Synthesis of the New Chiral (*R*)- and (*S*)-Aminodiphosphine Ligands *sec*-Butylbis(2-(diphenylphosphino)ethyl)amine, *sec*-Butylbis(2-(dicyclohexylphosphino)ethyl)amine, and (α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine and Their Organometallic Chemistry When Combined with Iridium

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The new chiral aminodiphosphine ligands (*R*)- and (*S*)-*sec*-butylbis(2-(diphenylphosphino)ethyl)amine, (*R*)- and (*S*)-*sec*-butylbis(2-(dicyclohexylphosphino)ethyl)amine, and (*R*)- and (*S*)-(α-methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine have been synthesized from optically pure (*R*)-(−)- and (*S*)-(+)-*sec*-butylamine or (*R*)-(+)- and (*S*)-(−)-(α-methylbenzyl)amine. The reactions between these PNP* ligands and $[Ir(COD)(OMe)]_2$ have been investigated in either aprotic or protic solvents (COD = cycloocta-1,5-diene). Depending on the substituents at either the carbon stereocenter or the phosphorus donors, iridium products with different structures and/or stabilities are obtained. Among the new complexes, there are monohydride, dihydride, and trihydride species. It is observed that (i) cyclohexyl substituents on the phosphorus donors favor the formation of complexes where the PNP* ligand adopts a meridional conformation; (ii) phenyl groups attached to the carbon stereocenter lead to the formation of thermodynamically stable ortho-metalated products. Irrespective of the phosphorus substituents, this C−H insertion reaction is reversible at room temperature. Both the new ligands and the iridium complexes have been characterized by various chemico−physical techniques, including multinuclear NMR spectroscopy. The structure of the monohydride complex [IrH(COD)(PNP*-**5a**)] (PNP*-**5a** = (*R*)-(−)-*sec*-butylbis(2-(diphenylphosphino)ethyl)amine) has been determined by single-crystal X-ray diffraction. The PNP*-**5a** ligand uses only the two phosphorus atoms for coordination, which is completed by a terminal hydride ligand and by the two olefinic ends of a COD molecule.

Introduction

Our continuing efforts to develop a range of asymmetric iridium catalysts with chiral aminophosphine ligands for the reduction of prochiral ketones and α,*β*-unsaturated ketones[3] has lead us to investigate the chemistry of the ligands (*R*)- and (*S*)-R′C*H(Me)N($CH_2CH_2PR_2$) (R′ = Et, R = Ph, PNP*-**5a**,**b**; R′ = Et, R = Cy, PNP*-**6a**,**b**; R′ = Ph, R = Cy, PNP*-**7a**,**b**) (Chart 1). The synthesis and characterization of these new aminodiphosphines are described in this work and follow our recent studies of the chiral ligands (*R*)- and (*S*)-PhC*H(Me)N($CH_2CH_2PPh_2$)$_2$ (PNP*-**I**)[3a] and the achiral ligand *n*-$C_3H_7N(CH_2CH_2PPh_2)_3$ (PNP-**II**).[3c] Both of these aminodiphosphines have been demonstrated to be suitable ligands for the preparation of iridium catalysts exhibiting excellent chemoselectivity for the reduction of the C=O functional group in benzylideneacetone. Using the chiral ligand PNP*-**I**, asymmetric induction was achieved with good enatioselectivity.[3a]

This paper also examines the organometallic chemistry, in association with $[Ir(COD)(OMe)]_2$, of these PNP* ligands bearing phenyl/methyl or ethyl/methyl (hydrogen and nitrogen) substituents on the chiral carbon atom and cyclohexyl or phenyl substituents on the phosphorus donors (COD = cycloocta-1,5-diene). The variation in the design of the new ligands in comparison with the already reported PNP*-**I** and PNP-**II** ligands was expected to change the organometallic chemistry with the associated metal as well as the mode of action or association between the catalysts and prochiral substrates. Indeed, the design of asymmetric catalysts relies on, as yet not fully understood, the transfer of

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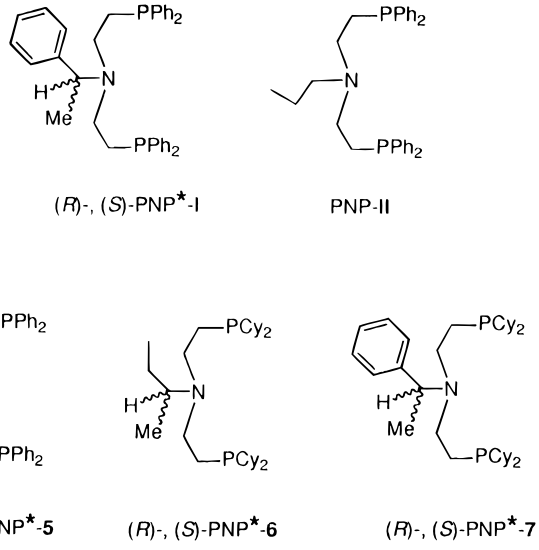
Chart 1



chiral information *via* either a through-space effect, depending on the chiral auxiliary and substrate to be proximally close in space, or an electronic (through-bond) effect.[4] Knowledge of both the mode and type of coordination of different PNP* ligands to iridium may thus be of paramount importance to increasing our knowledge of the factors that govern the enantioselective reduction of prochiral and α,β-unsaturated ketones by PNP*−Ir catalysts.

Experimental Section

All of the reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk-tube techniques. Optically pure (*R*)-(−)- and (*S*)-(+)-*sec*-butylamine (**1a** or **1b**, respectively) were obtained from Aldrich and used without further purification. Dicyclohexylphosphine was purchased from Strem Chemicals and distilled prior to use. Diphenylchlorophosphine was purchased from Fluka AG and distilled prior to use. All other chemicals were reagent grade and used as received from commercial suppliers. $[Ir(COD)(OMe)]_2$ was prepared according to a published procedure (COD = cycloocta-1,5-diene).[5]

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer interfaced to a Perkin-Elmer 3600 data station. Deuterated solvents for the NMR measurements (Merck and Aldrich) were dried over molecular sieves (4 Å). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200P spectrometer (operating at 200.13, 50.32, and 81.01 MHz, respectively); ^{2}H NMR spectra were acquired at 46.08 MHz on a Varian VXR 300 spectrometer using a broad-band 10-mm NMR probe. ^{1}H, ^{2}H, and ^{13}C NMR chemical shifts were reported relative to tetramethylsilane. ^{31}P NMR chemical shifts were reported relative to external 85% H_3PO_4, with downfield values taken as positive. ^{13}C-DEPT NMR experiments were run on a Bruker AC 200P spectrometer. The ^{1}H,^{1}H-2D COSY NMR experiments were routinely conducted on a Bruker AC 200P instrument in the absolute magnitude mode using a 45° or 90° pulse after the incremental delay or were acquired on an AVANCE DRX 500 Bruker spectrometer using the phase-sensitive TPPI mode with double quantum filter and no-spinning samples. The ^{1}H,^{1}H-2D NOESY NMR experiments were conducted on the same instrument in the phase-sensitive TPPI mode in order to discriminate between positive and negative cross peaks. The proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker AC200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device using the wide-band phosphorus decoupling sequence GARP.

In the numbering of the complexes, **a** and **b** refer to the two different stereoisomers that were synthesized when using optically pure ligands; **a** always assigned to the *R* isomer and **b** to the *S* isomer. The absence of such an addition indicates that the complex was synthesized with the racemic ligand. In the iridium complexes containing hydrides, the index A denotes the hydride ligand located *trans* to the nitrogen donor atom of the aminodiphosphine ligand.

In the ^{1}H NMR data presented for the iridium complexes, the resonances of the substituents on phosphorus as well as those of the organic backbone of the ligands have been generally omitted as they do not contain any important structural information.

Preparation of (*R*)-(−)- and (*S*)-(+)-*sec*-Butylbis-(2-(diphenylphosphino)ethyl)amine (PNP*-5a; PNP*-5b). (i) Preparation of (*R*)-(−)- and (*S*)-(+)-*sec*-Butylbis(2-hydroxyethyl)amine (2a,b). (*R*)-(−)-*sec*-Butylamine (**1a**) (8.0 g, 109 mmol) was dissolved in an ethanol/water mixture (1:2 v/v, 80 mL) under nitrogen, and the stirred reaction mixture was cooled to −10 °C. Ethylene oxide (12.5 g, 284 mmol, 2.6 equiv) was introduced directly into the reaction mixture (*ca.* 3.0 h) at such a rate to minimize the loss of unreacted oxirane. The reaction mixture was warmed to room temperature and stirred for a further 18 h. Ethanol and water were removed by distillation, and the crude diol was purified by fractional distillation under reduced pressure (139−140 °C/0.5 mmHg) to give (*R*)-(−)-*sec*-butylbis(2-hydroxyethyl)amine (**2a**) as a clear oil (14.9 g, 85%).

(*S*)-(+)-*sec*-Butylbis(2-hydroxyethyl)amine (**2b**) was prepared as a crude oil from its corresponding primary amine, **1b**, following a similar method to that described above, yield 83%. Anal. Calcd for $C_8H_{19}NO_2$: C, 59.63; H, 11.80; N, 8.70. Found: C, 59.26; H, 11.80; N, 8.46. MS (*m*/*e*): 130 (57), 74 (95), 56 (58), 28 (91), 18 (100). ^{1}H NMR ($CDCl_3$, 20 °C, 200.13 MHz; the numbering scheme of the hydrogen and carbon resonances for this product as well as all the other intermediates and ligands is given in Scheme 1 and in ref 6): δ 0.80 (d, $^3J_{H1,H2*}$ = 7.4 Hz, 3H1), 0.86 (dd, $^3J_{H3\alpha,H4}$ = 7.4 Hz, $^3J_{H3\beta,H4}$ = 7.4 Hz, 3H4), 1.18 (ddq, $^2J_{H3\alpha,H3\beta}$ = 14.5 Hz, $^3J_{H3\alpha,H2*}$ = 7.2 Hz, $^3J_{H3\alpha,H4}$ = 7.4 Hz, H3α), 1.43 (ddq, $^2J_{H3\alpha,H3\beta}$ = 14.5 Hz, $^3J_{H3\beta,H2*}$ = 7.7 Hz, $^3J_{H3\beta,H4}$ = 7.4 Hz, H3β), 2.45 (dt, $^2J_{H1'\alpha,H1'\beta}$ = 13.5 Hz, $^3J_{H1'\alpha,H2'}$ = 5.1 Hz, 2H1′α), 2.53 (dt, $^2J_{H1'\alpha,H1'\beta}$ = 13.5 Hz, $^3J_{H1'\beta,H2'}$ = 5.1 Hz, 2H1′β), 3.47 (dd, $^3J_{H1'\alpha,H2'}$ = 5.1 Hz, $^3J_{H1'\beta,H2'}$ = 5.1 Hz, 4H2′), 2.55 (ddq, $^3J_{H2*,H3\alpha}$ = 7.0 Hz, $^3J_{H2*,H3\beta}$ = 7.0 Hz, $^3J_{H1,H2*}$ = 7.0 Hz, H2*), 3.79 (br s, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 50.32 MHz): δ 11.6 (s, C4), 14.2 (s, C1), 26.5 (s, C3), 51.5 (s, 2C2′), 57.5 (s, C2*), 60.0 (s, 2C1′).

(ii) Preparation of (*R*)-(−)- and (*S*)-(+)-*sec*-Butylbis(2-chloroethyl)ammonium Chloride (3a,b). To a stirred solution of thionyl chloride (14.1 mL, 23.0 g, 193 mmol) in dry chloroform (15 mL) under nitrogen was added dropwise a solution of (*R*)-(−)-*sec*-butylbis(2-hydroxyethyl)amine (10.0 g, 62.1 mmol) (**2a**) in dry chloroform (15 mL). The reaction mixture was refluxed for 10 min then stirred at room temper-

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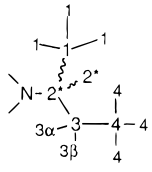
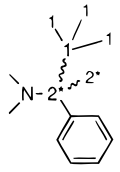
(6) Numbering schemes for the hydrogen and carbon atoms on the nitrogen tails in the ligands **5**, **6**, and **7**.



5, **6**



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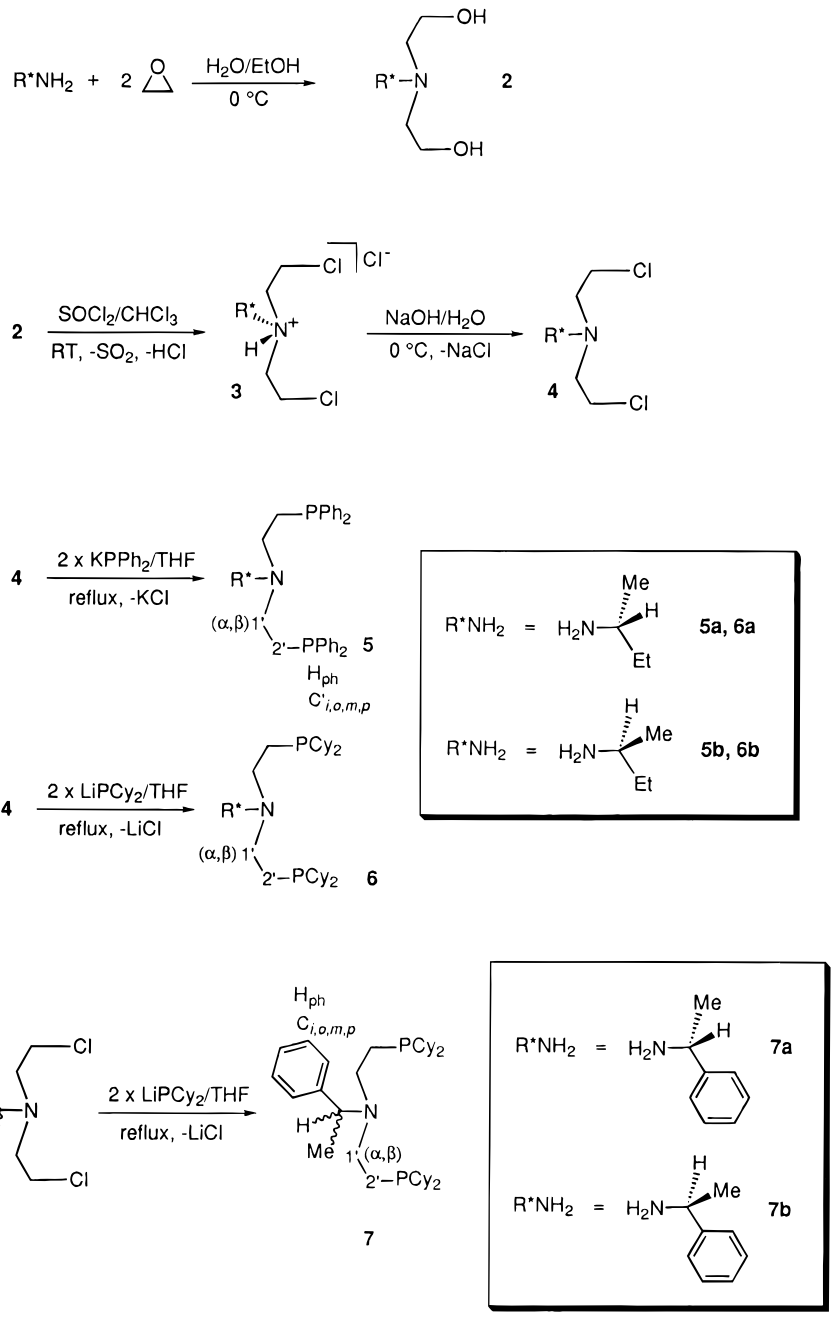
Scheme 1



ature for 18 h. The solvent was then removed *in vacuo* to leave the crude chloride salt of (*R*)-(−)-*sec*-butylbis(2-chloroethyl)ammonium (**3a**) as a white precipitate. Removal of excess thionyl chloride was achieved by repeated addition and evacuation of chloroform (3 × 20 mL) and ethanol (2 × 10 mL). The purified (*R*)-(−)-*sec*-butylbis(2-chloroethyl)ammonium chloride (**3a**) was dried to a constant weight with a pump. (*R*)-(−)-*sec*-butylbis(2-chloroethyl)ammonium chloride (**3a**) (11.6 g, 80%), as a white powder, was stored under nitrogen prior to use.

Correspondingly, (*S*)-(+)-*sec*-butylbis(2-chloroethyl)ammonium chloride (**3b**) (80%) was obtained as a white powder.

(iii) Preparation of (*R*)-(−)- and (*S*)-(+)-*sec*-Butylbis(2-chloroethyl)amine (4a,b). To a solution of (*R*)-(−)-*sec*-butylbis(2-chloroethyl)ammonium chloride (**3a**) (10.0 g, 42.7 mmol) in water (20 mL) was added an aqueous 7 M solution of sodium hydroxide (10 mL). The two immiscible layers which formed were separated, and the organic layer, (*R*)-(−)-*sec*-butylbis(2-chloroethyl)amine (**4a**), was dried over sodium hydroxide pellets. Anal. Calcd for $C_8H_{17}NCl_2$: C, 41.03; H, 7.69; N, 5.98. Found: C, 40.89; H, 7.52; N, 5.67. MS (*m*/*e*): 197 (1.1, M^+), 182 (11), 168 (84), 147 (19), 63 (40), 27 (100). ^{1}H NMR ($CDCl_3$, 20 °C, 299.94 MHz): δ 0.99 (dd, $^3J_{H3\alpha,H4}$ = 7.3 Hz, $^3J_{H3\beta,H4}$ = 7.3 Hz, 3H4), 1.37 (d, $^3J_{H1,H2*}$ = 6.4 Hz, 3H1), 1.56 (ddq, $^2J_{H3\alpha,H3\beta}$ = 13.7 Hz, $^3J_{H3\alpha,H2*}$ = 6.9 Hz, $^3J_{H3\alpha,H4}$ = 6.9 Hz, H3a), 2.07 (br m, H3β), 3.50 br m, H2*), 3.60 br m, 4H1′), 4.20 (t, $^3J_{H1',H2'}$ = 7.0 Hz, $^3J_{H1'\beta,H2'}$ = 5.1 Hz, 4H2′). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 50.32 MHz): δ 10.7 (s, C4), 13.1 (s, C1), 23.7 (s, C3), 37.3 (s, 2C2′), 52.0 (s, C2*), 61.6 (s, 2C1′).

(iv) Preparation of PNP*-5a and PNP*-5b. A solution of potassium diphenylphosphide in THF (130 mL) under nitrogen was prepared *in situ* from diphenylchlorophosphine (17.8 g, 80.8 mmol) and potassium metal (6.5 g, 165 mmol). To this stirred solution was added dropwise (*R*)-(−)-*sec*-butylbis(2-chloroethyl)amine (**4a**) (8.0 g, 40.4 mmol), and the temperature was maintained at 50 °C during the addition. During the course of the addition, the initial red solution gradually changed to a creamy color. The reaction mixture was then refluxed for 5 min and cooled to room temperature and water (100 mL) was added. The two layers were separated and the aqueous layer was extracted with ether (2 × 100 mL).

The combined organic layers were dried (Na_2SO_4) and filtered, and the ether/THF mixture was removed by distillation to leave a clear/ivory oil. The crude product was purified by recrystallization from acetone/ethanol (1:1 v/v) to give (*R*)-(−)-*sec*-butylbis(2-(diphenylphosphino)ethyl)amine (PNP*-**5a**) as white crystals (75%).

Following a similar method to that described above, (*S*)-(+)-*sec*-butylbis(2-(diphenylphosphino)ethyl)amine (PNP*-**5b**) was obtained as white crystals (78%). Anal. Calcd for $C_{32}H_{37}NP_2$: C, 77.26; H, 7.44; N, 2.82. Found: C, 78.84; H, 7.91; N, 2.94. MS (*m*/*e*): 468 (1.5), 312 (49.4), 298 (62.8), 185 (100). ^{1}H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ 0.80 (d, $^3J_{H1,H2*}$ = 6.5 Hz, 3H1), 0.85 (dd, $^3J_{H3\alpha,H4}$ = 7.3 Hz, $^3J_{H3\beta,H4}$ = 7.3 Hz, 3H4), 1.12 (ddq, $^2J_{H3\alpha,H3\beta}$ = 13.4 Hz, $^3J_{H3\alpha,H2*}$ = 7.0 Hz, $^3J_{H3\alpha,H4}$ = 7.3 Hz, H3a), 1.33 (ddq, $^2J_{H3\alpha,H3\beta}$ = 13.5 Hz, $^3J_{H3\beta,H2*}$ = 6.7 Hz, $^3J_{H3\beta,H4}$ = 7.3 Hz, H3β), 2.11 (dd, $^3J_{H1'\alpha,H2'}$ = 8.3 Hz, $^3J_{H1'\beta,H2'}$ = 8.2 Hz, 4H2′), 2.44 (dt, $^2J_{H1'\alpha,H1'\beta}$ = 13.1 Hz, $^3J_{H1'\alpha,H2'}$ = 7.0 Hz, 2H1′α), 2.53 (dt, $^2J_{H1'\alpha,H1'\beta}$ = 13.1 Hz, $^3J_{H1'\beta,H2'}$ = 7.0 Hz, 2H1′β), 2.63 (ddq, $^3J_{H2*,H3\alpha}$ = 7.0 Hz, $^3J_{H2*,H3\beta}$ = 6.7 Hz, $^3J_{H2*,H1}$ = 6.7 Hz, H2*), 7.27−7.45 (m, 20H_{ph}. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δ 12.9 (s, C4), 14.7 (s, C1), 27.5 (s, C3), 28.8 (d, $^1J_{P,C2'}$ = 12.2 Hz, 2C2′), 46.9 (d, $^2J_{P,C1'}$ = 22.9 Hz, 2C1′), 57.4 (s, C2*), 129.0 (s, 4C_p), 129.2 (s, 8C_m), 133.3 (d, $^2J_{P,C_o}$ = 3.1 Hz, 4C_o), 133.7 (d, $^2J_{P,C_o'}$ = 3.1 Hz, 4C_o'), 139.8 (d, $^1J_{P,C_i}$ = 14.2 Hz, 2C_i), 140.1 (d, $^1J_{P,C_i'}$ = 14.2 Hz, 2C_i'). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 81.01 MHz): δ −20.2 (s, 2P). **5a**: $[\alpha]_D^{20}$ = −24.7 (*c* = 1, $CHCl_3$). **5b**: $[\alpha]_D^{20}$ = +23.0 (*c* = 1, $CHCl_3$).

Preparation of (R)-(−)- and (*S*)-(+)-*sec*-Butylbis-(2-(dicyclohexylphosphino)ethyl)amine (PNP*-6a,b). A solution of lithium dicyclohexylphosphide in THF (100 mL) under nitrogen was prepared *in situ* from dicyclohexylphosphine (10.0 g, 50.4 mmol) and *n*-butyllithium (1.6 M in *n*-hexane solution, 31.3 mL, 50.5 mmol). To this stirred solution was added dropwise the free chloroamine (**4a** or **4b**) (6.2 g, 25.2 mmol), and the temperature was maintained at room temperature during the addition. During the course of the addition the initial yellow solution gradually became ivory colored. The reaction mixture was then refluxed for 5 min and cooled to room temperature, and the solvent was removed *in vacuo*. The resulting residue was washed with ethanol (2 × 50 mL). The crude product was purified by recrystallization from THF/ethanol (1:20, v/v) to give the corresponding aminodiphosphine ligand (*R*)-(−)- or (*S*)-(+)-*sec*-butylbis(2-((dicyclohexylphosphino)ethyl)amine (PNP*-**6a** or PNP*-**6b**) as a white crystalline compound in yield higher than >70%. Anal. Calcd for $C_{32}H_{61}NP_2$: C, 73.67; H, 11.79; N, 2.68. Found: C, 73.48; H, 11.72; N, 2.52.

^{1}H NMR ($CDCl_3$, 20 °C, 200.13 MHz): δ 0.85 (d, $^3J_{H1,H2*}$ = 7.3 Hz, 3H1), 0.95 (dd, $^3J_{H3\alpha,H4}$ = 5.6 Hz, $^3J_{H3\beta,H4}$ = 5.6 Hz, 3H4), 1.02−1.35 (m, 20CH_2(cyclohexyl)), 1.35−1.61 (m, 4CH_1-(cyclohexyl) and 4CH_2(P-N)), 1.61−1.93 (m, 20CH_2(cyclohexyl)), 2.40−2.83 (m, 4CH_2(P-N) and 1H2*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δ 12.4 (s, C4), 14.9 (s, C1), 22.6 (d, $^1J_{P,C2'}$ = 17.1 Hz, 2C2′), 27.4 (s, C3), 27.7 (s, 4CH_2(cyclohexyl)), 28.1 (d, J_{P,CH_2} = 7.3 Hz, 4CH_2(cyclohexyl)), 28.2 (d, J_{P,CH_2} = 11.0 Hz, 4CH_2(cyclohexyl)), 29.9 (d, J_{P,CH_2} = 7.3 Hz, 4CH_2-(cyclohexyl)), 31.3 (d, J_{P,CH_2} = 14.7 Hz, 4CH_2(cyclohexyl)), 34.1 (d, J_{P,CH_2} = 11.0 Hz, 4CH_2(cyclohexyl)), 49.9 (d, $^2J_{P,C1'}$ = 30.5 Hz, 2C1′), 57.6 (s, C2*). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 81.01 MHz): δ −7.19 (s, 2P). **6a**: $[\alpha]_D^{20}$ = −23.2 (*c* = 1, $CHCl_3$). **6b**: $[\alpha]_D^{20}$ = +23.7 (*c* = 1, $CHCl_3$).

Preparation of (*R*)-(+)- and (*S*)-(−)-(α-Methylbenzyl)-bis(2-((dicyclohexylphosphino)ethyl)amine (PNP*-7a and PNP*-7b). A solution of lithium dicyclohexylphosphide in THF (100 mL) under nitrogen was prepared *in situ* from dicyclohexylphosphine (10.0 g, 50.4 mmol) and *n*-butyllithium (1.6 M solution in *n*-hexane, 31.3 mL, 50.5 mmol). To this stirred solution was added dropwise either (*R*)-(+) or (*S*)-(−)-(α-methylbenzyl)bis(2-chloroethyl)amine[3a] (5.0 g, 25.2 mmol), and the temperature was maintained at room temperature during the addition. During the course of the addition, the initial yellow solution gradually became ivory colored. The reaction mixture was then refluxed for 5 min and cooled to room temperature, and the solvent was removed *in vacuo*. The resulting residue was washed with ethanol (2 × 50 mL). The crude product was purified by recrystallization from THF/ethanol (1:20 v/v) to give the corresponding aminodiphosphine ligand (*R*)-(+)- or (*S*)-(−)-α-methylbenzyl-bis(2-((dicyclohexylphosphino)ethyl)amine (PNP*-**7a** or PNP*-**7b**) as a white crystalline compound in a yield higher than 70%.

Anal. Calcd for $C_{36}H_{61}NP_2$: C, 75.89; H, 10.79; N, 2.46. Found: C, 75.76; H, 10.61; N, 2.34. ^{1}H NMR ($CDCl_3$, 20 °C, 200.13 MHz): δ 1.00−1.30 (m, 20CH_2(cyclohexyl) and 4CH_2-(P-N)), 1.35 (d, $^3J_{H1,H2*}$ = 6.6 Hz, 3H1), 1.40−1.57 (m, 4CH_1(cyclohexyl)), 1.57− 1.93 (m, 20CH_2(cyclohexyl)), 2.47−2.72 (m, 4CH_2(P-N)), 3.91 (q, $^3J_{H1,H2*}$ = 6.7 Hz, 1H2*), 7.1−7.39 (m, 5H_{ph}). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 50.32 MHz): δ 17.1 (s, C1), 18.0 (d, J_{P,CH_2} = 17.3 Hz, 4CH_2(cyclohexyl)), 25.3 (s, 4CH_2(cyclohexyl)), 25.9 (d, J_{P,CH_2} = 14.3 Hz, 4CH_2-(cyclohexyl)), 26.1 (d, J_{P,CH_2} = 14.3 Hz, 4CH_2(cyclohexyl)), 27.6 (d, $^1J_{P,C2'}$ = 7.5 Hz, 2C2′), 29.1 (d, J_{P,CH_2} = 14.7 Hz, 4CH_2-(cyclohexyl)), 31.8 (d, J_{P,CH_2} = 11.9 Hz, 4CH(cyclohexyl)), 47.5 (d, $^2J_{P,C1'}$ = 30.4 Hz, 2C1′), 58.5 (s, C2*), 125.5 (s, C_p), 126.3 (s, 2C_m), 127.1 (s, 2C_o), 144.0 (s, C_i). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 81.01 MHz): δ −9.53 (s, 2P). **7a**: $[\alpha]_D^{20}$ = +18.4 (*c* = 1, $CHCl_3$). **7b**: $[\alpha]_D^{20}$ = −19.4 (*c* = 1, $CHCl_3$).

The racemic aminodiphosphine ligands *rac*-**5**, **6**, and **7** were also prepared from the corresponding racemic amines following the same procedure.

Preparation of Iridium−PNP* Complexes. (*R*)- and (*S*)-[*sec*-Butylbis(2-(diphenylphosphino)ethyl)amine]-iridium Hydride Cycloocta-1,5-diene, [IrH(COD)(PNP*-5a,b)] (9a,b). [Ir(COD)(OMe)]$_2$ (663 mg, 1.0 mmol) was dissolved in dichloromethane (20 mL) under nitrogen. PNP*-**5a**,**b**, (1.00 g, 2.0 mmol) was added, and the yellow reaction mixture was stirred at room temperature for 1 h, during which time it became orange. After evaporation of the solvent to *ca*. 10 mL and addition of methanol (15 mL), a crystalline solid separated. This precipitate was filtered under nitrogen and washed with methanol and *n*-pentane to give [IrH(COD)-(PNP*-**5a**,**b**)] (**9a**,**b**) (124 mg, 78%). This was recrystallized from a dichloromethane/propan-2-ol mixture (2:1 v/v) to give white-creamy crystals (111 mg, 70%). IR (Nujol mull): ν(Ir−H) 2111 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{50}NIrP_2$: C, 60.07; H, 6.30; N, 1.75. Found: C, 59.85; H, 6.18; N, 1.49. ^{1}H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ −13.80 (t, $^2J_{H_{hydride},P}$ = 22.3 Hz, $H_{hydride}$), 0.48 (d, $^3J_{H1,H2*}$ = 6.4 Hz, 3H1), 0.62 (t, $^3J_{H3,H4}$ = 6.4 Hz, 3H4), 0.74 (dq, $^3J_{H2,H3}$ = 6.4 Hz, $^3J_{H3,H4}$ = 6.4 Hz, 2H3), 1.00−1.30, (m, 4H2′), 1.30−1.80 (m, 4H1′), 2.06 (m, 1H2*), 2.20−2.70 (m, 4CH_2(COD)), 3.15−3.60 (m, 4CH(COD)), 7.25−7.70 (m, 20CH_{ph}). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δ 12.3 (s, C4), 13.4 (s, C1), 26.2 (s, C2), 31.3 (dd, $J_{C,P}$ = 17.3 Hz, $^3J_{C,P}$ = 5.0 Hz, CH_2−P), 35.0 (d, $^2J_{C,P}$ = 18.1 Hz, CH_2-N), 35.5 (d, $^2J_{C,P}$ = 16.5 Hz, CH_2=N), 36.0 (dd, $J_{C,P}$ = 16.3 Hz, $^3J_{C,P}$ = 3.0 Hz, CH_2−P), 46.8 (d, $J_{C,P}$ = 5.8 Hz, 4CH_2(COD)), 47.0 (dd, $J_{C,P}$ = 24.7 Hz, $J_{C,P}$ = 7.4 Hz, 2CH_1(COD)), 58.3 (s, C1*), 78.8 (s, 2CH_1(COD)), 127.8− to 143.5 (m, 24C_{ph}). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 81.01 MHz): δ 0.61 (d, $^2J_{P,P}$ = 22.5 Hz, P), 2.34 (d, $^2J_{P,P}$ = 22.6 Hz, P).

(*R*)- and (*S*)-[*sec*-Butylbis(2-(diphenylphosphino)-ethyl)amine]iridium Trihydride, [IrH$_3$(PNP*-5a,b)] (10a,b). (**A**) Compound **9a**,**b** (600 mg, 0.75 mmol) was dissolved in THF (30 mL) under nitrogen. Hydrogen gas was slowly bubbled through the reaction mixture for 30 min. The reaction mixture was concentrated to one-half the original volume, and propan-2-ol (10 mL) was slowly added to induce precipitation of cream-colored microcrystals. This product was filtered and washed with propan-2-ol and *n*-hexane to give the iridium trihydride [IrH$_3$(PNP*-**5a**,**b**)] (**10a**,**b**). Recrystallization of the crude product from THF and propan-2-ol (2:1 v/v) gave pure **10a**,**b** (510 mg, 98%) as cream-colored crystals. GC/MS analysis of the reaction mixture showed the quantitative formation of cyclooctene (COE).

(**B**) Compound **9a**,**b** (200 mg, 0.25 mmol) was dissolved in THF (10 mL) and propan-2-ol (40 mL) under nitrogen. The reaction mixture was refluxed for 14 h and then cooled to room temperature. GC/MS analysis of a sample showed the presence of COE in the reaction mixture. After concentration to one-half the original volume under vacuum, *n*-hexane was added (20 mL). The crude product which separated was filtered and recrystallized (as described above) to give **10a**,**b** (140 mg, 80%). IR (Nujol mull): ν(Ir−H) 2160 (s), 2025 (s), 1993 (s), cm^{-1}. Anal. Calcd for $C_{32}H_{40}NIrP_2$: C, 55.41; H, 5.81; N, 2.02. Found: C, 55.30; H, 5.71; N, 1.84. ^1H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ −23.20 (dddd, $^2J_{H_A,P_{cis}}$ = 11.3 Hz, $^2J_{H_A,P_{cis}}$ = 11.3 Hz, $^2J_{H_A,H_B}$ = 5.7 Hz, $^2J_{H_A,H_{B'}}$ = 5.7 Hz, 1H_A), −9.75 (dddd, $^2J_{H_B,P_{trans}}$ = 129.6 Hz, $^2J_{H_B,P_{cis}}$ = 20.9 Hz, $^2J_{H_B,H_{B'}}$ = 38.9 Hz, $^2J_{H_B,H_A}$ = 6.0 Hz, 2H_B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δ 13.0 (s, C1), 15.9 (s, C4), 29.2 (s, C3), 34.8 (d, $^1J_{P,C2'}$ = 25.6 Hz, 1C2′), 35.8 (d, $^1J_{P,C2'}$ = 25.6 Hz, C2′), 54.7 (d, $^2J_{P,C1'}$ = 6.9 Hz, C1′), 56.9 (d, $^2J_{P,C1'}$ = 6.9 Hz, C1′), 69.7 (s, C2*), 128.0−142.0, 24C_{ph}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 81.01 MHz): δ 24.42 (d, $^2J_{P,P}$ = 5.7 Hz, P), 25.70 (d, $^2J_{P,P}$ = 5.7 Hz, P).

***In Situ* Formation of (*R*)- and (*S*)-[*sec*-Butylbis(2-(dicyclohexylphosphino)ethyl)amine]iridium Hydride Cycloocta-1,5-diene, [IrH(COD)(PNP*-6a,b)] (13a,b).** A 5-mm NMR tube was charged with $[Ir(COD)(OMe)]_2$ (6.6 mg, 0.01 mmol), PNP*-**6a**,**b** (10.4 mg, 0.02 mmol), and toluene-d_8 (0.75 mL) under nitrogen. The tube was flame sealed under nitrogen and heated to 37 °C for 1 h. $^{31}P\{^1H\}$ NMR analysis showed the formation of the five-coordinate monohydride complex [IrH(COD)(PNP*-**6a**,**b**)] (**13a**,**b**) as the only iridium-containing product. ^1H NMR (toluene-d_8, 20 °C, 200.13 MHz): δ −14.3 (dd, $^2J_{H_{hydride},P}$ = 23.9 Hz, $^2J_{H_{hydride},P}$ = 23.9 Hz, $H_{hydride}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 81.01 MHz): δ −1.51 ($^2J_{P,P}$ = 16.9 Hz, P), 1.52 ($^2J_{P,P}$ = 16.9 Hz, P).

Prolonged heating of this sample to a final temperature of 100 °C resulted in the transformation of this monohydride species into a number of other iridium−aminodiphosphine complexes which defied first-order analysis. During this thermal degradation, free COD was liberated into the solution (GC/MS).

***In Situ* Formation of (*R*)- and (*S*)-[(α-Methylbenzyl)-bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Hydride Cycloocta-1,5-diene, [IrH(COD)(PNP*-7a,b] (14a,b).** A 5-mm NMR tube was charged with $[Ir(COD)(OMe)]_2$ (6.6 mg, 0.01 mmol), PNP*-**7a**,**b** (11.2 mg, 0.02 mmol), and toluene-d_8 (0.75 mL) under nitrogen. The tube was flame sealed under nitrogen and heated to 37 °C for 1 h. $^{31}P\{^1H\}$ NMR analysis showed the formation of the five-coordinate monohydride [IrH(COD)(PNP*-**7a**,**b**)] (**14a**,**b**) as the only iridium-containing product. ^1H NMR (C_7D_8, 37 °C, 200.13 MHz): δ −15.3 (dd, $^2J_{H_{hydride},P_{cis}}$ = 25.1 Hz, $H_{hydride}$). $^{31}P\{^1H\}$ NMR (C_7D_8, 37 °C, 81.01 MHz): δ −1.00 ($^2J_{P,P}$ = 14.3 Hz, P), 0.75 ($^2J_{P,P}$ = 14.3 Hz, P).

Prolonged heating of this sample at 60 °C resulted in the selective transformation of the monohydride species to the dihydride ortho-metalated complex **15a**,**b** (see below). Following the thermal degradation of **14a**,**b**, free COD was detected in the reaction mixture by GC/MS.

Preparation of [IrH(COD)(PNP*-6a)] (13a). $[Ir(COD)(OMe)]_2$ (200 mg, 0.30 mmol) was dissolved in THF (15 mL) under nitrogen. The ligand PNP*-**6a** (350 mg, 0.67 mmol) was added, and the yellow reaction mixture became orange while stirring at room temperature for 1 h. The reaction mixture was concentrated, and *n*-pentane was added until a yellow solid precipitated. $^{31}P\{^1H\}$ NMR analysis showed it to contain **13a** (80%) together with some unidentified PNP*-**6a**/Ir products. Using MeOH in the place of *n*-pentane to induce precipitation, several unidentified products separated, none of which was the (hydride)COD complex **13a**.

Preparation of [IrH(COD)(PNP*-7a)] (14a). $[Ir(COD)(OMe)]_2$ (663 mg, 1.0 mmol) was dissolved in THF (15 mL) under nitrogen. The ligand PNP*-**7a** (1.12 g, 2.0 mmol) was added, and the yellow reaction mixture became orange while stirring at room temperature for 1 h. The reaction mixture was concentrated, and *n*-pentane was added to induce the precipitation of **14a** as a yellow solid in *ca.* 90% yield. In a separate experiment, MeOH was used instead of *n*-pentane. As a result, a distinct color change from orange to pink occurred. Evaporation of the solvent under a brisk current of nitrogen gave off-white crystals. The precipitate was filtered under nitrogen and washed with methanol and *n*-hexane to give the *mer*-dihydride complex, *mer*-$[IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**15a**), in almost quantitative yield (see below).

***(R)*- and (*S*)-[(α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Dihydride, $[IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (15a,b).** $[Ir(COD)(OMe)]_2$ (210 mg, 0.32 mmol) was dissolved in toluene (30 mL) under nitrogen. The ligand (PNP*-**7a**,**b**) (355 mg, 0.63 mmol) was added as a solid, and the yellow solution refluxed for 4 h under nitrogen. The solvent was removed (*in vacuo*) from the resultant dark brown solution to leave a creamy-colored residue. Recrystallization of this crude product from dichloromethane and methanol gave pure *mer*-$[IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**15a**,**b**) (410 mg, 85%) as cream-colored crystals. IR (Nujol mull): ν(Ir−H) 2096 (s), 1912.0 (s) cm^{-1}. Anal. Calcd for $C_{36}H_{60}NIrP_2$: C, 56.76; H, 7.94; N, 1.84. Found: C, 56.50; H, 7.76; N, 1.75. ^1H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ =21.43 (ddd, $^2J_{H_A,P_{cis}}$ 14.6 Hz, $^2J_{H_A,P_{cis}}$ 14.6 Hz, $^2J_{H_A,H_B}$ 5.4 Hz, H_A), −13.79 (ddd, $^2J_{H_B,P_{cis}}$ 19.2 Hz, $^2J_{H_B,P_{cis}}$ 19.2 Hz, $^2J_{H_B,H_A}$ 4.6 Hz, H_B), 6.28 (m, H_1), 6.47 (m, 2$H_{2/3}$), 7.51 (m, H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δ 11.4 (s, C1), 27.0−32.0 (all singlets, 20CH_2(cyclohexyl) and 2C2′), 33.6 (dd, $^1J_{P,CH}$ = 22.9 Hz, $^3J_{P,CH}$ = 7.6 Hz, CH_1(cyclohexyl)), 35.3 (dd, $^1J_{P,CH}$ = 21.9 Hz, $^3J_{P,CH}$ = 7.6 Hz, CH_1(cyclohexyl); 37.2 (dd, $^1J_{P,CH}$ = 26.7 Hz, $^3J_{P,CH}$ = 7.6 Hz, CH_1(cyclohexyl)), 40.2 (dd, $^1J_{P,CH}$ = 18.1 Hz, $^3J_{P,CH}$ = 8.6 Hz, CH_1(cyclohexyl)), 60.9 (dd, $^2J_{P,C1'}$ = 4.2 Hz, $^4J_{P,C1'}$ = 4.2 Hz, C1′), 61.3 (m, C1′), 66.9 (s, C2*), 118.9 (s, C_{ph}), 119.9 (s, C_{ph}), 125.5 (s, C_{ph}), 145.3 (s, C_{ph}), 156.4 (s, C_i), 162.3 (dd, $^2J_{P,C_{o,m}}$ = 8.6 Hz, $^2J_{P,C_{o,m}}$ = 8.6 Hz, $C_{o,m}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 81.01 MHz): AB system; δ 39.36 ($^2J_{P,P}$ = 348.6 Hz, P), 43.42 ($^2J_{P,P}$ = 348.6 Hz, P).

Deuterium Exchange Reaction of *rac,mer*-$[IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (15) with D_2O. (A). *In Situ* NMR Experiment. In a 5-mm screw-cap NMR tube, 10 mg (0.01 mmol) of *rac,mer*-$[IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**15**) was dissolved in THF-d_8 (0.6 mL) and the ^1H NMR spectrum recorded. One drop of D_2O was added through the serum cap to the solution, and the tube was agitated for 2 min before recording the ^1H spectrum again. The sample was then agitated for a further 10 min at room temperature and ^1H spectrum recorded again. Comparison of the proton NMR spectra clearly showed the exchange of the hydride ligands for deuteride ligands and the selective incorporation of deuterium into the *ortho*-position of the cyclometalated phenyl ring.

(B) Preparation of *rac,mer*-$[IrD_2\{C_6H_3DC^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (15-d_3). **15** (100 mg, 0.1 mmol) was dissolved in THF (5 mL), and 1 mL of D_2O was added. After vigorous stirring for 1h, the solution was evaporated to dryness under vacuum. The solid residue was washed with CH_3OD (2 × 2 mL) and recrystallized from CH_2Cl_2/CH_3OD to give **15-d_3** in *ca.* 80% yield. IR (Nujol mull): ν(Ir−D) not observed. ^2H NMR (THF, 20 °C, 46.08 MHz): δ −21.40 (m, D_A), −13.80 (m, D_B), 6.28 (m, D_1).

***rac,mer*-[(α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Dichloride, $[IrCl_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (18).** Complex **15** (250 mg, 0.33 mmol) was dissolved in $CHCl_3$ (10 mL) and heated at 65 °C for 2 h. The solvent was removed under nitrogen, and the residue was recrystallized from dichloromethane (8 mL) and methanol (5 mL) to give pure *rac,mer*-$[IrCl_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**18**) (196 mg, 72%) as small brick-like crystals. Anal. Calcd for $C_{36}H_{58}NCl_2IrP_2 \cdot 2CH_2Cl_2$:

C, 43.62; H, 6.25; N, 1.40. Found: C, 43.17; H, 6.34; N, 1.40. ^{1}H NMR (CD_2Cl_2, 20 °C, 200.13 MHz): δ 6.51 (m, H_1'), 6.83 (m, $H_{2/3}$), 6.92 (m, $H_{2/3}$), 7.91 (m, H_4). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C, 50.32 MHz): δ 11.4 (s, C1), 27.0−32.0 (all singlets, 20CH_2(cyclohexyl) and 2C2′), 33.5 (d, $^1J_{P,CH}$ = 23.2 Hz, CH_1(cyclohexyl)), 35.3 (d, $^1J_{P,CH}$ = 26.9 Hz, CH_1(cyclohexyl)), 38.0 (d, $^1J_{P,CH}$ = 26.9 Hz, CH_1(cyclohexyl)), 39.0 (d, $^1J_{P,CH}$ = 24.4 Hz, CH_1(cyclohexyl)), 60.9 (m, C1′), 62.2 (m, C1′), 69.5 (s, C2*), 120.4 (s, C_{ph}), 122.3 (s, C_{ph}), 126.8 (s, C_{ph}), 134.1 (dd, $^2J_{P,C_{o,m}}$ = 7.3 Hz, $^2J_{P,Co,m}$ = 7.3 Hz, $C_{o,m}$), 135.2 (s, C_{ph}), 151.5 (s, C_i). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 81.01 MHz): AB system; δ −2.34 ($^2J_{P,P}$ = 393.1 Hz, P), 4.90 ($^2J_{P,P}$ = 393.1 Hz, P).

Preparation of *rac,mer*-[(α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Hydride Chloride, [Ir(H)Cl{$C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2$}] (17). A 5-mm NMR tube was charged with $[Ir(COD)(OMe)]_2$ (6.6 mg, 0.01 mmol), PNP*-**7** (11.2 mg, 0.02 mmol), and dichloromethane-d_2 (0.75 mL) under nitrogen. The tube was flame sealed under nitrogen and heated to 95 °C for 14 h. ^{31}P{^{1}H} NMR analysis gave 60% conversion to the monohydride species *rac,mer*-[Ir(H)Cl{$C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2$}] (**17**). ^{1}H NMR ($CD_2Cl_2$, 20 °C, 200.13 MHz): δ −18.6 (dd, $^2J_{H_{hydride},P_{cis}}$ = 13.4 Hz, $^2J_{H_{hydride},P_{cis}}$ = 13.4 Hz, $H_{hydride}$), 6.60 (d, $^2J_{H-H}$ = 7.5 Hz, 1H_{ph}), 6.94 (t, $^2J_{H-H}$ = 7.3 Hz, 1H_{ph}), 7.02 (t, $^2J_{H-H}$ = 7.3 Hz, 1H_{ph}), 7.83 (d, $^2J_{H-H}$ = 7.4 Hz, 1H_{ph}). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 81.01 MHz): AB spin system; δ 28.00 ($^2J_{P,P}$ = 355.1 Hz, P), 30.13 ($^2J_{P,P}$ = 355.1 Hz, P).

On standing at room temperature overnight, white crystals of the (hydride)chloride **17** (6 mg) separated out of the orange solution. IR (Nujol mull): ν(Ir−H): 2080 (s) cm^{-1}. Anal. Calcd for $C_{36}H_{61}NClIrP_2$: C, 54.22; H, 7.71; N, 1.76. Found: C, 53.98; H, 7.85; N, 1.85.

***rac,fac*-[(α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Trihydride, [IrH_3(PNP*-7)] (16). (A).** $[Ir(COD)(OMe)]_2$ (200 mg, 0.30 mmol) was dissolved in THF (30 mL) under nitrogen. The ligand *rac*-α-methylbenzylbis(2-((dicyclohexylphosphino)ethyl)amine, PNP*-**7** (350 mg, 0.62 mmol), was added. Hydrogen gas was bubbled through this solution for 1 h, and the solution was heated to 50 °C for the first 15 min. GC/MS analysis of the reaction mixture showed the quantitative formation of COE. After complete evaporation of the solvent *in vacuo* at room temperature, a creamy-colored residue was obtained. ^{31}P{^{1}H} NMR analysis of the crude product showed the formation of **15** together with a minor amount of the trihydride *rac,fac*-[IrH_3(PNP*-**7**)] (**16**) (10%) as well as several other minor products. Recrystallization of this crude product from dichloromethane and methanol gave pure **15**.

(**B**) $[Ir(COD)(OMe)]_2$ (200 mg, 0.30 mmol) was dissolved in THF (30 mL) under nitrogen. The ligand PNP*-**7** (350 mg, 0.62 mmol) was added. Hydrogen gas was bubbled through this solution for 30 min, and the solution was heated to 30 °C. After complete evaporation of the solvent *in vacuo*, a yellow-colored residue was obtained. ^{31}P and ^{1}H NMR spectra of this residue showed the formation of **15** and **16** in a ratio of approximately 1:1 (70% based on integration of the ^{31}P resonances) together with several minor products. NMR data for **16**: ^{1}H NMR (CD_2Cl_2, 20 °C, 200.13 MHz) δ −25.12 (dddd, $^2J_{H_A,P_{cis}}$ = 11.6 Hz, $^2J_{H_A,P_{cis}}$ = 11.6 Hz, $^2J_{H_A,H_B}$ = 6.1 Hz, $^2J_{H_A,H_{B'}}$ = 6.1 Hz, H_A), −10.96 (dddd, $^2J_{H_B,P_{trans}}$ = 128.8 Hz, $^2J_{H_B,P_{cis}}$ = 26.9 Hz, $^2J_{H_B,H_{B'}}$ = 29.9 Hz, $^2J_{H_B,H_A}$ = 6.1 Hz, 2H_B. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 81.01 MHz): δ 37.2 (d, $^2J_{P,P}$ = 9.8 Hz, P), 29.7 (d, $^2J_{P,P}$ = 9.8 Hz, P).

Heating this NMR sample (prepared under nitrogen) converted all species to **15**.

(**C**) The above reaction was also carried out at 0 °C while hydrogen was bubbled through the THF solution. ^{31}P NMR showed that there was only *ca.* 30% conversion to the trihydride **16**, *ca.* 50% conversion to a monohydride species, and a small amount of the monohydride COD species. Once again, the NMR sample was heated (under nitrogen) and all species were converted to the dihydride **15**.

Table 1. Crystallographic Data and Details of Refinements for (*R*)-[IrH(COD){$C_2H_5C^*H(CH_3)N(CH_2CH_2PPh_2)_2$}] (9a)

formula	$C_{40}H_{50}IrNP_2$
fw	799.0
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
cryst dimens, mm	0.35 × 0.35 × 0.15
a, Å	9.852(2)
b, Å	12.689(3)
c, Å	15.776(3)
α, deg	68.66(2)
β, deg	75.27(2)
γ, deg	78.95(2)
V, Å^3	1765.8(8)
Z	2
D(calcd), g cm^{-3}	1.50
D(obs), g cm^{-3}	1.49
μ(Mo Kα), cm^{-1}	38.8
F(000)	808
θ range, deg	1.5−28.0
temp for data collect, K	293
no. of reflns collcd	8799
no. of reflns indep	8493
no. of reflns indep [$I > 3\sigma(I)$]	6521
data/restraints/params	6521/0/397
final *R* indices [$I > 3\sigma(I)$]	R1 = 0.037, wR2 = 0.041
largest diff peak and hole, e Å^{-3}	0.90 and −0.70

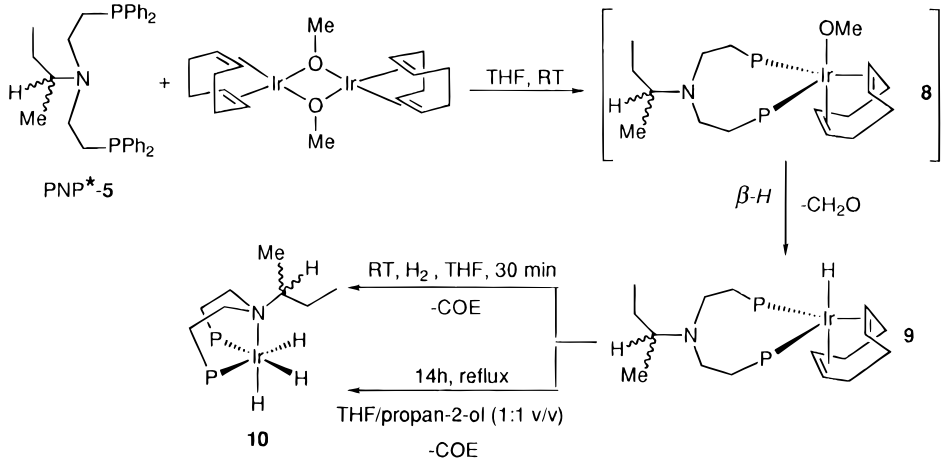
(**D**) A solution of **15** (200 mg, 0.26 mmol) in 30 mL of THF was pressurized with H_2 (20 atm) and then heated to 60 °C for 1 h. The solvent was removed *in vacuo* at room temperature. ^{31}P and ^{1}H NMR spectroscopy showed there was no conversion to the trihydride species and that the only phosphorus-containing product was the starting dihydride complex.

Attempted Preparation of *rac*-[*sec*-Butylbis(2-(dicyclohexylphosphino)ethyl)amine]iridium Trihydride [IrH_3(PNP*-6)]. $[Ir(COD)(OMe)]_2$ (200 mg, 0.30 mmol) was dissolved in THF (30 mL) under nitrogen. The ligand, *rac,sec*-bis(2-((dicyclohexylphosphino)ethyl)amine, PNP*-**6** (350 mg, 0.67 mmol), was added. Hydrogen gas was bubbled through this solution for 2 h at room temperature. ^{31}P NMR spectroscopy indicated that there was no conversion to a trihydride species (either *mer* or *fac*). Heating the NMR sample under a positive pressure of H_2 resulted in the formation of several products (some hydride bearing) that were not identified.

X-ray Data Collection and Processing. Crystals of **9a** were grown from a dichloromethane/methanol solution (2:1 v/v) at 25 °C under a nitrogen atmosphere. Intensities of the crystal were collected on an ENRAF-Nonius CAD4 diffractometer. Lattice parameters were obtained by a least-squares refinement of 25 accurately centered reflections. Three standard reflections were measured every 2 h for the orientation and intensity control. During data collection no decay of the specimen was observed. Intensity data were corrected for Lorentz−polarization factors, and the absorption correction based on a ψ scan was applied. Crystallographic details are reported in Table 1.

The stucture was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares procedures. The coordinated hydride was located from the difference Fourier map after anisotropic refinement. The positions of all of the other hydrogen atoms were calculated and confirmed by a difference Fourier map. Residual peaks were found only near the heavy atom. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The final cycles of refinement converged at R1(F_o) = 0.037 and wR2(F_o) = 0.041 for 6251 observed reflections with $I > 3\sigma(I)$. Scattering factors, anomalous dispersion terms, and programs were taken from the Enraf-Nonius MOLEN library.[7a] The program ORTEP[7b] was also used.

Scheme 2



Results and Discussion

Synthesis of Chiral Aminodiphosphine Ligands. Analogous to our methods previously employed to prepare the chiral (*R*)-(+)- and (*S*)-(−)-(α-methylbenzyl)bis(2-((diphenylphosphino)ethyl)amine ligands PNP*-**I**,[3a,c] the related ligands PNP*-**5a**,**b**, PNP*-**6a**,**b**, and PNP*-**7a**,**b** bearing different combinations of substituents on the phosphorus ends (phenyl for **5** and *cyclo*-C_6H_{11} for **6** and **7**) and/or on the stereoactive nitrogen-tail (*sec*-butyl for **5** and **6**; α-methylbenzyl for **7**) were prepared according to the general method shown in Scheme 1.

Descriptively, nucleophilic attack with the chiral primary amines **1a** or **1b** on 2.0 equiv of ethylene oxide (and consequent ring opening) in ethanol/water at 0 °C gives the corresponding chiral diols **2a** or **2b** as clear viscous oils in excellent yields (83 to 85%). Subsequent transformation of these diols into their dichloro−ammonium salts **3a** or **3b** is achieved using thionyl chloride in dry chloroform. Addition of concentrated sodium hydroxide to these ammonium salts **3a** or **3b** gives the corresponding dichlorides **4a** or **4b**. These dichloro tertiary amines are added immediately to stirred solutions of either potassium diphenylphosphide or lithium dicyclohexylphosphide in THF maintaining a temperature of 50 or 20 °C, respectively, during the addition. During the course of the reaction, the initial red solution gradually changes to a creamy color. After work-up, the crude PNP* ligands can be purified by recrystallization from acetone/ethanol to give off-white microcrystals (yields 70 to 78%).

Synthesis and Characterization of (*R*)- and (*S*)-[IrH(COD)(PNP*-5a,b)] (9a,b). (*R*)- and (*S*)-[IrH(COD)(PNP*-**5a**,**b**)] (**9a**,**b**) were routinely synthesized from the iridium dimer $[Ir(COD)(OMe)]_2$ and 2 equiv of the corresponding ligand PNP*-**5a**,**b** in good yields (Scheme 2). Compound **9a** is thermally stable in refluxing THF or toluene. Crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane/methanol under nitrogen.

The structure of **9a** was solved, and an ORTEP diagram of the molecule is shown in Figure 1. The structure of **9a** consists of the central iridium atom

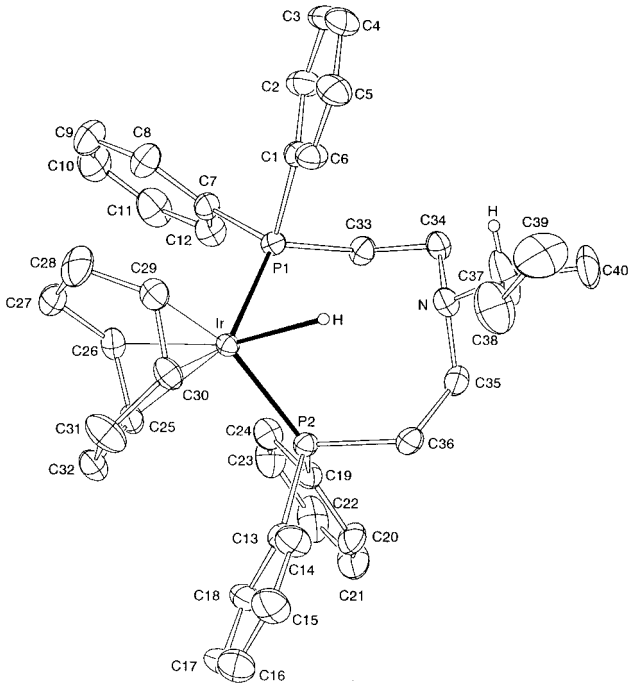


Figure 1. ORTEP drawing (thermal ellipsoid; 30% probability) and labeling scheme for (*R*)-[IrH(COD){$C_2H_5C^*H(CH_3)NCH_2CH_2PPh_2)_2$}] (**9a**).

coordinated with the COD and the PNP* ligand, *via* the two phosphorus atoms only. The hydride ligand is *cis* to the two phosphorus atoms and to one of the olefin bonds of the COD. The other unsaturated bond of the COD ligand is diagonally opposed to this hydride ligand. Descriptively, one may envisage dative bonding between the iridium metal and the center of the two unsaturated bonds of the COD ligand and thus describe the resulting structure as a distorted trigonal bipyramid. The iridium, two phosphorus atoms, two ethylene bridges, and nitrogen atom make up an eight-membered "pseudo-chair" ring system, with the stereocenter being pushed diagonally away from the COD ligand. The nitrogen atom is too far away from the hydride ligand to stabilize the complex *via* hydrogen bonding. The exclusive use of the phosphorus donors for coordination, with a free amine group, is not common for PNP ligands.[3c,8] Indeed, besides **9a**, the only X-ray authenticated metal complex containing an η^2-*P*,*P*-PNP ligand is $[TcNCl_2(PNP\text{-}\mathbf{II})]$.[9] In contrast, five-coordinate iridium complexes with η^4 COD ligands are much more numerous, with either

(7) (a) *MOLEN, An Interactive Intelligent System for Crystal Structure Analysis*; Enraf-Nonius: Delft, The Netherlands, 1990. (b) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (*R*)-[IrH(COD){$C_2H_5C^*H(CH_3)N(CH_2CH_2PPH_2$}] (9a)

Bond Lengths			
Ir−P1	2.315(1)	Ir−C29	2.150(6)
Ir−P2	2.286(1)	Ir−C30	2.148(6)
Ir−C25	2.240(8)	Ir−H	1.81(9)
Ir−C26	2.243(7)		
Bond Angles			
P1−Ir−P2	102.48(5)	P2−Ir−C29	148.5(2)
P1−Ir−C25	120.5(1)	P2−Ir−C30	110.2(2)
P1−Ir−C26	92.5(2)	P2−Ir−H	77(2)
P1−Ir−C29	105.9(2)	C25−Ir−H	160(2)
P1−Ir−C30	143.7(2)	C26−Ir−H	164(2)
P1−Ir−H	73(2)	C29−Ir−H	98(2)
P2−Ir−C25	85.3(2)	C30−Ir−H	99(2)
P2−Ir−C26	114.2(2)		

square-pyramidal or trigonal-bipyramidal coordination geometries.[10] In the case at hand, the bond distances and angles point to a distorted trigonal bipyramid. Selected bond distances and angles are listed in Table 2. The bond lengths and angles involving iridium, carbon, and phosphorus are in their usual range.[11] As expected from the different π-back-bonding contribution,[12] the Ir−C and C−C distances pertaining to the equatorial C−C double bond (C29−C30) are shorter and longer, respectively, than those pertaining to the axial C−C double bond (C25−C26). The hydride ligand has been located in the Fourier difference map and refined. The Ir−H distance, 1.81(9) Å, is somewhat long[11a] but comparable to that found in the Ir(III) octahedral complex *fac*,*exo*-(*R*)-[IrH_2{$C6H_4C^*H(CH_3)N(CH_2CH_2$-$PPh_2$}] (Ir−H, 1.64(9) Å, Ir−H1 1.8(2) Å) in which the hydride ligands are *trans* to nitrogen and phosphorus[3a] or in [1,1,1,1-(CO)$H(PPh_3)_2$-*arachno*-1-IrB_3H_7] (Ir−H 1.81(8) Å) in which the hydride is trans to CO.[11b]

Complex **9a** maintains the same structure in both the solid state and solution. The IR spectra (Nujol mulls or CH_2Cl_2 solution) contain the characteristic ν(Ir−H) band at 2110 cm^{-1}, while the ^1H NMR spectrum shows an upfield triplet corresponding to *cis* coupling between the hydride and the two phosphorus atoms (−13.80 ppm, $^2J_{H_{hydride},P}$ = 22.3 Hz). Evidence for the presence of a η^4-coordinated COD ligand is found in the ^{13}C NMR spectrum with diagnostic peaks at 46.8 ppm, corresponding to $4CH_2$, 47.0 ppm, corresponding to $2CH_1$, and 78.8 ppm, corresponding to $2CH_1$.[10] The AM spin system in the $^{31}P\{^1H\}$ NMR, acquired in CD_2Cl_2 at 25 °C ($J_{P,P}$ = 22.3 Hz), maintains its symmetry at higher temperatures (60 °C, THF-d_8, $J_{P,P}$ = 23.0 Hz). On lowering the temperature of a sample of **9a**,**b** in CD_2Cl_2 to a final temperature of −83 °C, the following changes in the $^{31}P\{^1H\}$ NMR spectra occur. The initial AM spin system is seen to slowly decrease in resolution such that at −33 °C two broad ($w_{1/2} \approx$ 80 Hz) peaks result. Further lowering the temperature of the sample results in coalescence of the two resonances at −53 °C. Below this temperature several peaks emerge from the base line, and at the final temperature of −83 °C, the spectrum shows two major peaks (13.00 and −10.00 ppm) and some minor peaks (between 0 and −16.00 ppm). The spectrum displayed at −83 °C compliments our recent observation and documentation of a similar series of events in the variable-temperature ^{31}P NMR spectra of the related (*R*)- and (*S*)-[IrH(COD)(PNP*-**I**)] complexes.[3a] As previously proposed for the latter complexes, the rapid equilibration of the eight-membered heterocycle at room temperature may be frozen out in one of a number of possible chair, boat, quasi-chair, or quasi-boat conformations on lowering the temperature of the sample of **9a**,**b** to −83 °C.[3a]

Like the PNP*-**I** derivative[3a] and in contrast to the achiral PNP-**II** complex [IrH(COD)(PNP-**II**)] (*vide infra*),[3b,c] one can exclude that in the temperature range investigated the terminal hydride ligand in **9a**,**b** may migrate to one of the two double bonds of the coordinated COD to give a cyclooctenyl ligand as in [Ir(σ,η^2-C_8H_{13})(PNP-**II**)] (see Scheme 6).[3c]

Synthesis and Characterization of (*R*)- and (*S*)-[IrH_3(PNP*-5a,b)] (10a,b). (*R*)- and (*S*)-[IrH_3(PNP*-**5a**,**b**)] (**10a**,**b**) were synthesized by either dissolving the corresponding (COD)hydride precursor **9a**,**b** in THF and bubbling hydrogen gas through the solution for 30 min or dissolving the monohydride **9a**,**b** in a mixture of THF/propan-2-ol (1:4) and refluxing for 14 h (Scheme 2). Reduction of COD to COE was obtained by both procedures and gave good yields (80 to 98%), with the crude products recrystallized to purity from THF/propan-2-ol. Characterization of the trihydride **10a** shows three strong absorptions in the IR spectrum at 1993, 2025, and 2160 cm^{-1}. Further diagnostic evidence for the formation of a trihydride complex is found in the ^1H NMR spectrum with the hydride *trans* to nitrogen (H_A) at −23.20 ppm and the two hydrides *cis* to nitrogen ($H_{B/B'}$) at −9.75 ppm. Hydride A gives rise to a seven-line multiplet that is interpreted as an overlapping doublet of doublets of doublets of doublets, with all the couplings constants consistent with *cis* configurations of both the phosphorus atoms and the two other hydride ligands. Hydrides B and B′ give rise to a doublet of doublets of doublets of doublets; one of the couplings is on the order of 130 Hz, consistent with a *trans* phosphorus−hydride coupling constant in iridium(III) complexes, with the other three coupling constants representing the *cis* couplings.[13] The $^{31}P\{^1H\}$ NMR spectrum shows an AM spin system with doublets of 5.7 Hz at 24.42 and 25.70 ppm, indicative of a facial orientation of the aminodiphosphine ligand.[8a,c]

The trihydride **10a**,**b** is thermally stable in refluxing THF or toluene. The low propensity to reductively eliminate H_2 as a thermal step is a typical characteristic of Ir(III) trihydrides with *fac* polydentate ligands, see

(8) (a) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585. (b) Bianchini, C.; Masi, D.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Acta Crystallogr.* **1996**, *C52*, 1973. (c) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272. (d) Bianchini, C.; Masi, D.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Acta Crystallogr.* **1995**, *C51*, 2514. (e) Bianchini, C.; Innocenti, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Gazz. Chim. Ital.* **1992**, *122*, 461.

(9) Marchi, A.; Marvelli, L.; Rossi, R.; Magon, L.; Uccelli, L.; Bertolasi, V.; Ferretti, V.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* **1993**, 1281.

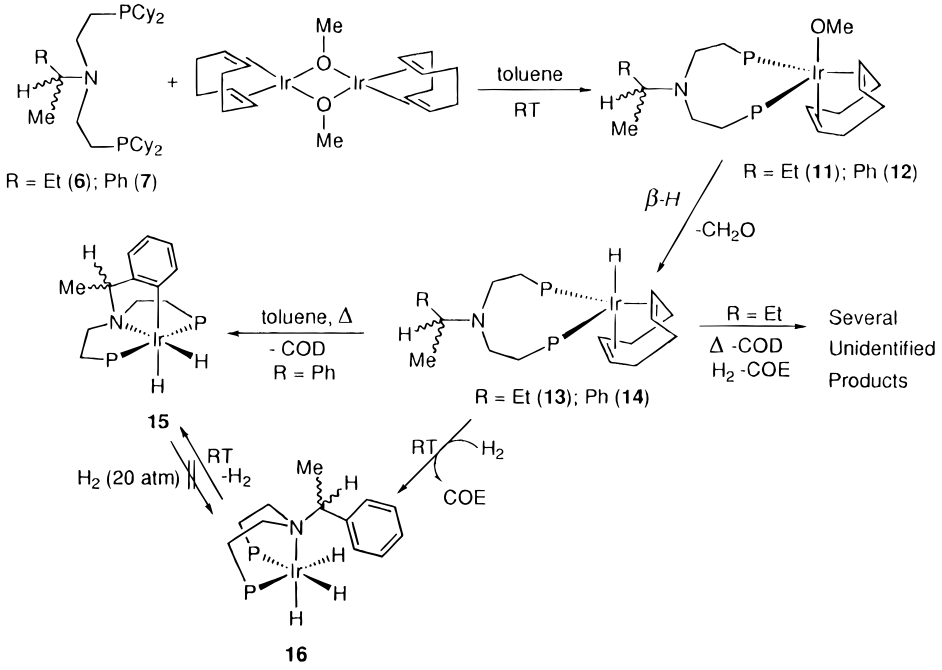
(10) (a) Gull, A. M.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1993**, *12*, 2121. (b) Wehman-Ooyevaar, I. C. M.; Kapteijn, G. C.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, 703.

(11) (a) Orpen G. A.; Brammer, L.; Allen, F. F.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. (b) Bould, J.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1985**, 1843.

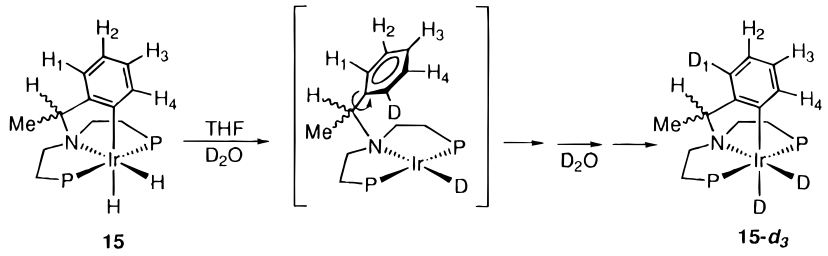
(12) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(13) (a) Pregosin, P. S.; Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1979. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Scheme 3



Scheme 4



for example the chemistry of [(triphos)IrH_3] (triphos = $MeC(CH_2PPh_2)_3$).[14]

Synthesis and Chacterization of *mer* (*R*)- and (*S*)-[$IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}$] (15a,b). Synthesis of the dihydride complexes (*R*)- and (*S*)-[α-methylbenzyl-bis(2-(dicyclohexylphosphino)ethyl)amine]iridium dihydride, [$IrH_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}$] (**15a**,**b**) (Scheme 3), was achieved by refluxing a 2:1 mixture of the corresponding ligand (either PNP*-**7a** or PNP*-**7b**) with the iridium dimer, $[Ir(COD)(OMe)]_2$, in toluene for 4 h. Removal of the solvent *in vacuo* gives **15a**,**b** which can be recrystallized from dichloromethane and methanol (yield 85%). The dihydride ortho-metalated complex has been characterized by NMR and IR spectroscopies. The $^{31}P\{^1H\}$ NMR spectrum consists of an AB spin system centered at about 42 ppm with $^2J_{P,P} = 348.6$ Hz, indicating that the two phosphorus atoms of the PNP* ligand are in a *trans* disposition.[3a,13] Important features of the ^1H NMR spectrum show that there are two hydride resonances at high field, −21.43 ppm (H_A, the hydride *trans* to nitrogen of the PNP ligand) and −13.79 ppm (H_B, the hydride *trans* to the cyclometalated ring), as well as only four aromatic protons appearing as two doublets and two triplets, the aromatic protons pattern being consistent with an ortho-metalated phenyl ring.[3a] Both of the hydride resonances appear as an overlapping doublet of doublets of doublets; a doublet due to the coupling to the other hydride and a doublet of doublets due to the coupling to the two different phosphorus atoms. A 2D-^1H-^1H phase-sensitive NOESY spectrum showed a clear cross-peak between the hydride resonance at −21.43 ppm (H_A) and the hydride at −13.79 ppm (H_B) as well as the aromatic proton at 7.51 ppm. The latter interaction confirms that the most downfield of the aromatic−hydrogen resonances is in fact proton H4 (for the labeling scheme adopted, see Scheme 4). The 2D-^1H-^1H COSY NMR spectra showed all of the expected couplings between the aromatic protons. A very similar proton spectrum is observed for the dichloride derivative **18** (*vide infra*), and the *o*-metalation in this complex has been confirmed by a single-crystal X-ray diffraction analysis,[15] thus further supporting the determined structure for the dihydride complex **15a**,**b**. The $^{13}C\{^1H\}$ NMR spectrum also supports the structure determined as in the low-field region it contains an overlapping doublet of doublets attributable to the carbon atom of an ortho-metalated phenyl group (δ 162.3 (dd, $^2J_{P,C_{o,m}} = 8.6$ Hz, $^2J_{P,C_{o,m}} = 8.6$ Hz).

On the basis of this spectroscopic evidence, it can thus be concluded that the PNP*-**7** ligand in **15a**,**b** is oriented

(14) (a) Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993**, *115*, 1753. (b) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1995**, *14*, 2342.

(15) Bianchini, C. *et al.* X-ray crystal structure of *rac*-[$IrCl_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}$], manuscript in preparation. Crystal data: space group *Pnma* (No. 62); $a = 17.887(9)$ Å, $b = 24.305(3)$ Å, $c = 9.806(1)$ Å, $\alpha = 90.00(2)°$, $\beta = 90.00(1)°$, $\gamma = 90.00(2)°$; $V = 4263.05(3)$ Å^3; $d_{calcd} = 1.428$ g cm^{-3}; $Z = 4$; R [$I > 2\sigma(I)$] = 0.094, R (all data) = 0.143.

in a meridional fashion, with two hydride ligands *cis*-coordinated to iridium and the sixth coordination site occupied by the carbon atom of the ortho-metalated phenyl substituent attached to the chiral center. No *mer* to *fac* isomerization of the polydentate ligand in the ortho-metalated complex was observed in toluene-d_8 to the final temperature of 110 °C.

Deuterium Exchange Reaction. Reaction of the Dihydride 15 with D_2O. When a THF-d_8 solution of the *rac*-dihydride **15** is shaken with a drop of D_2O and the ^1H NMR followed, it is observed that the resonances arising from the two hydride ligands disappear along with the aromatic resonance at 6.28 ppm assigned to proton H1 (the assignment follows from analysis of both the NOESY and COSY spectra). Removal of the solvent from a THF solution of **15** previously treated with D_2O affords $[IrD_2\{C_6H_3DC^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**15-*d*$_3$**). A ^2H NMR spectrum recorded in THF on this sample, confirmed that the loss of the proton resonances were in fact matched with corresponding resonances in the ^2H NMR spectrum. This indeed shows deuterium incorporation exclusively for the two hydrides and proton H1 (Scheme 4). The selective incorporation of deuterium in the *ortho* position of the metalated phenyl ring suggests that the dihydride is in rapid equilibrium with a de-ortho-metalated species, most presumably a four-coordinate species similar to that previously proposed for the intermediate square-planar complex [IrH(P-NP*-**I**)].[3a] This species was observed by ^{31}P and ^1H NMR before *o*-metalation occurred to give the corresponding dihydride complex. During the conversion of the COD−hydride complex **14** to the dihydride **15**, which involves the decoordination of COD, no intermediate was observed by ^{31}P NMR spectroscopy, however. A similar case of reversible ortho-metalation occurring at room temperature has recently been reported by Caulton *et al*. for the Ir(III)−hydride complex $[IrH(\eta^2\text{-}C_6H_4P^tBu_2)(C_2Ph)(P^tBu_2Ph)]$.[16]

Synthesis and Chacterization of *mer,rac*-[(α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Dichloride, $[IrCl_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (18). The dichloride complex $[IrCl_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**18**) was synthesized by dissolving the ortho-metalated dihydride complex **15** in $CHCl_3$ and heating at 65 °C for 2 h. After removal of the solvent, recrystallization from dichloromethane and methanol gave **18** as brick-like crystals. The ^{31}P and ^1H NMR spectra of this complex are very similar to those acquired for the dihydride complex (see above), with the obvious exception that there are no hydride resonances at high field in the ^1H NMR spectra. The ^{13}C NMR spectrum also supports the ortho-metalated structure as it shows in the low-field region an overlapping doublet of doublets attributable to the carbon atom of an ortho-metalated phenyl group (δ 134.1 (dd, $^2J_{P,C_{o,m}}$ = 7.3 Hz, $^2J_{P,C_{o,m}}$ = 7.3 Hz)).

A crystal structure was determined for this complex[15] and showed that the PNP ligand is in a meridional orientation about an octahedral iridium center and that the phenyl ring is indeed metalated through one of the *ortho* carbons. The two chloride ligands are found to be in a *cis* disposition to one another: one is *trans* to the nitrogen and the other is *trans* to the ortho-metalated phenyl ring. A molecular sketch of the complex cation is reported in Figure 2.

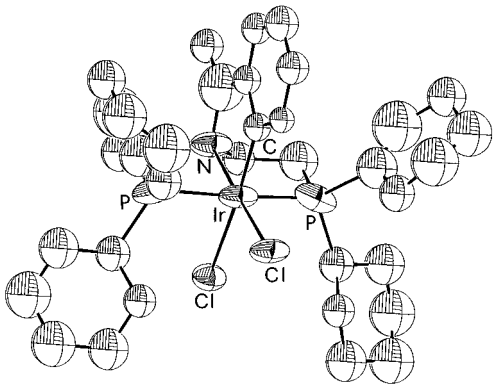
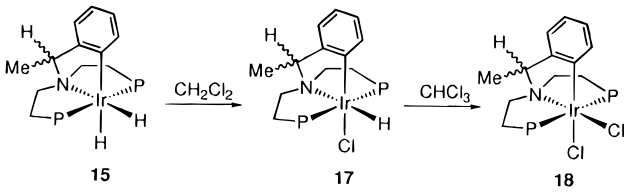


Figure 2. ORTEP drawing (thermal ellipsoid; 30% probability) for $[IrCl_2\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**18**).

Scheme 5



Identification of *rac*-[(α-Methylbenzyl)bis(2-(dicyclohexylphosphino)ethyl)amine]iridium Hydride Chloride, $[Ir(H)Cl\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (17). In the conversion of dihydride **15** to dichloride **18**, an intermediate species was detected, and this was determined to be the (hydride)chloride complex *rac*-$[Ir(H)Cl\{C_6H_4C^*H(CH_3)N[CH_2CH_2P(C_6H_{11})_2]_2\}]$ (**17**) (Scheme 5). Although this complex was only isolated in a very small amount (precipitated within an NMR tube), it was unambiguously characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies as well as elemental analysis. As expected, the hydride/chloride exchange in dichloromethane occurs to a lesser extent than that in chloroform. Indeed, warming dihydride **15** in dichloromethane causes only a partial exchange of the hydride ligand *trans* to the carbon atom of the cyclometalated ring. The $^{31}P\{^1H\}$ NMR spectrum shows an AB system at slightly higher field then the corresponding dihydride, indicating that the PNP* ligand remains in a meridional orientation. The ^1H NMR spectrum features the disappearence of the hydride resonances of **15** and the appearance of a new hydride resonance at −18.6 ppm, appearing as an overlapping doublet of doublets (coupled to the two different phosphorus atoms). A 2D-^1H-^1H NOESY NMR experiment showed that the hydride has a NOE effect to proton H4 of the ortho-metalated phenyl ring, indicating that it is the hydride *cis* to nitrogen to be exchanged in the process affording **17**. The selectivity of H substitution agrees with the greater *trans effect* of the metalated carbon atom as compared to nitrogen.[17]

***In Situ* Variable-Temperature NMR Study for the Formation of the Ortho-Metalated Dihydride 15.** Variable-temperature ^1H and ^{31}P NMR measurements were carried out on a solution prepared by

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dissolving the iridium dimer $[Ir(COD)(OMe)]_2$ in toluene-d_8 with 2 equiv of PNP*-**7**. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum showed the presence of the free aminodiphosphine ligand (singlet at −9.53 ppm) as well as the presence of another species (singlet at *ca.* 10 ppm). The corresponding ^1H NMR spectrum showed that there were no hydride ligands present, and thus the signal is tentatively assigned to the COD−methoxy species [Ir(COD)(OMe)(PNP*-**7**)] (**12**) (Scheme 3). Heating the sample to 37 °C, the ^{31}P NMR spectrum showed the presence of an AM spin system at 1.4 ppm and a decrease in the intensity of the signals at *ca.* 10 and −9.53 ppm. Correspondingly, the ^1H NMR spectrum showed hydride resonance growing in at *ca.* −13.8 ppm, appearing as an overlapping doublet of doublets. This is consistent with the methoxy complex **12** β-eliminating formaldehyde to give the monohydride COD species **14**.[3] Heating the sample further to a temperature of 78 °C, the ^{31}P NMR spectrum showed the appearance of the AB spin system of **15** centered at *ca.* 42 ppm and the disappearance of the AM spin system at 1.4 ppm.

***In Situ* Variable-Temperature NMR Study for the Characterization of (*R*)- and (*S*)-[IrH(COD)(PNP*-6a,b)] (13a,b) and (*R*)- and (*S*)-[IrH(COD)(PNP*-7a,b)] (14a,b).** *In situ* variable-temperature NMR experiments allowed for the NMR (^1H and ^{31}P) characterization of the COD−monohydride species **13a**,**b** and **14a**,**b**, which can also be isolated in the solid state in the absence of protic solvents (Scheme 3). In a typical experiment, 2:1 mixtures of the appropriate PNP* ligand and the dimer $[Ir(COD)(OMe)]_2$ were mixed in toluene-d_8 at room temperature under a nitrogen atmosphere. The $^{31}P\{^1H\}$ NMR spectra of these solutions showed the free PNP* ligands at *ca.* −9 ppm as a sharp singlet as well as another singlet resonance shifted about 20 ppm downfield ($\delta \approx 10$). The latter resonance had no associated hydride resonances in the ^1H NMR spectrum, and a likely candidate for this species is indeed the methoxy−COD complex [Ir(OMe)(COD)(PNP*)] (PNP* = PNP*-**6**, **11**; PNP*-**7**, **12**). Careful heating of the NMR tube in the probe of the spectrometer allowed the quantitative formation of each of the monohydrides (**13a**,**b** and **14a**,**b**) to be observed (^1H and ^{31}P NMR) at a stabilized temperature of 37 °C. Further heating of the solution containing **14a**,**b** at 60° C in an external oil bath quantitatively yielded **15a**,**b**. By contrast, prolonged heating of the **13a**,**b** samples resulted in a number of transformations, during the course of the experiment, giving rise to various products which defied first-order analysis.

Attempted Formation of the Iridium Trihydride Complex *rac*-[IrH$_3$(PNP*-6)] (16). The trihydride [IrH$_3$(PNP*-**6**)] (**16**) was formed *in situ*, but it was never isolated in the pure form. One method that was used in an attempt to form **16** was to take a THF solution of dihydride **15** and put this under 20 atm of hydrogen with the idea of forcing the oxidative addition of molecular hydrogen by the spectroscopically undetected (but inferred, *via* the deuterium exchange experiment previously described) four-coordinate monohydride species. This, however, failed to give the trihydride, and only the starting material was recovered. Reacting PNP*-**6** with $[Ir(COD)(OMe)]_2$ under hydrogen in order to form the trihydride from the COD-hydride species **14** before it could form the dihydride **15** was also attempted, as it was clear that once the dihydride formed this would not react with hydrogen. This was attempted at several temperatures, the details of which are reported in the Experimental Section. The most successful attempt did in fact form *ca.* 30% of trihydride **16** which could be characterized by ^{31}P and ^1H NMR spectroscopies, particularly with the use of $^1H\{^{31}P\}$ and selective ^1H homonuclear decoupling experiments. A direct comparison was made with the ^{31}P NMR spectra as well as the hydride region of the ^1H NMR spectra acquired for the isolated trihydride **10** and were found to be very similar, thus giving additional supporting evidence for the *fac* structural assignment of **16** generated *in situ*. However, on warming a sample of **16** generated *in situ* to only 40 °C, the complex rapidly eliminates dihydrogen and cyclometalation to give the stable ortho-metalated complex **15**, indicating that the range for the thermal stability of the trihydride **16** is extremely narrow.

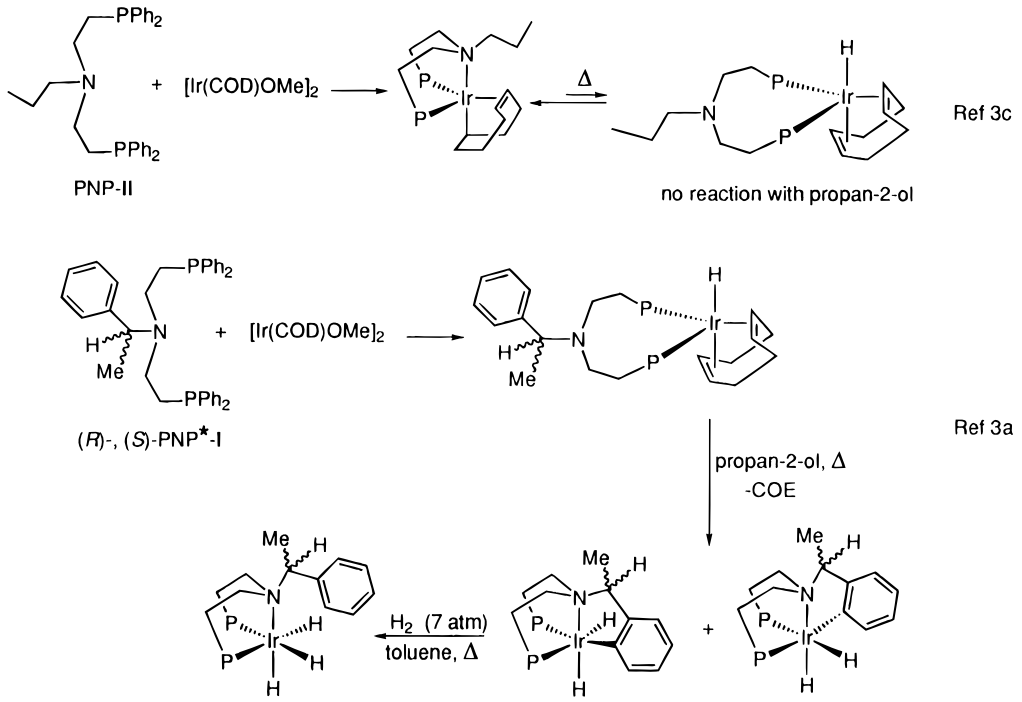
From the attempted reactions to form trihydride **16** species, it is clear that the most thermodynamically stable species is **15**. Although the deuterium exchange reaction showed that the latter compound is in rapid equilibrium with a (proposed) four-coordinate monohydride species (following the selective incorporation of deuterium at the *ortho* position), it was not possible to trap this proposed species with hydrogen, indicating that the reductive elimination of hydrogen from the trihydride is a much more facile process than that of the reductive elimination of the metalated ring, thus making the dihydride complex **15** the thermodynamic sink of the reaction of PNP*-**7** with $[Ir(COD)(OMe)]_2$ in either protic or aprotic solvents.

Conclusions

From a comparison of the reactions illustrated in Scheme 6 with those reported in Schemes 2 and 3, one may draw out a number of interesting conclusions regarding the influence of the substituents at either the stereocenter or the phosphorus donors on the coordination chemistry of these aminodiphosphine ligands (Scheme 6).

At first glance, it is clearly apparent that irrespective of the nature of the other coligands the steric bulk generated at the terminus of the PNP donor system by the cyclohexyl substituents favors a meridional conformation of the ligands. This thermodynamic control on the bonding mode of the PNP ligands is so efficient that the Ir(III) *fac* trihydride complexes, generally stable with the phenylated ligands,[14] with the cyclohexyl-substituted ligands either are not formed at all (PNP*-**6**) or spontaneoulsy lose H_2 at room temperature (PNP*-**7**). On the other hand, *mer* trihydride complexes have never been seen with this type of PNP ligands, most likely because they would bear an overload of the *trans influence*.[17] In a sense, this result was desired prior to the synthesis of PNP*-**6** and PNP*-**7**. One of the reasons for the proposed formulation of these ligands was, in fact, to derive a series of chiral iridium complexes which, due to the steric bulk of the large cumbersome cyclohexyl groups, would drive the ketone or any other prochiral substrate into a "molecular pocket" different from that of the PNP*-**I** and PNP-**II** ligands already investigated.[3] Moreover, the most energetically favored *mer* conformation of the ligands

Scheme 6



bearing cyclohexyl substituents might decrease the risk of poor enantioface discrimination due to configurational instability of the catalysts during the reactions.[18] Analogously, the facility with which trihydride **16** thermally loses H_2 is expected to increase the activity of metal catalysts derived from the cyclohexyl-substituted ligands PNP*-**6** and PNP*-**7** in homogeneous reduction reactions under a high pressure of H_2.

The influence of the substituent(s) at the R′R″*C*HN-$(CH_2CH_2PR_2)_2$ carbon atom on the coordination chemistry of the PNP* ligands is even more pronounced than that exerted by the phosphorus substituents. First of all, no intramolecular cyclometalation occurs with the alkyl substituents, a finding that is in line with the thermodynamics of the insertion of metal centers into C−H bonds from either sp^2- or sp^3-hybridized carbon atoms.[19] When the alkyl substituent at this carbon atom is associated with cyclohexyl substituents at the phosphorus donors, extremely reactive metal fragments are formed, which represents an attractive characteristic of any efficient catalyst precursor. On the other hand, the phenyl substituent at the stereocenter does not seem to inhibit the reactivity of the iridium complexes with PNP*-**I** or PNP*-**7**, as the C−H insertion is a reversible process through which the metal is chemically and stereochemically stabilized.

Finally, it is worth noticing the striking effect played by the alkyl substituent at the nitrogen atom on the reaction with $[Ir(COD)(OMe)]_2$. The linear *n*-propyl group favors the formation of the hydride-migration cyclooctenyl product [Ir(PNP-**II**)(σ,η^2-C_8H_{13})], which only at high temperature produces small equilibrium concentrations of the hydride−COD complex (Scheme 6).[3c] The branched *sec*-butyl group in PNP*-**5** forms a very reactive hydride−COD species that, unlike the PNP-**II** one, is hydrogenated by propan-2-ol. A clear cut explanation for this contrasting behavior cannot be provided by us at this stage, although it seems highly probable that steric effects may play a major role in driving the two distinct reactivities.

In light of the results presented in this paper, we are, at present, continuing our investigations of the hydrogen-transfer reduction of prochiral and α,β-unsaturated ketones by iridium catalysis. Preliminary results show that the catalytic activity decreases in the order PNP*-**I** > PNP*-**7** > PNP*-**6** > PNP*-**5**, while the chemo- and enatioselectivities greatly depend on the nature of the alkyl or aryl substituents at either the ketone or the chiral ligand. Studies also include the synthesis of other chiral PNP* ligands either bearing different substituents at the stereogenic carbon atom or containing the stereocenter incorporated into the P-N arm, *i. e.*, closer to the site of reduction.

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Supporting Information Available: Tables of crystallographic data, positional parameters, bond distances, bond angles, and anisotropic thermal parameters for (*R*)-[IrH(COD)(C_2H_5C*H(CH_3)N($CH_2CH_2PPh_2$)$_2$)] (**9a**) (6 pages). Ordering information is given on any current masthead page.

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