only sluggishly react with Tl$^+$.[15] This would seem to indicate that an N-bonded pyrrole-type ring is a much stronger electron-withdrawing group than a phenyl, making it difficult to remove Cl$^-$.

In conclusion, reactions shown in eq 1 leading to compounds **1a–d** show that oxidative additions of N–H bonds to iridium in Ir[(COD)(PMe$_3$)$_3$]Cl are facile. We are continuing our investigations into this system with special attention directed toward making the amine hydride complexes more reactive so that we may explore the possibility of N–H addition across unsaturated molecules.

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Supplementary Material Available: Listings of final atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for **1b** (3 pages). Ordering information is given on any current masthead page.

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(11) A suspension of 0.25 g (0.44 mmol) of [Ir(COD)(PMe$_3$)$_3$]Cl and 0.058 g (0.49 mmol) of 7-azaindole was refluxed under N$_2$ in 3 mL of mesitylene for 15 h. After 15 h, the reaction mixture was a pale yellow solution with a white precipitate. The precipitate was filtered out and washed with pentane to yield 0.13 g (0.23 mmol, 52%) of (Me$_3$P)$_3$Ir(H)(Cl)(NC$_7$H$_5$N) (**1d**), identified on the basis of the following information. ^{1}H NMR (270 MHz at 20 °C in CDCl$_3$): δ −20.66 (dt, $J_{\text{P-H}}$ = 16, 14 Hz, 1 H, Ir–H), 1.14 (t, $J_{\text{P-H}}$ = 3.5 Hz, 18 H, trans PMe$_3$), 1.72 (d, $J_{\text{P-H}}$ = 9.6 Hz, cis PMe$_3$), 6.36 (d, $J_{\text{H-H}}$ = 2.9 Hz, 1 H, H(3), N$_2$C$_7$H$_5$), 6.74 (dd, $J_{\text{H-H}}$ = 7.4, 4.6 Hz, 1 H, H(5), N$_2$C$_7$H$_5$), 7.75 (dd, $J_{\text{H-H}}$ = 7.1, 1.1 Hz, 1 H, H(2), N$_2$C$_7$H$_5$), 8.19–8.23 ppm (m, 2 H, H(4) and H(6), N$_2$C$_7$H$_5$). ^{31}P{^{1}H} NMR (81 MHz at 20 °C in CDCl$_3$): δ −49.09 (br t, $J_{\text{P-P}}$ = 22 Hz, 1 P, cis PMe$_3$), −33.82 ppm (d, $J_{\text{P-P}}$ = 22 Hz, 2 P, trans PMe$_3$). Anal. Calcd (found): C, 33.48 (33.25); H, 5.79 (5.84). IR (CH$_2$Cl$_2$): $\nu_{\text{Ir-H}}$ not observed.

(12) Crystal structure data for **1b**, C$_{17}$H$_{34}$Cl$_1$Ir$_1$N$_1$P$_3$, are as follows. Crystals were grown by slow diffusion of pentane into a CHCl$_3$ solution of **1b**. A pale yellow distorted cube of approximate dimensions 0.2 × 0.2 × 0.2 mm was chosen for the X-ray diffraction study. The crystal belongs to the monoclinic space group $P2_1/c$, with a = 9.316 (3) Å, b = 13.647 (3) Å, c = 18.288 (4) Å, β = 95.75 (2)°, V = 2313 (1) Å^3, and d_{calcd} = 1.645 g cm^{-3} for Z = 4. Data were collected at 298 K on a Nicolet R3m/V diffractometer with Mo Kα radiation (λ = 0.71073 Å) and θ–2θ scans. A total of 4097 independent reflections were collected with 3541 observed ($F > 3.0\sigma(F)$). A semiempirical absorption correction based on a series of ψ scans was applied to the data. The structure was solved by using Patterson methods and refined by using full-matrix least-squares procedures employing the SHELXTL-Plus software as supplied by Nicolet Corp. The hydride hydrogen atom and the indole hydrogen atoms were located and refined isotropically. All other hydrogen atoms (PMe$_3$ ligands) were placed at calculated positions. Non-hydrogen atoms were refined anisotropically. The solution refined with the final residuals R = 0.0262 and R_w = 0.0356.

(13) Merola, J. S. Unpublished results.

(14) Modeling was done with Chem-X distributed by Chemical Design Ltd., Oxford, England.

(15) While Ir(H)(Cl)(phenyl)(PMe$_3$)$_3$ reacts rapidly and quantitatively at room temperature with Tl[PF$_6$] in CH$_2$Cl$_2$ solution in the presence of ligands,[5] compounds **1a–d** show little reaction after several days under those conditions.