convention, recommended by IUPAC, has been used in reporting all chemical shifts. Infrared spectra were recorded from mineral oil mulls or dichloromethane solutions with a Perkin-Elmer 180 or IBM IR32 spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8450A spectrophotometer. Emission spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrophotometer. Electrochemical measurements were made with an EG&G Princeton Applied Research Model 173 potentiosat/galvanostat with a Model 179 digital coulometer plug-in. For cyclic voltammetric measurements a Model 175 universal prorammer was used also. All potentials reported are for degassed dichloromethane solutions containing 0.5 mM compound and 0.1 *M* tetrabutylammonium perchlorate. An Ag/AgCl reference electrode was used in all measurements. The ferrocenium/ferrocene potential was measured as 0.49 (1) V under these conditions.

X-ray Structure Determination and Refinement. Well-formed green plates were obtained from a green dichloromethane solution of the complex which was layered with 1 drop of methanol followed by several mL of diethyl ether. The crystals were handled while immersed in a hydrocarbon oil in order to retard loss of lattice solvent and prevent fracture. A suitable crystal was mounted on a glass fiber with use of silicone grease and placed in the cold stream of the diffractometer. No decay in the intensities of two standad reflections was observed during the course of data collection. Crystal data and information regarding data collection are given in Table V.

The usual corrections for Lorentz and polarization effects were applied to the data. Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer. Scattering factors and corrections for anomalous dispersion were from the *International Tables*.[29]

Solution of the structure was accomplished by a combination of Patterson and Fourier methods. The species of interest, the trirhodium cation, displays no disorder. However, the structure exhibits disorder in the remaining region of the crystal lattice. Although only three PF_6^- groups are required by stoichiometry, there are actually four sites (some with partial occupancy) for these anions. All of these PF_6^- groups have different types of disorder. This is depicted in a figure in the supplementary material. In addition there are three partially occupied sites for molecules of dichloromethane. Figure 2 of the supplementary material is a stereoview of the region of the lattice that contains these disordered molecules.

Six low-angle reflections affected by extinction were omitted from the data. An absorption correction was applied.[30] In the final cycles of refinement, rhodium, phosphorus, fluorine, and chlorine (except Cl(6a and b)) atoms were assigned anisotropic thermal elipsoids. Hydrogen atoms in the cation were included in the structure factor calculation by use of a riding model, with C–H of 0.96 Å and $U_{iso} = 1.2U_{iso}$ for the bonded carbon. In the final difference map there were several features of ca. 1.0 eÅ^{-3} in height, all in the region of the disordered anions and dichloromethane. In view of the severe disorder present, the final *R* value of 0.095 is not unreasonable.

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Registry No. **2**, 115559-93-8; **2**·1.3CH_2Cl_2, 115649-39-3; **4a**, 115590-24-4; **4b**, 115559-95-0; **4c**, 115559-97-2; **5**, 115559-98-3; **6**, 115590-25-5; $[Rh_3(CO)_3(\mu\text{-}Cl)Cl(\mu\text{-}dpmp)_2][BPh_4]$, 84774-75-4.

Supplementary Material Available: Listings of all bond distances, bond angles, hydrogen atom positions, and anisotropic thermal parameters and figures showing the disordered regions (11 pages); listing of structure factors (53 pages). Ordering information is given on any current masthead page.

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(30) The program XABS obtains an absorption tensor from $F_o - F_c$. Hope, H.; Moezzi, B., Department of Chemistry, University of California, Davis, CA.

Rational Design in Homogeneous Catalysis. Ir(I)-Catalyzed Addition of Aniline to Norbornylene via N–H Activation

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Abstract: The first successful demonstration of the amination of an olefin by a transition-metal-catalyzed N–H activation mechanism was accomplished in a stepwise manner with an Ir(I) catalyst and the substrates aniline and norbornylene. The initial N–H oxidative addition step envisioned in such a mechanism was demonstrated for the complexes $Ir(PMe_3)_4PF_6$, $Ir(PMe_3)_3(C_8H_{14})Cl$, and $Ir(PEt_3)_3Cl$, all of which gave rise to stable cis anilido hydride complexes when reacted with aniline. The second step, olefin insertion, was accomplished from the reaction of $Ir(PEt_3)_2(C_2H_4)_2Cl$ (**1**) with aniline and norbornylene. The resulting insertion product, $Ir(PEt_3)_2(NHPhC_7H_{10})(H)Cl$ (**6**), was characterized by NMR spectroscopy and single-crystal X-ray diffraction and was found to have an azoiridacyclobutane type structure. The relevant crystal data for **6** are $a = 10.702$ (3) Å, $b = 13.176$ (21) Å, $c = 19.498$ (5) Å, $\beta = 98.61$ (2); $P2_1/c$, $T = -70$ °C, $d_c = 1.591$ g/cm^3, $\mu = 51.21$ cm^{-1}; 3029 reflections, $R = 0.039$ and $R_w = 0.036$. Decomposition studies of **6** established two competing reaction pathways. C–N and Ir–C bond breaking, the microscopic reverse of the formation of **6**, gave norbornylene and a reactive Ir intermediate. The competing pathway of C–H reductive elimination occurs by prior ligand dissociation and yields the amination product, *exo*-2-(phenylamino)norbornane (**7**). Labeling studies indicated an overall cis addition of the N–H group across the exo face of norbornylene. The individual steps for this reaction were elaborated into a catalytic cycle for the addition of aniline to norbornylene and a mechanism based on these individual steps proposed.

Rational design of transition-metal homogeneous catalysis is an attractive but generally difficult goal to accomplish. Our initial results on the activation of ammonia by an electron-rich Ir complex prompted us to investigate such a design for the amination of olefins.[1] Here we report on the results of this study, leading to the first successful demonstration of the catalytic amination of an olefin by N–H activation.

Transition-metal-promoted amination of olefins is generally stoichiometric and is based on nucleophilic attack of a free amine on an olefin coordinated to a high-valent metal center.[2] A

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(1) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.

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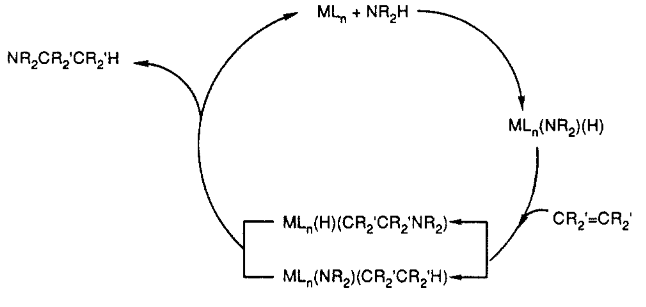
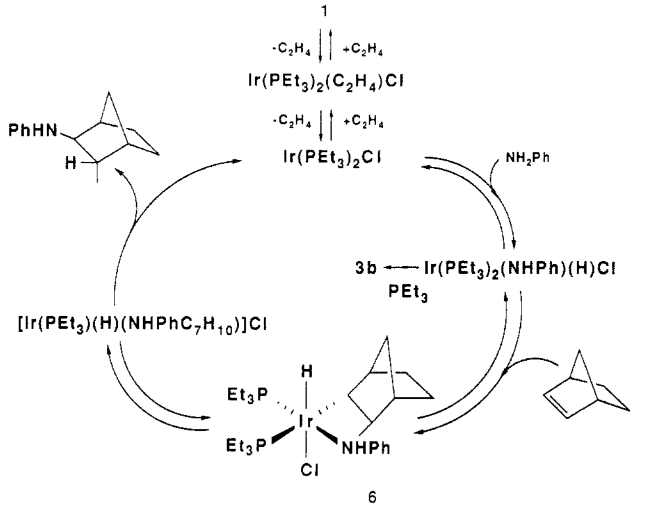
Scheme I



Scheme II



potentially different approach, based on N–H activation, is shown in Scheme I.

To date, there are no examples of such a mechanism for the catalytic amination of olefins, though some of the individual steps have been observed. The oxidative addition reactions of ammonia and aniline to the late transition-metal complexes $M_3(CO)_{12}$ (M = Ru, Os) have been reported, and we have found that certain electron-rich Ir(I) complexes will undergo this reaction.[1,3a–e] We have previously reported, for example, the oxidative addition of NH_3 by **1** (eq 1).[1] The oxidative addition reaction of imides and

$$Ir(PEt_3)_2(C_2H_4)_2Cl + NH_3(l) \rightarrow [Ir(PEt_3)_2(H)(NH_3)(\mu\text{-}NH_2)]_2(Cl)_2 + C_2H_4 \quad (1)$$

chelate assisted N–H oxidative addition reactions to group VIII metals have also been reported.[3f–i] Recently, the formal insertion of acrylonitrile into the Pt–N bond of *trans*-$Pt(PEt_3)_2(H)(NHPh)$ and the subsequent reductive elimination of 3-anilinopropionitrile was reported.[4] A catalytic cycle was not possible in this system, however, since N–H oxidatve addition is thermodynamically unfavorable. In the case of complex **2**, it was possible to introduce unsaturated ligands into the metal coordination sphere; however, insertion does not take place, perhaps because of the high stability of the amido bridge.[1] In an effort to overcome this problem and promote olefin amination by N–H activation, further modifications of this system were explored.

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere by using either Schlenk techniques or a Vacuum Atmospheres drybox. Solvents were dried and degassed before use. Zinc chloride, norbornylene, 5-methyl-2-norbornene, and *exo*-2-aminonorbornane were obtained from Aldrich and were used without further purification. Aniline, also obtained from Aldrich, was distilled from CaH_2 and passed through alumina prior to use. $TIPF_6$ was obtained from Strem Chemicals and used without further purification. Aniline-^{15}N (96.6%) was obtained from Stohler Isotope Chemicals and aniline-N,N-d_2 (99%) was obtained from MSD Isotopes. $Ir(PEt_2)(C_2H_4)_2Cl$,[1] $[Ir(PMe_3)_4]PF_6$,[5] $Ir(PMe_3)_3(C_8H_{14})Cl$,[5] and $Cr(CO)_3(C_6H_5F)$[6] were prepared according to published procedures. $Ir(PEt_3)_3Cl$ was prepared by adding 6 equiv of PEt_3 to $[Ir(C_8H_{14})_2Cl]_2$ in diethyl ether. IR, ^1H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra were recorded on Perkin-Elmer 983G and QE 300, and Nicolet 300 spectrometers. GC analyses were obtained using a Hewlett Packard 5890 gas chromatograph with a high-performance cross-linked methyl silicone capillary column. GC yields were determined with *m*-xylene as an internal standard.

I. $Ir(PMe_3)_3(NHPh)(H)Cl$ (3a). A solution of $Ir(PMe_3)_3(C_8H_{14})Cl$ (0.500 g, 0.88 mmol) in 10 mL of aniline was stirred at 0 °C overnight. Excess aniline was extracted with two 75-mL portions of pentane. The residue was then slurried in 50 mL of Et_2O and the resulting off-white precipitate was filtered, washed with Et_2O, and dried vacuo. Yield 320 mg (65%). IR (Nujol) ν_{N-H} 3349, ν_{Ir-H} 2227, ν_{Ir-Cl} 227 cm^{-1}. ^1H NMR (C_5D_5N) −21.59 (d of t, J_{P-H} = 19.8, 14.1 Hz, 1 H, IrH), 1.47 (t, J_{P-H} = 4, 18 H, PCH_3), 1.58 (d, J_{P-H} = 9.5, 18 H, PCH_3), 2.81 (s, 1 H, NH), 6.30 (t, J_{H-H} = 7.0, 1 H), 6.51 (d (br), 7.8, 1 H), 6.72 (d (br), 7.8, 1 H), 7.03 (t (br), 7.5, 1 H), 7.22 (t (br), 7.5, 1 H). $^{31}P\{^1H\}$ (C_5D_5N) −37.4 (d, J_{P-P} = 20, 2 P), −53.0 (t, J_{P-H} = 20, 1 P). $^{13}C\ \{^1H\}$ (C_5D_5N) 15.9 (t, J_{P-C} = 18.4, PCH_3), 20.23 (d of t, J_{P-C} = 36.5, 2.0, PCH_3), 112.8 (s, Ar-C), 115.7 (s, Ar-C), 115.8 (s, Ar-C), 129.0 (s, Ar-C), 129.4 (s, Ar-C), 158.5 (d, 3.2, Ar-C). With aniline-^{15}N:$^{31}P\{^1H\}$ (THF-d_8) −34.7 (d, J_{P-P} = 20, 2 P), −50.5 (d of t, J_{P-P} = 20, J_{N-P} = 45.4, 1 P). ^1H (THF-d_8) as before except 2.28 (d, J_{N-H} = 76, 1 H, NH).

II. $Ir(PEt_3)_3(NHPh)(H)Cl$ (3b). The complex **3b** was not isolated in a pure form in the solid state; however, solutions containing **3b** as the major species were prepared in two ways.

(i) $Ir(PEt_3)_3Cl$ (0.200 g, 0.343 mmol) and aniline (0.100 g, 1.07 mmol) were dissolved together in 2 mL of THF and heated at 50 °C for 12 h. The resulting light-orange solution was stripped in vacuo and then analyzed by ^{31}P NMR in THF-d_8 solution. **3b** was found to be the major phosphorus-containing product present (about 80% of total phosphorus species present). The other species were not identified.

(ii) **6** (0.025 g, 0.038 mmol) and PEt_3 (0.010 g, 0.085 mmol) were dissolved together in an NMR tube with THF-d_8. The solution was heated at 80 °C for 1 h and then analyzed by ^1H and ^{31}P NMR. These spectra were consistent with the presence of PEt_3, norbornylene, and **3b** as the major products (~90%). ^1H (THF-d_8) −21.47 (d of t, J_{P-H} = 13.2, 17.6 Hz, 1 H, IrH), 1.09 (m, 27 H, CH_3), 1.85 (m, 18 H, PCH_2), 2.29 (s, 1 H, NH), 5.81 (t, J_{H-H} 7.0, 1 H, ArH_{para}), 6.15 (d, J_{H-H} = 7.4, 1 H, ArH_{ortho}), 6.28 (d, J_{H-H} = 8.1, 1 H, ArH_{ortho}), 6.59 (t, J_{H-H} = 7.3, 1 H, ArH_{meta}), 6.74 (t, J_{H-H} = 7.4, 1 H, ArH_{meta}). ^{31}P (THF-d_8) −14.9 (d, J_{P-P} = 18.5, 2 P), −23.4 (t, J_{P-P} = 18.5 1 P). With aniline-^{15}N: −14.8 (d, J_{P-P} = 18.5, 2 P), −23.4 (d of t, J_{P-P} = 18.5, J_{P-N} = 43.9, 1 P).

III. *cis*-$[Ir(PMe_3)_4(NHPh)(H)PF_6$ (4). A deep red solution of $[Ir(PMe_3)_4]PF_6$ (0.680 g, 1.06 mmol) in 20 mL of aniline was heated at 75 °C for 36 h. The resulting light-orange solution was cooled to room temperature, and the excess aniline was extracted with two 50-mL portions of pentane. Diethyl ether was added to the gummy, pale-yellow residue to give a light-orange powder. The solid was filtered and washed with Et_2O. Analysis of this crude product showed it to be an approximately 50/50 mixture of complexes **4** and **5**. The two complexes were separated by slurrying the crude solid in 5 mL of THF followed by filtration. The remaining solid, found to be pure **4** by subsequent analysis, was dried in vacuo. Yield 380 mg (49%). IR (Nujol) ν_{N-H} = 3401, ν_{Ir-H} = 2094 cm^{-1}. ^1H NMR (C_5D_5N) −11.27 (d of q, J_{P-H} = 140, 18.5, 1 H, Ir-H), 1.54 (t, 3.5, 18 H, PCH_3), 1.57 (d, 8.5, 9 H, PCH_3), 1.74 (d, 8.5, 9 H, PCH_3), 6.45 (t, 7.0, 1 H, Ar-H), 6.58 (d (v br), 1 H, Ar-H), 6.71 (d (v br), 1 H, Ar-H), 7.08 (t (v br), 1 H, Ar-H), 7.25 (t (v br), 1 H, Ar-H). $^{31}P\ \{^1H\}$ (C_5D_5N) −45.3 (t, J_{P-P} = 19.5 2 P) −56.0 (s (v br), 1 P) −57.9 (q, 16.0, 1 P).

IV. $[Ir(PMe_3)_3(PMe_2CH_2)(H)]PF_6$ (5). Complex **5** was obtained from $[Ir(PMe_3)_4]PF_6$ as the major product in the presence of aniline when long reaction times or elevated temperatures were employed. For example, a solution of $[Ir(PMe_3)_4]PF_6$ (0.740 g, 1.15 mmol) and 3 mL

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of aniline in 20 mL of THF was heated at 100 °C in a Fisher-Porter pressure tube for 12 h. The resulting light-orange solution was cooled to room temperature and filtered. THF was removed from the filtrate in vacuo and aniline was extracted from the residue with pentane (3 × 50 mL) followed by Et_2O (3 × 50 mL). Drying in vacuo gave **5** as a pale-orange powder. Yield 630 mg (85%). Complex **5** could also be generated in the absence of aniline in solvents such as THF or pyridine; however, lower yields and purity were obtained. IR (Nujol) ν_{Ir-H} = 2054, 2044 (sh) cm^{-1}. ^1H THF-d_8 −13.54 (d of q, 18.0, 125, 1 H, IrH), 0.31 (m (br), 1 H, IrCH), 0.70 (m (br), 1 H, IrCH), 1.52 (d, 7.5, 9 H, PCH_3), 1.65–1.80 (m, 21 H, PCH_3), 1.89 (d of d, 4.5, 18.0, 3 H, PCH_3). $^{31}P\{^1H\}$ (THF-d_8) −68.5 (d of d of d, 19.3, 32.0, 237.5, 1 P), −59.7 (d of t, 19.3, 21.3, 1 P), −52.5 (d of d of d, 5.0, 19.3, 32.0, 1 P), −49.6 (d of d of d, 5.0, 21.3, 237.6, 1 P). FAB/MS 495, 497 (M^+).

V. $Ir(PEt_3)_2(NHPhC_7H_{10})(H)Cl$ (6). A solution of aniline (0.054 g, 0.58 mmol) in 1 mL of Et_2O was added to a slurry of $Ir(PEt_3)_2(C_2H_4)_2Cl$ (0.300 g, 0.58 mmol) and norbornylene (1.00 g, 10.6 mmol) in 5 mL of *n*-hexane. The mixture was heated to reflux giving, intially, a homogeneous red-orange solution. The solution was refluxed for 24 h during which time a white powder precipitated from the solution. The solution was filtered and the solid washed with Et_2O. Drying in vacuo gave 0.190 g (50%) of a white powder which contained **6** in about 90% purity and about 10% of an unidentified $Ir(PEt_3)_2$ hydride species.[7] This powder was sufficiently pure to use in subsequent reactivity studies. Single crystals of **6** were obtained by stirring $Ir(PEt_3)_2(C_2H_2)_2Cl$ (0.527 g, 1.07 mmol), norbornylene (1.00 g, 10.6 mmol), and aniline (0.500 g, 5.37 mmol) together in 5 mL of Et_2O at room temperature overnight and then allowing the solution to stand undisturbed for several weeks. Crystals of **6**, having an IR spectrum identical with the bulk powder described above, and the starting Ir complex **1** slowly formed during this time. The colorless, air-stable needles of **6** were separated from **1** under a microscope. IR (Nujol) ν_{N-H} = 3275, ν_{Ir-H} = 2181, ν_{Ir-Cl} = 227 cm^{-1}. With aniline-*N,N*-d_2) ν_{N-D} = 2432, ν_{Ir-D} = 1565 cm^{-1}. ^1H (THF-d_8) −20.86 (d of d, 12.2, 18.3, 1 H, IrH), 0.93 (d of t, 6.0, 14.0, 9 H, CH_3), 1.12 (d of t, 6.0, 14.0, 9 H, CH_3), 1.37 (m, 6 H, PCH_2), 1.66 (m, 6 H, PCH_2), 1.8-2.1 (m, 5 H), 2.33 (s, 1 H), 2.40 (d, 10.0, 1 H), 4.21 (t (br), 6.3, 1 H), 4.68 (t (br), 7.0, 1 H), 7.02 (t, 7.2, 1 H, Ar-H), 7.16 (t, 7.8, 2 H, Ar-H), 7.89 (d, 7.8, 2 H, Ar-H). $^{31}P\{^1H\}$ (THF-d_8) −6.7 (s (br), 1 P), −10.0 (s (br), 1 P).

VI. *exo*-2-(Phenylamino)norbornane (7). The synthesis of **7** was adapted from a literature procedure.[8] To a solution of $Cr(CO)_3(C_6H_5F)$ (1.5 g, 6.47 mmol) in 30 mL of DMF was added a solution of *exo*-2-aminonorbornane (2.15 g, 19.37 mmol). The solution was stirred at room temperature for 24 h. After removing DMF in vacuo, the yellow-orange residue was taken up in 100 mL of Et_2O, filtered over Celite to remove fluoride salts, and washed with Et_2O. Iodine (1.64 g, 6.47 mmol) was slowly added to the Et_2O filtrate. After CO evolution had ceased, the dark solution was stirred for 2 h, filtered over Celite, and rotovapped to a dark, viscous liquid. Vacuum distillation (85 °C, (0.05 mm Hg)) gave 0.44 g of **7** as a viscous pale-yellow liquid (36%). ^1H (C_6D_6) 0.60–1.0 (m, 4 H), 1.19 (m, 1 H), 1.27 (m, 2 H), 1.46 (d of d of d, 12.5, 8.0, 2.5, 1 H, C_3H endo), 1.99 (s, 1 H, $C_{1,4}H$), 2.04 (s, 1 H, $C_{1,4}H$), 2.97 (m, 1 H, C_2H), 3.08 (s (br), 1 H, NH), 6.44 (d, 8.0, 2 H, Ar-H), 6.72 (t, 7.4, 1 H, Ar-H), 7.15 (t, 7.6, 2 H, Ar-H). $^{13}C\{^1H\}$ (C_6D_6) 26.5 (s), 28.8 (s), 35.5 (s), 35.9 (s), 41.1 (s), 41.5 (s) 56.7 (s), 113.5 (s), 117.2 (s), 129.4 (s), 148.0 (s). MS 187 (M^+).

VII. Decomposition Kinetics for $Ir(PEt_3)_2(H)(NHPhC_7H_{10})Cl$ (6). The decomposition of **6** in CD_2Cl_2 at 45 °C was monitored by ^1H NMR with use of a sample of **6** sealed under N_2. Anisole was added as an internal standard and $C[(acac)_3$ was added so that T_1 (norbornylene) < 1 s. A kinetic model for the decomposition was obtained by using the GEAR and GIT modeling programs.[9]

VIII. Ir(I)-Catalyzed Addition of Aniline to Norbornylene. The following procedure is a typical example of a catalytic run with $Ir(PEt_3)_2(C_2H_4)_2Cl$ (**1**) as the catalyst precursor. **1** (0.100 g, 0.192 mmol), norbornylene (1.00 g, 10.64 mmol), $ZnCl_2$ (0.005g, 0.037 mmol), aniline (0.180 g, 1.92 mmol) were dissolved in 10 mL of THF and then heated to reflux under a slow stream of N_2. The orange solution was refluxed for 3 days during which time the solution turned brown. In four experiments, two, three, five, and six turnovers of **7** were obtained as determined by GC analysis of the reaction mixture.

IX. X-ray Crystallography. A colorless needle with dimenstions 0.15, 0.15, 0.40 mm obtained from Et_2O was mounted in a glass capillary under N_2 and placed on an ENRAF-NONIUS CAD4 diffractometer equipped with a Mo Kα source, graphite monochromator, and FTS gas-cooled low-temperature unit operating at −70 °C. The diffractometer routines indicated a monoclinic cell with dimensions a = 10.702 (3) Å, b = 13.176 (21) Å, c = 19.498 (5) Å, β = 98.61 (2)°, which were verified by partial rotation photographic projections along each of the three reciprocal axes. With Z = 4, the calculated density for $IrClP_2NC_{25}H_{47}$ is 1.591 g/cm^3. Preliminary scans of selected peaks showed broad half-heights with typical widths of 0.48ω. The cause of the broadening was not determined but undoubtedly affected the refinement (vide infra).

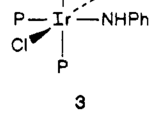
A total of 4646 data was collected over the range $2.1 < 2\theta < 48.0°$ with use of the ω-scan method with a scan width 1.20–1.50° ω and scan speeds 1.70–5.00 deg/min. The data were treated in the usual manner for Lorentz-polarization as well as for a 4% decrease in intensity as indicated by the two monitor reflections. In addition, with m = 51.21 cm^{-1}, the data were collected for absorption via the method of Walker and Stuart (REF) yielding a range of transmission factors of 0.25–0.55. The merged data (R_{merge} = 1.9%, 105 duplicates) yielded 3029a unique reflections with $I < 3.0\sigma(I)$.

The solution was accomplished via an automated Patterson analysis and was complicated by noise near the Ir. The asymmetric unit consists of one molecule lying in a general position separated by normal van der Waals contacts. The hydride atom was inferred from its geometry about the Ir, while the remaining hydrogen atoms were calculated in their ideal positions with N,C–H = 0.95 Å. The coordinates and thermal parameters were refined via full-matrix least-squares analysis on F with scattering factors taken from the *International Table for Crystallography*, Vol. IV, and included anomalous dispersions terms for Ir, Cl, and P. The final refinement allowed anisotropic temperature factors for all non-hydrogen atoms and included the carbon hydrogens as fixed atom contributors with isotropic B values fixed at 3.0 Å. Due to the broadening of the diffraction peaks, the weights were modified according to the method of Prince and Nicholson which indicated 31 outliers to the model. Although the hydride atom coordinates refined successfully, its isotropic temperature factor refined to a negative value, undoubtedly a reflection of the quality of the data, and hence its temperature factor was fixed to B = 1.0 Å. The final refinement with 274 parameters yielded R = 0.039 and R_w = 0.036 with the standard deviation of an observation of unit weight 1.33. The average shift/error in the last cycle was 0.02 and the largest residual density on the final difference map was 1.7 e/Å^3, 1.12 Å from the iridium.

Atomic coordinate and equivalent isotropic thermal parameters are listed in Table I, and selected interatomic distances and intramolecular angles are listed in Table II. A table of anisotropic temperature factors for the non-hydrogen atoms and tables of observed and calculated structure factor amplitudes are given in the supplementary material.

Results and Discussion

One reasonable approach to inhibiting the formation of amido dimers would be the use of a sterically more hindered amine, and so the oxidative addition of aniline with some electron-rich Ir(I) complexes was tried. Indeed, the reaction of aniline with the complexes $Ir(PEt_3)_3Cl$, $Ir(PMe_3)_3(C_8H_{14})Cl$, and $[Ir(PMe_3)_4]PF_6$ gave, in good to moderate yield, the monomeric anilido hydride isomer **3**, in the case of the tris(phosphine) complexes, and isomer **4**, in the case of $[Ir(PMe_3)_4]PF_6$. Formation of the thermodynamically more stable C–H oxidative addition product **5** occurs from either **4** or $[Ir(PMe_3)_4]PF_6$ after prolonged heating or at elevating temperatures. The overall compositions and stereochemistry of **3** and **4** were readily ascertained from the IR, ^1H, and ^{31}P NMR spectra and by the use of ^{15}N-labeled aniline. For example, the presence of a doublet of triplets at −21.59 ppm with P–H coupling constants of 19.8 and 14.1 Hz in the ^1H NMR spectrum of **3a** (P = PMe_3) indicates a cis orientation of the hydride ligand to two non-equivalent sets of phosphine ligands as shown below. The use of ^{15}N-labeled aniline in the synthesis of **3a** had no effect on the hydride resonance of **3a** but did give rise to an additional splitting of the trans phosphorus resonance in the $^{31}P\{^1H\}$ NMR spectrum of **3a** (−50.5, d of t, J_{P-P} = 20, J_{N-P} = 45.4 Hz, 1 P).



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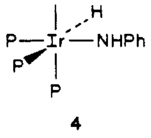

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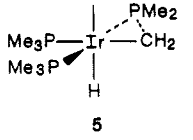

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[7] Some of the identifiable ^1H NMR resonances for this species are (THF-d_8): −21.31 (dd, J_{P-H} = 10.7, 21.4 Hz, 1 H, IrH), 2.86 (d, J_{P-H} = 8, 1 H), 5.19 (m (br), 1 H), 5.30 (m (br), 1 H).

[8] Bunnett, J. F.; Hermann, H. *J. Org. Chem.* **1971**, *36*, 4081 and references therein.

[9] (a) McKinney, R. J.; Weigert, F. J. *QCPE Bull.* **1986**, *6*, 136. (b) McKinney, R. J.; Weigert, F. J. *Ibid.* **1986**, 141.

Table I. Fractional Coordinates (×10000) and Isotropic Thermal Parameters for **6**

atom	*X*	*Y*	*Z*	B_{ISO}
Ir(1)	3221.7 (3)	1487.4 (3)	2541.2 (1)	1.3 (1)′
Cl(1)	3428 (2)	−404 (2)	2423 (1)	2.2 (1)′
P(1)	1420 (2)	1310 (2)	2982 (1)	1.6 (1)′
P(2)	2409 (2)	1766 (2)	1375 (1)	1.7 (1)′
N(1)	5210 (6)	1795 (5)	2444 (3)	1.3 (2)′
C(1)	5651 (7)	1392 (7)	3170 (4)	1.5 (2)′
C(2)	6477 (7)	2155 (7)	3619 (4)	2.2 (2)′
C(3)	6899 (8)	1642 (8)	4331 (4)	2.7 (3)′
C(4)	5662 (7)	1610 (8)	4660 (4)	2.5 (2)′
C(5)	4668 (7)	2089 (8)	4097 (4)	2.3 (2)′
C(6)	4455 (7)	1313 (6)	3491 (4)	1.3 (2)′
C(7)	5459 (8)	2891 (7)	3799 (4)	2.1 (2)′
C(11)	5952 (6)	1490 (8)	1904 (3)	1.5 (2)′
C(12)	5832 (8)	544 (8)	1624 (4)	2.3 (2)′
C(13)	6476 (8)	277 (8)	1097 (4)	2.6 (3)′
C(14)	7298 (8)	965 (8)	859 (4)	2.5 (3)′
C(15)	7436 (8)	1914 (8)	1154 (4)	2.5 (3)′
C(16)	6747 (7)	2185 (7)	1678 (4)	2.1 (2)′
C(21)	1605 (7)	834 (8)	3868 (4)	2.2 (2)′
C(22)	1944 (9)	−300 (8)	3958 (5)	3.0 (3)′
C(23)	215 (7)	451 (7)	2539 (4)	2.0 (2)′
C(24)	−979 (8)	290 (8)	2864 (5)	2.9 (3)′
C(25)	558 (7)	2485 (8)	3075 (4)	2.5 (3)′
C(26)	1282 (9)	3257 (8)	3542 (5)	3.1 (3)′
C(31)	2270 (8)	681 (8)	773 (4)	2.4 (2)′
C(32)	1261 (9)	−87 (8)	873 (4)	3.0 (3)′
C(33)	881 (7)	2421 (7)	1162 (4)	2.1 (2)′
C(34)	440 (8)	2686 (9)	411 (4)	3.5 (3)′
C(35)	3430 (8)	2584 (8)	940 (4)	2.3 (2)′
C(36)	3602 (8)	3652 (9)	1219 (5)	3.5 (3)′
H	3232 (58)	2776 (57)	2620 (31)	1.0
H(1)	6086	734	3151	3.0
H(1′)	5256	2532	2485	3.0
H(2)	7139	2483	3410	3.0
H(3)	7516	2078	4607	3.0
H(3′)	7192	990	4257	3.0
H(4)	5761	2020	5074	3.0
H(4′)	5437	927	4724	3.0
H(5)	3917	2375	4243	3.0
H(6)	4296	650	3658	3.0
H(7)	5030	3161	3382	3.0
H(7′)	5833	3335	4151	3.0
H(12)	5299	36	1809	3.0
H(13)	6369	−399	884	3.0
H(14)	7798	780	495	3.0
H(15)	7996	2397	992	3.0
H(16)	6828	2865	1882	3.0
H(21)	864	941	4071	3.0
H(21′)	2233	1198	4160	3.0
H(22)	2019	−493	4425	3.0
H(22′)	2713	−427	3783	3.0
H(22″)	1285	−695	3690	3.0
H(23)	594	−219	2504	3.0
H(23′)	5	622	2076	3.0
H(24)	−1545	−164	2611	3.0
H(24′)	−1405	942	2885	3.0
H(24″)	−784	55	3337	3.0
H(25)	−238	2326	3227	3.0
H(25′)	307	2772	2612	3.0
H(26)	808	3853	3573	3.0
H(26′)	2054	3422	3373	3.0
H(26″)	1499	2969	3998	3.0
H(31)	3092	333	813	3.0
H(31′)	2159	919	301	3.0
H(32)	1248	−625	545	3.0
H(32′)	462	247	803	3.0
H(32″)	1420	−354	1328	3.0
H(33)	868	3028	1444	3.0
H(33′)	219	2029	1341	3.0
H(34)	−364	3015	347	3.0
H(34′)	363	2074	136	3.0
H(34″)	1040	3117	244	3.0
H(35)	3125	2590	451	3.0
H(35′)	4247	2256	956	3.0
H(36)	4147	4025	963	3.0
H(36′)	3964	3637	1693	3.0
H(36″)	2803	3982	1170	3.0

Table II. Selected Interatomic Distances (Å) and Intramolecular Angles (deg) for **6**

Ir(1)–Cl(1)	2.515 (5)	Cl(1)–Ir(1)–H	175 (2)
Ir(1)–P(1)	2.238 (2)	P(1)–Ir(1)–P(2)	100.02 (7)
Ir(1)–P(2)	2.339(2)	P(1)–Ir(1)–N(1)	162.1 (2)
Ir(1)–N(1)	2.202 (6)	P(2)–Ir(1)–N(1)	96.3 (2)
Ir(1)–C(6)	2.120 (7)	P(1)–Ir(1)–C(6)	96.4 (2)
Ir(1)–H	1.705 (75)	P(2)–Ir(1)–C(6)	163.5 (2)
N(1)–C(1)	1.520 (9)	N(1)–Ir(1)–C(6)	67.2 (2)
N(1)–C(11)	1.465 (9)	Ir(1)–N(1)–C(1)	91.4 (4)
C(1)–C(2)	1.525 (11)	Ir(1)–N(1)–C(11)	130.3 (5)
C(1)–C(6)	1.510 (10)	Ir(1)–C(6)–C(1)	94.9 (4)
C(5)–C(6)	1.553 (11)	Ir(1)–C(6)–C(5)	126.5 (6)

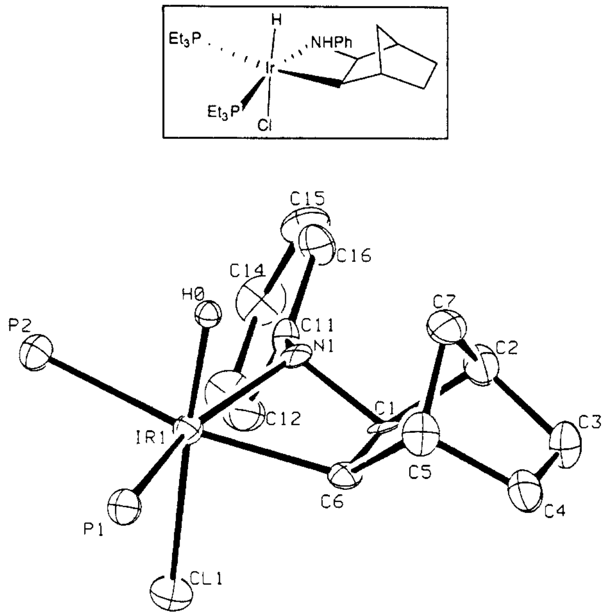

Figure 1. ORTEP and stick drawings of the solid-state structure of **6**. H atoms and ethyl groups have been omitted from the ORTEP drawing for clarity.

Since the complexes of **3** and **4** are coordinatively saturated and sterically hindered,[10] it was not suprising that these species were unreactive toward unsaturated substrates. Since it is likely that N–H oxidative addition to Ir(I) proceeds through an unsaturated $14e^-$ intermediate to give an unsaturated, pentacoordinate, $16e^-$ Ir(III) complex, we reasoned that in the absence of a trapping phosphine ligand, such a $16e^-$ Ir anilido species might undergo further reaction with a suitable unsaturated substrate. The reaction of aniline and norbornylene with $Ir(PEt_3)_2(C_2H_4)_2Cl$ a molecule that dissociates ethylene to form a $14e^-$ intermediate,[1] was therefore tried.

Refluxing a solution of **1**, aniline, and a large excess of norbornylene in *n*-hexane overnight resulted in the precipitation of a new Ir complex, **6**, as a white solid in 50% overall yield (~90% purity) together with an unidentified $Ir(PEt_3)_2$ hydride species (~10%).[7] IR and ^1H NMR spectroscopic analyses of this solid indicated the presence of Ir–H, N–H, and N–Ph groups (IR (Nujol) ν_{N-H} = 3275, ν_{Ir-H} = 2181 cm^{-1}; ^1H (THF-d_8) −20.86 (d of d, J_{P-H} = 12.2, 18.3, IrH). $^{31}P\{^1H\}$ and ^1H NMR spectra were also consistent with the presence of two non-equivalent PEt_3 ligands, both of which were cis relative to the hydride ligand. A number of other somewhat complex resonances, potentially consistent with a norbornyl fragment, were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **6**. However, a complete and unambiguous structural assignment based on these data was not possible. Fortunately, single crystals of **6**, suitable for X-ray diffraction analysis and having an IR spectrum identical with the bulk powder,

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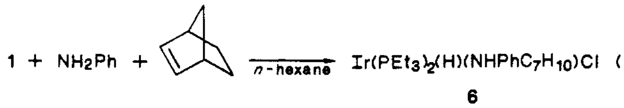
[10] ^1H NMR spectra of complexes **3** and **4** indicated hindered rotation of the phenyl group. Construction of molecular models suggests an unfavorable interaction between the ortho H's and phosphine ligands.

Table III. Effect of Added Reagents on Decomposition of **6**

reagent[a]	norboprnylene (%)	**7** (%)	major inorganic product
none	53	43	
PEt_3	92	3	**3b**
C_2H_4[b]	88	11	**1**
1,5-cyclooctadiene	44	56	$Ir(PEt_3)_x(COD)Cl$[f]
LiCl[c]	82	12	
$ZnCl_2$[d]	0	100	
$TlPF_6$[d]	0	100	
CH_2Cl_2[e]	95	5	

[a] THF solution of **6** and 2 equiv of reagent heated at 80 °C for 1 h. [b] 60 psi. [c] Saturated THF solution. [d] Reaction carried out at room temperature in THF. [e] Decomposition of **6** in CH_2Cl_2 at 45 °C. [f] Same species observed from the addition of 1,5-cyclooctadiene to **1**.

were obtained by the slow reaction of **1**, aniline, and norbornylene in diethyl ether.



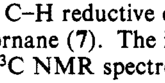
(2)

Description of the Structure

The solid-state structure of complex **6**, shown in Figure 1, is consistent with the IR and solution NMR data. The norbornyl fragment is incorporated as part of an azoiridacyclobutane ring in which the N and C_3 atoms are bonded to Ir and a single bond exists between N and C_2 of the norbornyl fragment. Significantly, the N and Ir atoms are bonded to the exo face of the norbornyl group, corresponding to an overall cis addition to norbornylene. Relevant bond angles and distances for this azometallacyclobutane are given in Table II. The P atoms are approximately trans to N and C_2 of the azometallacyclobutane. The stronger trans effect of C_2 vs N is reflected in an Ir–P_2 distance 0.1 Å longer than that of Ir–P1. The hydride ligand was located and is approximately trans of the Cl. The overall coordination geometry about Ir is distorted octahedral.

The importance of **6** as a possible intermediate in a potential catalytic addition of aniline to norbornylene was established by studies of the thermal and Lewis acid catalyzed decomposition of **6**. THF and THF-d_8 solutions of **6** were decomposed alone and in the presence of several trapping ligands by heating these solutions at 80 °C for 1 h. The resulting solutions were analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as well as by GC. Alternatively, these solutions of **6** were decomposed at room temperature by the addition of 1 equiv of $TlPF_6$ or a catalytic amount of $ZnCl_2$. Decomposition was very rapid under these conditions, with complete decomposition occurring in a few mintues. The results of these experiments are shown in Table III.

In every case the only organic products detected were aniline, norbornylene, and the C–H reductive elimination product *exo*-2-(phenylamino)norbornane (**7**). The identity of **7** was verified by GC/MS, ^1H and ^{13}C NMR spectroscopy, as well as an independent synthesis of **7**. Authentic samples of **7** were obtained from the reaction of $Cr(CO)_3(C_6H_5F)$ and *exo*-2-aminonorbornane. Oxidative workup of the resulting Cr arene complex, $Cr(CO)_3(C_6H_5NHC_7H_{11})$, gave **7** in moderate yield.



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The total conversion of **6**, calculated from the yields of **7** and norbornylene, was greater than 90% in all cases. In some cases it was possible to identify the major inorganic species present. In general, the major inorganic species present after the decomposition corresponded, formally, to the reaction of either the $Ir(PEt_3)_2Cl$ or $Ir(PEt_3)_2(NHPh)(H)Cl$ group with the appropriate trapping ligand.[11] Thus, the use of C_2H_4 as a trapping ligand regenerates the starting complex **1**, whereas, the use of PEt_3 yields the hydride complex $Ir(PEt_3)_3(H)(NHPh)Cl$, (**3b**), the same compound obtained from the reaction of aniline and $Ir(PEt_3)_3Cl$ (vide supra).

The effects of added PEt_3, C_2H_4, and LiCl on the product distribution of the thermal decomposition were particularly marked, giving norbornylene and about 10% or less of the reductive elimination product **7**. In contrast, the use of the Lewis acids $TlPF_6$ or $ZnCl_2$ gave exclusively **7**. Furthermore, the addition of 1 equiv of $TlPF_6$ to **6** in the presence of 6 equiv of PEt_3 at 25 °C also gave **7**, exclusively. A marked solvent effect on the decomposition was also observed. Whereas a roughly 60/40 distribution of norbornylene to **7** was obtained after 24 h in THF at 45 °C, a 95/5 distribution was obtained in CH_2Cl_2 under the same conditions.

The reaction of aniline-*N*,*N*-d_2 with norbornylene and **1** was carried out as described above to give the Ir–D analogue of **6**. Lewis acid decomposition of this compound followed by chromatographic workup of the nonvolatile reaction products afforded a pure sample of deuterium-labeled **7** (ca. 95% $C_{13}H_{16}DN$ by GC/MS). A single resonance at δ 0.867 (s, br) was observed in the ^2H NMR spectrum of this compound (C_6H_6). The $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 showed a 1:1:1 triplet (J_{C-D} = 18.5 Hz) at 40.9 ppm. This ^{13}C resonance was assigned to C_3 of **7** on the basis of APT, 2D $^1H/^{13}C$ correlation, and COSY NMR experiments. 2D NOESY NMR spectra of **7** in C_6D_6 allowed the assignment of the deuterium resonance at 0.867 ppm to the exo position on C_3. Thus **1** promotes a stereospecific cis addition of the N–H group across the exo face of norbornylene.

Crossover studies of the thermal and Lewis acid catalyzed reductive elimination of **7** were consistent with an intramolecular process. Mixtures of ^{15}N-labeled **6** and deuterium-labeled **6** (Ir–D) were decomposed under both conditions. Product **7** was then analyzed by GC/MS. In both cases, approximately 95% of **7** corresponded to a singly labeled species (either D or ^{15}N). In a related experiment, the thermal decomposition of **7** was studied in the presence of 5-methyl-2-norbornene. About 75% of the (phenylamino)norbornanes detected corresponded to 5-methyl derivatives when neat alkene was used, as determined by GC/MS; however, no crossover products were observed with 3 equiv of alkene (0.06 M) were used.

Having demonstrated the individual steps for the stoichiometric addition of aniline to norbornylene, the catalytic process was examined. Indeed, the addition of aniline to norbornylene occurs catalytically, though slowly, in the presence of **1** and $ZnCl_2$. Thus, orange THF solutions containing **1** (1 equiv), $ZnCl_2$ (0.2 equiv), aniline (5–40 equiv), and norbornylene (55 equiv) gave from 2 to 6 turnovers of **7**, exclusively, after 48 h of reflux. A slow color change from orange to brown was observed during this time and the resulting solutions were found to be completely inactive.[12] As observed with complex **6**, the use of aniline-*N*,*N*-d_2 gave **7** labeled exclusively in the 3-exo position. Control experiments conducted in the absence of **1** did not yield any of the addition product **7**. The formation of **7** was irreversible under these conditions since the reaction of **7** with **1** under reflux did not yield aniline or norbornylene.

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(11) Smaller amounts of unidentified Ir hydride species were observed in the ^1H NMR spectra, however.

(12) Pathways for catalyst deactivation are not well understood; however, at least one decomposition pathway arises from the presence of water. Small amounts of water give rise to catalytically inactive Ir anilido species. ^{15}N, ^{31}P, and ^1H NMR characterization as well as single-crystal X-ray diffraction data (included in supplementary material) are in agreement with the formulation $[[Ir(PEt_3)_2(H)]_2(\mu\text{-}NHPh)(\mu\text{-}OH)(\mu\text{-}Cl)]Cl$ for this species. Crystal data: $Ir_4Cl_4P_8O_3N_3C_{58}H_{153}$, from THF/$Et_2O$/pentane, white parallelopiped, ~0.35 × 0.19 × 0.38 mm, triclinic, P_1 (No. 2), a = 15.375 (2) Å, b = 16.117 (3) Å, c = 10.778 (1) Å, α = 105.94 (1)°, β = 90.45 (1)°, γ 72.07 (1)°, from 25 reflections, T = −70 °C, V = 2434.8 Å^3, Z = 1, FW = 2099.28, D_c = 1.431 g/cm^3, μ(Mo) = 57.01 cm^{-1}, 8045 unique reflections with $I \geq 3.0\sigma(I)$, Mo Kα radiation, 2.8° $\leq 2\theta \leq$ 55.0°, corrected for absorption (DIFABS), range of transmission fators = 0.24–0.61, refinement by full-matrix least squares on F, 486 parameters, refined anisotropic: all non-hodrgeon atoms, isotropic: H, fixed atoms: H, final R = 0.031, R_w = 0.030, error of fit = 1.09, max Δ/σ = 0.31, largest residual density = 1.28 e/Å^3.

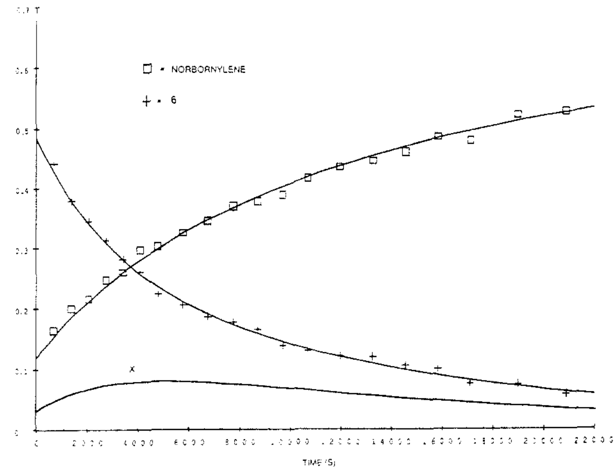
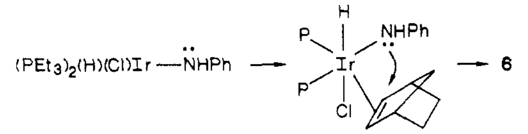


Figure 2. Decomposition kinetics of **6** in CD_2Cl_2 at 45 °C showing the disappearance of **6** and the production of norbornylene and the unknown species X (calculated fit only).[17] The solid lines are the calculated fit for the kinetic model shown in the text with $k_2 = 1.13 \times 10^{-4}\ s^{-1}$, $k_1 = 8.6 \times 10^{-5}\ s^{-1}$, and $k_{-1} = 2.24 \times 10^{-4}\ s^{-1}$.

From these data it is possible to construct, in a qualitative manner, a fairly detailed mechanism for the catalytic addition of aniline to norbornylene. This mechanism is shown in Figure 2. Stepwise dissociation of ethylene from the catalyst precursor **1** results in an equilibrium mixture of **1**, $Ir(PEt_3)_2(C_2H_4)Cl$, and the active catalyst $Ir(PEt_3)_2Cl$. The monoethylene adduct can be synthesized directly from **1** and is detectable in small amounts in solutions of **1**.[1] The $14e^-$ species $Ir(PEt_2)_2Cl$ has not been detected directly; however, the related compounds $M(i\text{-}Pr_3P)_2Cl$ (M = Rh, Ir) are known[13] and such $14e^-$ species are important in C–H and H–H oxidative addition reactions of Rh(I) and Ir(I).[14]

In the next step, aniline is oxidatively added to $Ir(PEt_3)Cl$ to form the intermediate $Ir(PEt_3)_2(H)(NHPh)(Cl)$ which, though not directly observed, is readily trapped by PEt_3 or norbornylene to give $Ir(PEt_3)_3(H)(NHPh)(Cl)$, **3b**, and **6**, respectively. The available data also suggest that N–H oxidative addition is reversible. Generation of $Ir(PEt_3)_2(H)(NHPh)(Cl)$ via the decomposition of **6** (vide supra) in the presence of ethylene gave aniline and **1** as the final products. This same decomposition reaction carried out with ^{15}N-labeled **6** in the presence of PEt_3 and unlabeled aniline gave unlabeled complex **3** and free aniline-^{15}N. Also, the formation of $[Ir(PMe_3)_3(PMe_2CH_2)(H)]PF_6$ (**5**) from *cis*-$[Ir(PMe_3)_4(NHPh)(H)]PF_6$ (**4**) suggests that N–H oxidative addition is reversible in this system as well.

The intermediate $16e^-$ anilido hydride compound reacts with norbornylene to form the isolated Ir complex **6**. Addition of norbornylene takes place across the sterically less hindered exo face. Formation of the azometallacyclobutane may proceed in the following manner as depicted below. Coordination of norbornylene to the electron-deficient Ir(III) center followed by intramolecular attack of the nitrogen lone pair on the adjacent olefin seems the most likely mechanism for the formation of complex **6**.[15] In this model, the Ir center plays a dual role in first activating the nitrogen lone pair by N–H oxidative addition and then activating norbornylene via electrophilic attack on the π system.



Decomposition of **6** proceeds along two competing pathways: Ir–C/N–C bond breaking and C–H reductive elimination. Cleavage of the N–C and Ir–C bonds, the microscopic reverse of the formation of **6**, leads to formation of norbornylene and $Ir(PEt_3)_2(NHPh)(H)Cl$.[16] The reversibility of this reaction step is also consistent with the observed formation of 5-methyl derivatives of **6** from the decompopsition of **6** in the presence of a large excess of 5-methyl-2-norbornylene (vida supra). By the principle of microscopic reversibility, Ir–C and N–C bond cleavage would proceed directly from the $18e^-$ complex **6**. Kinetic studies of the decomposition of **6** in CD_2Cl_2 suggest, however, that the mechanism is somewhat more complicated than a simple first-order process.

The decomposition of **6** in CD_2Cl_2 at 45 °C, in the presence of the unidentified $Ir(PEt_3)_2$ hydride species,[7] was monitored by ^1H NMR and the results from this experiment are shown in Figure 2. Under these conditions **7** forms at a very slow rate, so the decomposition of **6** to form norbornylene can be measured directly. The formation of a low concentration of a new hydride species, which then slowly decreased over time, was observed during the decomposition. The ^1H NMR resonances associated with this species strongly suggest that it is an isomer of **6** (–22.29 (dd, J(P–H) = 10 Hz, IrH, 1 (H), 4.14 (m (br), 1 H), 4.57 (tr (br), 7.5 Hz 1 H). In fact, attempts to model the reaction as a simple first-order decomposition of **6** into norbornylene were unsuccessful. The simplest kinetic model that fits the data, shown below, involves the reversible formation of a second species in combination with a first-order decomposition of **6** into norbornylene. A value of 1.13 (5) × $10^{-4}\ s^{-1}$ for the first-order decay constant k_2 was obtained from the fit, shown in Figure 2, corresponding to $\Delta G^{\ddagger}$ (45 °C) = 24.5 kcal/mol.[17] The results of the kinetic modeling should be viewed with caution, however, because of the presence of the unknown $Ir(PEt_3)_2$ hydride species.

$$\begin{tikzcd}
6 \arrow[r, shift left, "k_1"] \arrow[d, "k_2"'] & X \arrow[l, shift left, "k_{-1}"] \\
\text{norbornylene} &
\end{tikzcd}$$

Reductive elimination of a C–H bond, the competing pathway, results in the production of **7** and the regeneration of $Ir(PEt_3)_2Cl$ to complete the catalytic cycle. Studies of the reductive elimination of **6** from **7** are consistent with an initial, reversible, ligand-dissociation step followed by an irreversible C–H reductive elimination from the resulting $16e^-$ intermediate as observed for C–H reductive elimination from Rh(III).[14] Although PEt_3 dissociation cannot be rigorously excluded, the available data support dissociation of the Cl ligand as the slow step. Thus, while Lewis acids dramatically accelerate C–H reductive elimination, the phosphine scavengers $Rh(acac)(C_2H_4)_2$, $[Rh(C_8H_{14})_2Cl]_2$, and $[Rh(C_8H_{10})Cl]_2$ were ineffective at accelerating C–H reductive elimination relative to Ir–C/N–C bond breaking. Dissociation of the Cl ligand is not unexpected since it occupies a coordination site trans to the hydride. Also, in the case of C–H reductive elimination from Rh(III), it is the ligand trans to the hydride that

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[15] An intriguing alternative for the formation of **6** is to consider the electronically unsaturated $16e^-$ species to have some N–Ir multiple bond character:

$$Ir{-}NHPh \leftrightarrow Ir(-){=}NHPh(+)$$

Formation of **6** may then proceed in a manner similar to the formation of a metallocyclobutane from an olefin and metallocarbene. Such titanocyclobutanes derived from norbornylene are important intermediates in the ring-opening polymerization of norbornylene. Ring-opening polymerization was not observed in this Ir system, however. See: Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

[16] Though the reaction is reversible, it appears that the reaction rate of the intermediate $Ir(PEt_3)_2(NHPh)(H)Cl$ with norbornylene is significant only at high concentrations of norbornylene. This intermediate reacts much more readily with trapping ligands such as PEt_3. For example, the reaction of $Ir(PEt_3)_3Cl$ with aniline and a large excess of norbornylene gives $Ir(PEt_3)_3(NHPh)(H)Cl$, (**3b**) and a trace amount of (**7**), but complex **6** is not observed.

[17] Due to the lack of accurate, quantitative data on the concentration of the species X, the kinetic model was relatively insensitive to the rate constants k_1 and k_{-1}. In general, the best fits were obtained with k_1/k_{-1} = 0.4. The model was very sensitive, however, to the decay constant k_2.

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dissociates prior to reductive elimination.[14] In the absence of a Lewis acid, a lower bound of about 27 kcal/mol on $\Delta G^{\ddagger}$ (45 °C) for the overall reductive elimination of dichloromethane is suggested by the kinetic studies of the decomposition of **6** in CD_2Cl_2, as compared with $\Delta G^{\ddagger}$ (31 °C) = 23.4 kcal/mol for the overall C–H reductive elimination from *cis*-$Rh(H)(PMe_3)_2(CH_2COCH_3)Cl$.[14]

According to this model, ligands such as PEt_3 decrease the rate of reductive elimination by intercepting the intermediate, cationic $16e^-$ species. Apparently, this species reacts readily with a variety of simple two-electron donors to give $18e^-$ species which, like **6**, do not diretly give C–H reductive elimination. At room temperature and in the presence of a Lewis acid, the effective barrier for C–H reductive elimination from **6** is greatly reduced while the barrier to Ir–C/N–C bond breaking remains relatively large. The observation of exclusive C–H reductive elimination from **6** in the presence of $TlPF_6$ and PEt_3 at room temperature suggests that PEt_3 binds reversibly to the cationic, intermediate $16e^-$ complex. The differing effects of THF and CH_2Cl_2 are probably due to the greater ability of THF to support a charged species.

In summary, a new approach to the synthetically important amination of olefins has been demonstrated. For this purpose, the various steps envisioned to be involved in such a transformation were individually discovered and elaborated in a catalytic cycle. The major steps involved are N–H oxidative addition, reaction of the resulting amido hydride complex with an olefin to form an azometallacycle, and finally C–H reductive elimination, resulting in cis addition of aniline to the exo face of norbornylene.

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Supplementary Material Available: APT, 2D $^1H/^{13}C$ correlation, 2D NOESY, and COSY NMR spectra of **7**, tables of anisotropic temperature factors and structure factor amplitudes for complex **6**, crystal structure of $[Ir(PEt_3)_2(H)]_2(\mu\text{-}NHPh)(\mu\text{-}OH)(\mu\text{-}Cl)]Cl$[12] including tables of atomic coordinates, thermal parameters, and distances and angles (14 pages); listing of structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

Mechanism of the Oxidation of CO by $PtCl_4^{2-}$. An Investigation into the Nature of the Intermediates by Isotopic Labeling

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Abstract: The oxidation of CO by $PtCl_4^{2-}$–$CuCl_2$ in the presence of ^{18}O-enriched water produces CO_2 of which the ^{18}O distribution indicates that statistically 1.5 of the 2 oxygens are derived from water. During the reaction, $PtCl_3(CO)^-$ may be isolated by quenching with $(AsPh_4)^+Cl^-$. This monocarbonyl species undergoes oxygen exchange with ^{18}O-enriched water reaching isotopic equilibrium within 5 min at ambient temperature. Under a ^{13}CO atmosphere, a solution of $PtCl_3(CO)^-$ yields CO_2 of which the ^{13}C abundance reveals that half the CO_2 comes from gaseous CO and the other half is from $PtCl_3(CO)^-$. These results strongly imply that $PtCl_3(CO)^-$ reacts with gaseous CO to give $PtCl_2(CO)_2$ prior to CO_2 formation. The rapid oxygen exchange of $PtCl_3(CO)^-$ with water and the irreversible attack of $PtCl_2(CO)_2$ by water to give CO_2 are proposed to explain the observation that statistically 1.5 of the 2 oxygens in CO_2 are from water. Isotopic analysis of the CO_2 produced from the reaction of ^{13}CO with $PtCl_3(CO)^-$ in ^{18}O-enriched aqueous solution demonstrates that one oxygen in [^{13}C]carbon dioxide is originally from water, while both oxygens in [^{12}C]carbon dioxide are derived from water. This double-labeling experiment further confirms the results obtained from ^{18}O and ^{13}C labeling studies. A detailed mechanism based on the results of these isotopic labeling studies is proposed.

The conversion of CO to CO_2 assisted by metal complexes is a basic process in several important reactions. These include the water–gas shift reaction,[1] the Reppe-modified hydroformylation,[2] the reduction of aromatic nitro compounds by carbon monoxide,[3] the hydrogenation of olefins by carbon monoxide and water,[4] the reduction of metal ions by carbon monoxide,[5] and the reduction of nitric oxide or nitrous oxide by carbon monoxide.[6,7] Nevertheless, there are only a few examples in the literature[8] concerning the mechanism of the production of CO_2 from coordinated CO

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