NMR Analyses. NMR spectra in toluene-d_8 were recorded on a JEOL GX 400 spectrometer (^{1}H, 400 MHz). Chemical shifts are referenced to the solvent (toluene-d_8) signals: δ = 2.03 ppm (^{1}H, C_6D_5-CHD_2) and δ = 125.2 ppm (^{13}C, para-C). Crystals of **7** (130 mg, ^{6}Li-enriched material) were placed under argon in a dry 5-mm NMR tube fitted with a serum cap. Dry toluene-d_8 (0.6 mL) was added. The compound is only slightly soluble.

NMR spectra in THF-d_8 were recorded on a Bruker AC 200 spectrometer (^{1}H, 200 MHz). Chemical shifts are referenced to the solvent (THF-d_8) signals: δ = 1.73 ppm (^{1}H, 3-H THF-d_7) and δ = 25.2 ppm (^{13}C, β-CD_2). Crystals of **7** (129 mg, ^{6}Li-enriched material) were placed under nitrogen in a dry 5-mm NMR tube and dissolved readily in 0.6 mL of THF-d_8.

Cryoscopy Measurements. Cryoscopy measurements in THF and benzene were carried out in an apparatus described by Bauer et al.[27]

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Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters, bond distances, bond angles, and torsional angles (8 pages); a listing of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Synthesis and Reaction Chemistry of Iridium(III) Hydrides Formed by the Intramolecular N-H Addition of Hybrid Phosphine Amines to Iridium(I)

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Monovalent P-bonded iridium and rhodium complexes MCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHR$) (R = CH_2Ph, Et) have been prepared from [M(μ-Cl)(1,5-COD)]$_2$ and *o*-$Ph_2PC_6H_4NHR$. New P,N-chelate complexes [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHR$)]ClO_4 are formed upon reaction of the iridium complexes with $AgClO_4$. The amine arm of the chelate can be substituted by added ligands L to give [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHR$)L]ClO_4 (L = pyridine, acetonitrile). Solution thermolysis of [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]ClO_4 results in cyclometalation of the benzyl ring. The complex IrHCl(*o*-$Ph_2PC_6H_4NR$)(*o*-$Ph_2PC_6H_4NHR$) (R = CH_2Ph, Et) has been obtained from the reaction between [Ir(μ-Cl)(C_8H_{12})$_2$]$_2$ and *o*-$Ph_2PC_6H_4NHR$. The pathway involves N-H addition to iridium(I). Reversible protonation of IrHCl(*o*-$Ph_2PC_6H_4NR$)(*o*-$Ph_2PC_6H_4NHR$) with HX gives [IrHCl(*o*-$Ph_2PC_6H_4NHR$)$_2$]X. The chloride ligand is replaced by CO to give two isomers of [IrH(*o*-$Ph_2PC_6H_4NR$)CO(*o*-$Ph_2PC_6H_4NHR$)]Cl. The reaction between [Rh(μ-Cl)(C_8H_{14})]$_2$ and *o*-$Ph_2PC_6H_4NHCH_2Ph$ gives the unstable complex [Rh(*o*-$Ph_2PC_6H_4NHCH_2Ph$)$_2$]Cl, which reacts with CO to give *trans*-RhCl(CO)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)$_2$. Crystal data for [IrHCl(*o*-$Ph_2PC_6H_4NHCH_2Ph$)$_2$]Cl·2$CDCl_3$: $P2_1/n$, a = 10.111 (4) Å, b = 25.886 (3) Å, c = 19.939 (3) Å, β = 93.03 (2)°, Z = 4, refined to R = 0.036, R_w = 0.054.

Introduction

The insertion of a low-valent metal center into an N-H bond is an important reaction for the development of catalytic processes involving the carbonylation or alkylation of amines with carbon monoxide or alkenes.[1] Despite this potential significance there are very few examples of such reactions.[2] Low-valent complexes are more prevalent for later transition metals, but such metals are likely to disfavor N-H addition because of the formation of a relatively weak metal-nitrogen amide bond.[3] The best current estimates of N-H, M-H, and M-N bond enthalpies suggest that the reaction is approximately thermoneutral for the platinum group metals.[4] Our decision to focus on these metals is based on the logic that not only is the N-H addition reaction thermodynamically feasible but also the metal-amide bond formed is sufficiently weak that subsequent insertion reactions into it are possible.

In this paper we present our results on the reactions of phosphine amines with low-valent complexes of rhodium and iridium.[5] These ligands are chosen because they can undergo intramolecular "chelate-assisted" oxidative addition of the N-H bond from a tertiary phosphine anchor to give 5-membered ring complexes.[6]

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Experimental Section

All reactions were carried out on a Schlenk line by using a high-purity nitrogen atmosphere. $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 3H_2O$ were purchased from Matthey Bishop, Inc. The solvents THF, benzene, and toluene were dried by refluxing over sodium/benzophenone or $LiAlH_4$. The compounds *o*-$Ph_2PC_6H_4NHCH_2Ph$, *o*-$Ph_2PC_6H_4NHC(O)Me$, $[M(\mu\text{-}Cl)(cyclooctene)_2]_2$, and $[M(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (M = Rh, Ir) were prepared by literature procedures.[7] ^1H, ^{31}P, and ^{13}C NMR spectra were measured on a Bruker AC200 spectrometer in $CDCl_3$ solvent unless noted otherwise. Deuterated solvents and DABCO were purchased from Aldrich Chemical Co. Infrared spectra were measured on Perkin-Elmer Model 683 and Mattson Cygnus 100 spectrometers. Conductivity measurements were performed in a cell with platinized electrodes connected to an Industrial Instruments conductivity bridge (Model RC-16B2). All measurements were done in a dichloromethane solution (concentration = (0.53–0.58) × 10^{-3} mol) at 25 °C under nitrogen atmosphere. The cell constant was 0.417 cm^{-1} as determined in a 0.100 M KCl(aq) solution. The molar conductivity of $(n\text{-}Bu)_4NI$ (0.57 × 10^{-3} mol in CH_2Cl_2) was 27.1 Ω^{-1} cm^2 mol^{-1} at 25 °C.

***o*-(Diphenylphosphino)-*N*-ethylaniline (*o*-$Ph_2PC_6H_4NHEt$).** *o*-(Diphenylphosphino)-*N*-acetylaniline (3.20 g, 10 mmol) was placed in a dried 100-mL two-neck round-bottom flask fitted with a reflux condenser, a nitrogen bubbler, a septum, and a magnetic stir bar. A solution of borane in THF (20 mL of 1.0 M) was added by syringe through the septum into the nitrogen-purged flask. The reaction mixture was refluxed for 2 h under nitrogen. To the cool reaction mixture was slowly added hydrochloric acid (26 mL of 20%) by means of a syringe. The THF was removed by distillation, and solid sodium hydroxide was added to the reaction mixture to give a saturated solution. The solution was refluxed under nitrogen for 1 h, cooled, and extracted with dichloromethane. The dichloromethane layer was dried over $MgSO_4$ and filtered. After rotary evaporation a pale yellow oil was obtained, which was dissolved in benzene (5 mL) and passed through a silica gel column. The colorless eluant was evaporated to give an oil, which was dissolved in hot 95% ethyl alcohol to give a saturated solution. Upon storing in the refrigerator for 12 h a white precipitate formed. This final product was filtered and dried in vacuo: yield 2.2 g (72%); mp 68–69 °C. Anal. Calcd for $C_{20}H_{20}NP$: C, 78.7; H, 6.60; N, 4.59. Found: C, 78.7; H, 6.65; N, 4.58. IR: ν(NH) 3356 cm^{-1}. ^1H NMR: δ 6.5–7.4 (m, 14 H, phenyl), 4.56 (br, 1 H, N*H*), 3.13 (q, 2 H, CH_2), 1.14 (t, 3 H, CH_3, $^3J(HH)$ = 7.1 Hz). $^{31}P\{^1H\}$ NMR: δ −20.3 (s).

Chloro(1,5-cyclooctadiene)[*o*-(diphenylphosphino)-*N*-benzylaniline]rhodium(I) [1, RhCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]. A mixture of $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (100 mg, 0.204 mmol) and *o*-$Ph_2PC_6H_4NHCH_2Ph$ (149 mg, 0.406 mmol) was placed in a 50-mL Schlenk flask fitted with a filter stick assembly and a magnetic stir bar. Oxygen-free dry dichloromethane (20 mL) was added via syringe and the reaction mixture stirred 1 h. The solution volume was reduced to 5 mL, and an orange complex formed by the addition of a mixture of hexane and diethyl ether. The solid product was washed with hexane, recrystallized from dichloromethane/*n*-hexane, and dried in vacuo; yield 195 mg (78%). Anal. Calcd for $C_{33}H_{34}ClNPRh$: C, 64.6; H, 5.58; N, 2.28. Found: C, 64.5; H, 5.53; N, 2.21. IR: ν(NH) 3163 cm^{-1}. ^1H NMR: δ 6.6–7.8 (m, 19 H, phenyl), 4.50 (d, 2 H, CH_2, $^3J(HNCH)$ = 5.5 Hz), 1.7–2.2 (m, 8 H, CH_2), 5.5 and 3.5 (br, C*H* and N*H*). $^{31}P\{^1H\}$ NMR: δ 21.7 (d, ^1J(RhP) = 145 Hz).

Chloro(1,5-cyclooctadiene)[*o*-(diphenylphosphino)-*N*-ethylaniline]rhodium(I) [2, RhCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)·$^2/_3CH_2Cl_2$. A similar procedure using $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (100 mg, 0.204 mmol) and *o*-$Ph_2PC_6H_4NHEt$ (125 mg, 0.408 mmol) gave the pure complex, yield 169 mg (75%). Anal. Calcd for $C_{28.67}H_{33.33}Cl_{2.33}NPRh$: C, 56.6; H, 5.52; N, 2.30. Found: C, 56.7; H, 5.53; N, 2.29. IR: ν(NH) 3150 cm^{-1}. ^1H NMR: δ 6.7–7.7 (m, 14 H, phenyl), 3.24 (dt, 2 H, CH_2, $^3J(HH)$ = 7.1 Hz, $^3J(HNCH)$ = 5.1 Hz), 1.24 (t, 3 H, CH_3), 1.9–2.1 (m, 8 H, CH_2), 5.6 and 4.2 (br, C*H* and N*H*). $^{31}P\{^1H\}$ NMR: δ 25.3 (d, ^1J(RhP) = 150 Hz).

Chloro(1,5-cyclooctadiene)[*o*-(diphenylphosphino)-*N*-benzylaniline]iridium(I) [3, IrCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]. A similar procedure using $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (100 mg, 0.15 mmol) and *o*-$Ph_2PC_6H_4NHCH_2Ph$ (110 mg, 0.3 mmol) gave the pure complex, yield 137 mg (65%). The complex is extremely air sensitive. Anal. Calcd for $C_{33}H_{34}ClIrNP$: C, 56.4, H, 4.87; N, 1.99. Found: C, 56.0; H, 4.87; N, 1.95. IR: ν(NH) 3120 cm^{-1}. ^1H NMR: δ 6.2–7.7 (m, 19 H, phenyl), 4.56 (d, 2 H, CH_2, $^3J(HNCH)$ = 5.6 Hz), 1.5–1.9 (m, 8 H, CH_2), 5.6 and 2.9 (br, C*H* and N*H*). ^{31}P NMR: δ 14.9 (s).

Chloro(1,5-cyclooctadiene)[*o*-(diphenylphosphino)-*N*-ethylaniline]iridium(I) [4, IrCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)]. A similar procedure using $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (100 mg, 0.15 mmol) and o-$Ph_2PC_6H_4NHEt$ (92 mg, 0.3 mmol) gave a solution of the complex. The product is soluble in all organic solvents and is extremely air sensitive. ^1H NMR: δ 6.6–7.7 (14 H, phenyl), 3.36 (t, 2 H, CH_2), 1.28 (t, 3 H, CH_3), 1.7–2.3 (m, 8 H, CH_2). $^{31}P\{^1H\}$ NMR: δ 12.0 (s).

(1,5-Cyclooctadiene)[*o*-(diphenylphosphino)-*N*-benzylaniline]iridium(I) Perchlorate [5, [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]ClO_4·$^1/_2CH_2Cl_2$]. A mixture of $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (100 mg, 0.15 mmol) and silver perchlorate (62 mg, 0.3 mmol) was placed in a 50-mL Schlenk flask fitted with a filter stick assembly and a magnetic stir bar. Tetrahydrofuran (30 mL), freshly distilled from sodium/benzophenone, was added via syringe. Following filtration, the yellow solution was transferred to a Schlenk flask containing *o*-(diphenylphosphino)-*N*-benzylaniline (110 mg, 0.3 mmol). After being stirred for 30 min, the solution volume was reduced to ca. 10 mL. The orange complex was precipitated by addition of hexane and filtered. Recrystallization from dichloromethane/hexane gave the pure complex, yield 189 mg (82%). Anal. Calcd for $C_{33.5}H_{35}Cl_2IrNO_4P$: C, 49.7; H, 4.36; N, 1.73. Found: C, 49.9; H, 4.64; N, 1.50. IR: ν(NH) 3168 cm^{-1}, $\nu(ClO_4)$ 1100 cm^{-1}. ^1H NMR: δ 7.96 (br, 1 H, N*H*), 7.0–8.1 (m, 19 H, phenyl), 5.88 (m), 4.11 (m), 4.24 (m), and 3.25 (m) (4 H, C*H*), 1.4–2.3 (8 H, CH_2), 4.69 (dd, 1 H, CH_A, $^3J(HNCH_A)$ = 4.1 Hz), 4.21 (dd, 1 H, CH_B, $^3J(HNCH_B)$ = 5.8 Hz, $^2J(H_AH_B)$ = 13 Hz). $^{31}P\{^1H\}$ NMR: δ 27.7 (s). Λ_M = 12.3 Ω^{-1} cm^2 mol^{-1} (CH_2Cl_2).

(1,5-Cyclooctadiene)[*o*-(diphenylphosphino)-*N*-ethylaniline]iridium(I) Perchlorate [6, [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)]ClO_4·$^2/_3CH_2Cl_2$]. A similar procedure using $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (100 mg, 0.15 mmol), silver perchlorate (62 mg, 0.3 mmol), and *o*-(diphenylphosphino)-*N*-ethylaniline (92 mg, 0.3 mmol) gave the pure complex, yield 171 mg (81%). Anal. Calcd for $C_{28.67}H_{33.33}Cl_{2.33}IrNO_4P$: C, 45.2; H,4.41; N, 1.84. Found: C, 44.7; H, 4.45; N, 1.97. IR: ν(NH) 3191 cm^{-1}, $\nu(ClO_4)$ 1100 cm^{-1}. ^1H NMR: δ 7.2–7.8 (m, 14 H, phenyl), 5.87 (m), 5.06 (m), 3.90 (m), and 3.05 (m) (4 H, C*H*), 1.5–2.4 (m, 8 H, CH_2), 3.53 (ddq, 1 H, CH_A, $^3J(HNCH_A)$ = 3.5 Hz, $^3J(HH)$ = 7.3 Hz), 3.32 (ddq, 1 H, CH_B, $^3J(HNCH_B)$ = 5.3 Hz, $^2J(H_AH_B)$ = 13 Hz). $^{31}P\{^1H\}$ NMR: δ 29.4 (s). Λ_M = 13.9 Ω^{-1} cm^2 mol^{-1} (CH_2Cl_2).

(1,5-Cyclooctadiene)[*o*-(diphenylphosphino)-*N*-ethylaniline](pyridine)iridium(I) Perchlorate [7, [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)py]ClO_4]. Pyridine (0.05 mL) was added to a solution of [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)]ClO_4 in $CDCl_3$ contained in an NMR tube. Observation of the product complex in this solution occurred when equivalent methylenic ^1H NMR resonances for the ethyl group were observed. ^1H NMR: δ 7.2–7.7 (m, 19 H, phenyl), 4.5 (br, 4 H, C*H*), 3.41 (q, 2 H, CH_2), 1.8–2.3 (m, 8 H, CH_2), 1.08 (t, 3 H, CH_3, $^3J(HH)$ = 7.3 Hz).

(1,5-Cyclooctadiene)[*o*-(diphenylphosphino)-*N*-ethylaniline](acetonitrile)iridium(I) Perchlorate [8, [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)MeCN]ClO_4]. Acetonitrile (0.05 mL) was added to a solution of [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHEt$)]ClO_4 in $CDCl_3$ contained in an NMR tube. Observation of the product complex in this solution occurred when equivalent methylenic ^1H NMR resonances for the ethyl group were observed. ^1H NMR: δ 7.4–7.7 (m, 14 H, phenyl), 4.4 (br, 4 H, C*H*), 3.4 (dq, 2 H, CH_2), 1.8–2.3 (m, 8 H, CH_2), 1.08 (t, 3 H, CH_3, $^3J(HNCH_2)$ = 4.7 Hz, $^3J(HH)$ = 7.3 Hz). $^{31}P\{^1H\}$ NMR: δ 30.1 (s).

Hydrido(1,5-cyclooctadiene)[*o*-(diphenylphosphino)-*N*-benzylaniline]iridium(III) Perchlorate [9, [IrH(1,5-

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COD)(*o*-$Ph_2PC_6H_4NHCH_2C_6H_4$-*o*)]ClO_4]. Solutions of this complex have been prepared by keeping **5** in $CDCl_3$ at ambient temperature for 3 days or by refluxing the solution for 3 h. The complex began to decompose before complete conversion was achieved. IR: ν(NH) 3216 cm^{-1}, ν(IrH) 2183 cm^{-1}. ^1H NMR: δ 8.45 (br, 1 H, N*H*), 6.2–8.6 (18 H, phenyl), −15.1 (d, 1 H, Ir*H*, ^2J(PH) = 11 Hz), 5.22 (dd, 1 H, CH_A, $^3J(HNCH_A)$ = 6 Hz), 4.45 (d, 1 H, CH_B, $^3J(HNCH_B)$ unobserved; $^2J(HCH)$ = 16 Hz), 4.97 (m), 4.40 (m), 4.08 (m), and 3.76 (m) (4 H, C*H*), 2.2–3.2 (m, 8 H, C*H*). $^{31}P\{^1H\}$ NMR: δ 26.7 (s).

Hydridochloro[*o*-(diphenylphosphino)-*N*-benzylanilido][*o*-(diphenylphosphino)-*N*-benzylaniline]iridium(III) [10, IrHCl(*o*-$Ph_2PC_6H_4NCH_2Ph$)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]. A mixture of $[Ir(\mu\text{-Cl})(cyclooctene)_2]_2$ (50 mg, 0.056 mmol) and *o*-(diphenylphosphino)-*N*-benzylaniline (82.3 mg, 0.224 mmol) were placed in a 50-mL Schlenk flask fitted with a filter stick and a magnetic stir bar. Dry oxygen-free toluene was added via syringe and the reaction mixture stirred for 1 h. Addition of hexane gave a yellow precipitate. The filtered complex was recrystallized from toluene/hexane and dried in vacuo; yield 96 mg (89%). Anal. Calcd for $C_{50}H_{44}ClIrN_2P_2$: C, 62.4; H, 4.61; N, 2.91. Found: C, 62.4; H, 4.76, N, 2.77. IR: ν(NH) 3182 cm^{-1}, ν(IrH) 2192 cm^{-1}. ^1H NMR: δ −22.2 (pseudotriplet, 1 H, Ir*H*, $^2J(PH)$ = 20 Hz). $^{31}P\{^1H\}$ NMR: δ 7.2 (br), 9.02 (br).

Hydridochloro[*o*-(diphenylphosphino)-*N*-ethylanilido][*o*-(diphenylphosphino)-*N*-ethylaniline]iridium(III) [11, IrHCl(*o*-$Ph_2PC_6H_4NEt$)(*o*-$Ph_2PC_6H_4NHEt$)]. A similar procedure using $[Ir(\mu\text{-Cl})(cyclooctene)_2]_2$ (50 mg, 0.056 mmol) and *o*-(diphenylphosphino)-*N*-ethylaniline (69 mg, 0.224 mmol) gave the pure complex, yield 76 mg (81%). Anal. Calcd for $C_{40}H_{40}ClIrN_2P_2$: C, 57.3; H, 4.81; N, 3.34. Found: C, 57.4; H, 4.94; N, 3.21. IR: ν(NH) 3221 cm^{-1}, ν(IrH) 2217 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.8–7.6 (28 H, phenyl), 3.59 (br, 4 H, CH_2), 1.10 (br, 6 H, CH_3), −22.4 (t, 1 H, Ir*H*, ^2J(PH) = 20 Hz). $^{31}P\{^1H\}$ NMR: δ 10.6 (br).

Hydridochlorobis[*o*-(diphenylphosphino)-*N*-benzylaniline]iridium(III) [12, [IrHCl(*o*-$Ph_2PC_6H_4NHCH_2Ph)_2$]X (X = Cl, OH, $MeCO_2$)]. Solutions of this complex have been prepared by adding hydrogen chloride, water, or acetic acid to a dichloromethane solution of complex **10**. Evaporation of the solvent, or the addition of hexane, gave the complex as a colorless solid. IR: ν(NH) 3345 cm^{-1}, ν(IrH) 2217 cm^{-1}. ^1H NMR: δ 10.5 (br, (2 H, N*H*), 6.7–7.9 (m, 38 H, phenyl), 5.17 (dd, 2 H, CH_A, $^3J(HNCH_A)$ = 3.0 Hz), 4.08 (dd, 2 H, CH_B, $^2J(H_AH_B)$ = 13.1 Hz, $^3J(H_BNCH)$ = 8.6 Hz), −19.7 (t, 1 H, Ir*H*, $^2J(PH)$ = 18.4 Hz). $^{31}P\{^1H\}$ NMR: δ 7.4 (s).

Hydridochlorobis[*o*-(diphenylphosphino)-*N*-ethylaniline]iridium(III) [13, [IrHCl(*o*-$Ph_2PC_6H_4NHEt)_2$]Cl]. This complex was observed in solution by adding hydrogen chloride to a dichloromethane solution of complex **11**. ^1H NMR: δ 9.7 (br, 2 H, N*H*), 6.6–7.9 (m, 28 H, phenyl), 3.76 (dq, 2 H, CH_A), 3.14 (ddq, 2 H, CH_B, $^2J(H_AH_B)$ = 13 Hz, $^3J(HNCH_B)$ = 7.8 Hz), 1.00 (t, 6 H, CH_3, $^3J(HH)$ = 7.1 Hz), −20.2 (t, 1 H, Ir*H*, $^2J(PH)$ = 18.5 Hz). $^{31}P\{^1H\}$ NMR: δ 8.1 (s).

Hydrido[*o*-(diphenylphosphino)-*N*-benzylanilido][*o*-(diphenylphosphino)-*N*-benzylaniline]carbonyliridium(III) Chloride [14, [IrH(*o*-$Ph_2PC_6H_4NCH_2Ph$)CO(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]Cl]. A $CDCl_3$ solution of complex **10** contained in a 5-mm NMR tube was saturated with carbon monoxide, and the ^1H and $^{31}P\{^1H\}$ NMR spectra were monitored every 10 min. Three products formed in solution. One complex was identified as $[IrHCl(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl$ (**12**). The other products were two different isomers, A and B, formed sequentially, of the product iridium carbonyl complex **14**. From $^{31}P\{^1H\}$ NMR spectroscopy in CH_2Cl_2/CD_2Cl_2 solution we observed the following relative amounts of **10** + **12**/**14A**/**14B** being formed in solution after 10 min, 20 min, and 30 min, respectively: 58/28/14, 38/12/50, 30/0/70. The spectral resolution is insufficient to separately estimate **10** and **12**. After 30 min the conductivity of a dichloromethane solution containing **10** (0.57 mmol) and carbon monoxide was 5.20 Ω^{-1} cm^2 mol^{-1}. The yield of **12** was reduced if excess DABCO was added to the reaction mixture prior to the addition of $CDCl_3$ and CO. The relative amounts of **10** + **12**/**14A**/**14B** formed after 10 min, 20 min, and 30 min, respectively were as follows: 14/48/38, 10/18/72, 0/4/96. After 12 h in $CDCl_3$, complex **14** had decomposed to a mixture of products. The rate of formation of **14** was reduced by the presence of [*n*-Bu_4N]Cl in the solution. Kinetic isomer (A): IR ν(IrH) 2071 cm^{-1}, ν(CO) 1996 cm^{-1}; ^1H NMR δ −7.80 (t, Ir*H*, $^2J(PH)$ = 18.3 Hz); $^{31}P\{^1H\}$ NMR δ 16.3 (s). Thermodynamic isomer (B): IR ν(IrH) 2108 cm^{-1}, ν(CO) 2031 cm^{-1}; ^1H NMR δ 4.75 (dd, 1 H, CH_A, $^3J(HNCH_A)$ = 6.1 Hz), 4.22 (d, 1 H, CH_B, $^2J(H_AH_B)$ = 18.3 Hz), 4.24 (d, 1 H, $CH_{A'}$), 3.57 (d, 1 H, $CH_{B'}$, $^2J(H_{A'}H_{B'})$ = 18.3 Hz), −14.0 (dd, 1 H, IrH, $^2J(HP_A)$ = 18.3 Hz, $^2J(HP_B)$ = 11.0 Hz). $^{31}P\{^1H\}$ NMR: δ 24.9 (d, P_A), 5.65 (d, P_B, $^2J(P_AP_B)$ = 21.4 Hz).

Hydrido[*o*-(diphenylphosphino)-*N*-ethylanilido][*o*-(diphenylphosphino)-*N*-ethylaniline]carbonyliridium(III) Chloride [15, [IrH(*o*-$Ph_2PC_6H_4NEt$)CO(*o*-$Ph_2PC_6H_4NHEt$)]Cl]. A similar procedure using IrHCl(*o*-$Ph_2PC_6H_4NEt$)(*o*-$Ph_2PC_6H_4NHEt$) (**13**) led to two isomers of the complex being sequentially formed in the solution. Kinetic isomer (A): IR ν(IrH) 2098 cm^{-1}, ν(CO) 2005 cm^{-1}; ^1H NMR δ −7.95 (t, Ir*H*, $^2J(PH)$ = 17.7 Hz); $^{31}P\{^1H\}$ NMR δ 16.7 (s). Thermodynamic isomer (B): IR ν(IrH) 2132 cm^{-1}, ν(CO) 2036 cm^{-1}; ^1H NMR δ 4.21 (ddq, 1 H, CH_A, $^3J(HNCH_A)$ = 6.1 Hz, $^2J(H_AH_B)$ = 14.7 Hz, $^3J(HH)$ = 6.7 Hz), ~3.0 (dq, 1 H, CH_B), ~3.0 (dq, 1 H, $CH_{A'}$), 2.52 (dq, 1 H, $CH_{B'}$, $^2J(H_{A'}H_{B'})$ = 14.6 Hz), 1.22 (t, 3 H, CH_3, $^3J(HH)$ = 6.7 Hz), 0.85 (t, 3 H, $CH_{3'}$, $^3J(HH')$ = 6.9 Hz), −13.9 (dd, 1 H, Ir*H*, $^2J(HP_A)$ = 16.4 Hz, $^2J(HP_B)$ = 9.8 Hz); $^{31}P\{^1H\}$ NMR δ 24.7 (d, P_A), 6.15 (d, P_B, $^2J(PP)$ = 22 Hz).

***trans*-Chlorocarbonylbis[*o*-(diphenylphosphino)-*N*-benzylaniline]rhodium(I) [16, RhCl(CO)(*o*-$Ph_2PC_6H_4NHCH_2Ph)_2$].** The same procedure was followed as that used for **10** except that $[Rh(\mu\text{-Cl})(cyclooctene)_2]_2$ (200 mg, 0.28 mmol) and *o*-$Ph_2PC_6H_4NHCH_2Ph$ (410 mg, 1.12 mmol) were used in dichloromethane solution. After 1 h at ambient temperature the solution contained the unstable complex [Rh(*o*-$Ph_2PC_6H_4NHCH_2Ph)_2$]Cl. This complex was too thermally unstable to be characterized by microanalysis, and it was not isolated in a pure state. $^{31}P\{^1H\}$ NMR: δ 53.7 (d, $^1J(RhP)$ = 176 Hz). Bubbling carbon monoxide through this solution for 10 min gave the yellow product complex, yield 267 mg (54%). Anal. Calcd for $C_{51}H_{44}ClN_2OP_2Rh$: C, 68.0; H, 4.92; N, 3.11. Found: C, 68.0; H, 5.11; N, 2.92. IR: ν(NH) 3210 cm^{-1}, ν(CO) 1963 cm^{-1}. ^1H NMR: δ 6.5–7.6 (m, 38 H, phenyl), 6.47 (br, 2 H, N*H*), 4.26 (d, 4 H, CH_2, $^3J(HNCH)$ = 4.7 Hz). $^{31}P\{^1H\}$ NMR: δ 19.8 ($^1J(RhP)$ = 118 Hz).

Crystal Structure Determination. A single crystal of complex **12** (X = Cl) was grown by slow evaporation from a solution in $CDCl_3$. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromator by ω–2θ scans of variable rates with a maximum scan time of 90 s. The data were collected in the region from $0 < h < 11$, $0 < k < 29$, and $-22 < l < 22$. Three standard reflections were monitored every 200 reflections and showed a 7.3% linear decrease in the intensity of the standards over the period of the data collection due to loss of solvent of crystallization. The data were corrected for Lorentz–polarization, background and absorption effects, and linear absorption decay. The absorption correction was based on ψ scans of reflections near $\chi = 90°$. The space group $P2_1/n$ was uniquely determined by systematic absences. Other details of the experiment are given in Table I.

The position of the Ir atom was determined by direct methods (MULTAN '82). A combination of full-matrix least-squares refinement and difference electron density syntheses was used to locate the remaining non-hydrogen atoms. Atomic scattering factors were corrected for the effects of anomalous dispersion.[8,9] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in a combination of observed and calculated positions then held positionally and thermally invariant. The compound crystallizes with two molecules of deuterated chloroform per molecule of complex. The solvent molecules have been located and refined. The final least-squares cycle converged with a maximum shift of 0.08σ with final residual values of R = 3.6 and R_w = 5.4. The crystal data are collected in Table I and the final atomic positions in Table II. Selected bond distances and angles are collected in Table III.

(8) All calculations were performed by using the Enraf-Nonius Structure Determination Package.

(9) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

Table I. Crystallographic Data for $[IrHCl(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl \cdot 2CDCl_3$

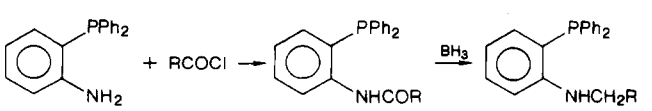
formula	$C_{50}P_2N_2Cl_2IrH_{45}\cdot 2CDCl_3$
mol wt, amu	1237.72
cryst dimens, mm	0.40 × 0.23 × 0.17
cryst system	monoclinic
space group	$P2_1/n$
cell dimens	
a, Å	10.111 (4)
b, Å	25.886 (3)
c, Å	19.939 (3)
β, deg	93.03 (2)
V, Å^3	5211
Z	4
ρ(calcd), g cm^{-3}	1.58
radiatn	Mo Kα, λ(Mo Kα_1) = 0.709 30
2θ range, deg	3–48
scan type	ω–2θ
scan angle, deg	0.8 + 2 tan θ
scan speed, deg min^{-1}	4.0
total data collected	8693
unique data	7663
obsd data with $I_o > 3\sigma_I$	6184
μ, cm^{-1}	27.5
transmissn coeff	0.9994–0.7668
F(000)	2460
R^a	0.036
$R_w{}^b$	0.054

$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ ($w = 1/\sigma(F^2)$).

Results and Discussion

The low-valent d^8 compounds chosen for this project are chloro-bridged alkene complexes that have the potential to generate several coordination sites both by chloro bridge cleavage and by alkene substitution. The availability of multiple coordination positions is a particularly favorable situation because the intramolecular N–H addition reaction from a tertiary phosphine anchor requires three coordination positions at the metal center. The phosphine amines used by us as ligands in this project are ortho-substituted (diphenylphosphino)anilines. The tertiary phosphine moiety is suitable because it will form strong complexes with rhodium and iridium, and P,N-chelation will be favored with these ligands because of the formation of a planar five-membered ring in the product complexes. Intramolecular N–H activation bears a strong resemblance to the well-known cyclometalation of C–H bonds, a reaction which is favored by bulky substituents on the carbon.[10] We have therefore used a synthetic strategy for our new phosphine amines such that different alkyl substituents can be readily incorporated onto the nitrogen heteroatom of the ligands. Characteristic spectroscopic data for the ligands and complexes are shown in Table IV.

Ligand Synthesis. The new phosphine amines which we have synthesized have the general formula *o*-$Ph_2PC_6H_4NHR$ (R = CH_2Ph, Et). These compounds are obtained by first treating *o*-$Ph_2PC_6H_4NH_2$ with benzoyl or acetyl chloride, followed by reduction of the carbonyl group in *o*-$Ph_2PC_6H_4NHC(O)R$ with borane (eq 1). The



(1)

R = Ph, Me

pure colorless solids are air stable and soluble in a wide range of organic solvents. Each compound shows a characteristic infrared band in the 3300–3500 cm^{-1} region due to ν(NH) and a single resonance upfield of H_3PO_4 in the $^{31}P\{^1H\}$ NMR spectrum (Table I).

(10) Bottomley, A. R. H.; Crocker, C.; Shaw, B. L. *J. Organomet. Chem.* **1983**, *250*, 617–626.

Table II. Positional Parameters and Their Estimated Standard Deviations for $[IrHCl(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl \cdot 2CDCl_3$[a]

atom	x	y	z	B, Å^2
Ir	0.93574 (2)	0.10766 (1)	0.24398 (1)	2.365 (5)
Cl1	0.6988 (2)	0.08382 (8)	0.2466 (1)	3.84 (4)
Cl2	0.7124 (2)	0.24903 (9)	0.2281 (1)	4.80 (5)
Cl3	0.2931 (3)	0.2770 (1)	0.1492 (1)	7.42 (8)
Cl4	0.3665 (4)	0.1769 (1)	0.1969 (2)	8.37 (9)
Cl5	0.3185 (4)	0.2586 (2)	0.2903 (2)	9.7 (1)
Cl6	0.9751 (4)	0.3417 (2)	0.2210 (2)	10.6 (1)
Cl7	1.1119 (6)	0.4030 (2)	0.3141 (3)	16.6 (2)
Cl8	1.0887 (5)	0.4370 (3)	0.1818 (3)	22.7 (2)
P1	0.9963 (2)	0.06437 (7)	0.33811 (9)	2.75 (4)
P2	0.9812 (2)	0.05252 (7)	0.16088 (9)	2.75 (4)
N1	0.8827 (5)	0.1661 (2)	0.3160 (3)	2.8 (1)
N2	0.8761 (5)	0.1564 (2)	0.1580 (3)	2.9 (1)
C1	0.8993 (7)	0.0968 (3)	0.3997 (3)	3.2 (2)
C2	0.8746 (8)	0.0782 (3)	0.4635 (4)	4.2 (2)
C3	0.7847 (9)	0.1039 (4)	0.5028 (4)	4.9 (2)
C4	0.7212 (8)	0.1477 (4)	0.4776 (4)	4.4 (2)
C5	0.7476 (7)	0.1670 (3)	0.4166 (4)	3.4 (2)
C6	0.8399 (6)	0.1424 (3)	0.3782 (3)	2.8 (1)
C7	0.9988 (7)	0.2037 (3)	0.3329 (4)	3.4 (2)
C8	0.9750 (8)	0.2382 (3)	0.3918 (4)	3.7 (2)
C9	1.0293 (8)	0.2238 (3)	0.4549 (4)	4.5 (2)
C10	1.0003 (9)	0.2525 (4)	0.5105 (4)	5.0 (2)
C11	0.9188 (9)	0.2946 (4)	0.5051 (4)	5.3 (2)
C12	0.862 (1)	0.3085 (3)	0.4441 (4)	5.3 (2)
C13	0.8924 (9)	0.2810 (3)	0.3866 (4)	4.3 (2)
C14	0.8729 (7)	0.0768 (3)	0.0934 (4)	3.0 (1)
C15	0.8246 (8)	0.0473 (3)	0.0375 (4)	4.1 (2)
C16	0.7324 (8)	0.0672 (4)	−0.0085 (4)	4.3 (2)
C17	0.6859 (8)	0.1169 (3)	0.0007 (4)	3.9 (2)
C18	0.7298 (7)	0.1475 (3)	0.0557 (4)	3.8 (2)
C19	0.8245 (7)	0.1257 (3)	0.1013 (3)	3.0 (1)
C20	0.9881 (7)	0.1913 (3)	0.1379 (4)	3.5 (2)
C21	0.9604 (7)	0.2234 (3)	0.0752 (4)	3.5 (2)
C22	1.0125 (8)	0.2081 (3)	0.0157 (4)	4.2 (2)
C23	0.9873 (9)	0.2383 (4)	−0.0422 (4)	5.3 (2)
C24	0.915 (1)	0.2817 (4)	−0.0409 (4)	5.5 (2)
C25	0.8649 (9)	0.2981 (3)	0.0200 (4)	5.2 (2)
C26	0.8875 (8)	0.2678 (3)	0.0775 (4)	4.3 (2)
C27	1.1488 (7)	0.0554 (3)	0.1311 (4)	3.0 (1)
C28	1.1740 (8)	0.0686 (3)	0.0661 (4)	4.5 (2)
C29	1.3062 (9)	0.0711 (4)	0.0463 (5)	6.6 (2)
C30	1.4113 (9)	0.0596 (4)	0.0917 (6)	6.3 (3)
C31	1.3841 (8)	0.0474 (4)	0.1568 (5)	5.8 (2)
C32	1.2531 (7)	0.0440 (3)	0.1763 (4)	4.2 (2)
C33	0.9469 (7)	−0.0165 (3)	0.1625 (3)	3.0 (1)
C34	0.8270 (8)	−0.0341 (3)	0.1846 (5)	4.6 (2)
C35	0.798 (1)	−0.0861 (4)	0.1843 (5)	6.2 (2)
C36	0.889 (1)	−0.1217 (4)	0.1658 (5)	5.8 (2)
C37	1.008 (1)	−0.1054 (4)	0.1445 (6)	6.4 (3)
C38	1.0379 (9)	−0.0519 (3)	0.1425 (4)	5.0 (2)
C39	1.1679 (7)	0.0653 (3)	0.3715 (4)	3.3 (2)
C40	1.2668 (7)	0.0909 (3)	0.3373 (4)	3.7 (2)
C41	1.3971 (8)	0.0901 (4)	0.3622 (4)	4.8 (2)
C42	1.4322 (9)	0.0658 (4)	0.4213 (5)	5.3 (2)
C43	1.333 (1)	0.0422 (4)	0.4575 (5)	6.9 (3)
C44	1.2041 (9)	0.0418 (4)	0.4320 (4)	5.3 (2)
C45	0.9523 (8)	−0.0036 (3)	0.3465 (4)	3.4 (2)
C46	0.8221 (8)	−0.0161 (3)	0.3598 (4)	4.7 (2)
C47	0.792 (1)	−0.0689 (4)	0.3662 (5)	5.9 (2)
C48	0.879 (1)	−0.1060 (3)	0.3538 (5)	6.4 (3)
C49	1.007 (1)	−0.0922 (4)	0.3384 (6)	6.6 (3)
C50	1.0423 (9)	−0.0407 (4)	0.3337 (5)	5.2 (2)
C51	0.3827 (9	0.2429 (4)	0.2128 (5)	5.5 (2)
C52	1.111 (1)	0.3840 (6)	0.2345 (8)	10.0 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[IrHCl(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl \cdot 2CDCl_3$

Bond Distances			
Ir-H	1.60 (4)	C6-N1	1.469 (6)
Ir-Cl1	2.477 (1)	P2-C14	1.803 (5)
Ir-P1	2.243 (1)	C14-C15	1.416 (8)
Ir-P2	2.253 (1)	C15-C16	1.372 (8)
Ir-N1	2.173 (8)	C16-C17	1.385 (9)
Ir-N2	2.187 (4)	C17-C18	1.406 (8)
P1-C1	1.818 (6)	C18-C19	1.404 (7)
C1-C2	1.395 (8)	C19-N2	1.457 (7)
C2-C3	1.399 (9)	N1-C7	1.547 (7)
C3-C4	1.384 (9)	C7-C8	1.506 (8)
C4-C5	1.355 (8)	N2-C20	1.519 (7)
C5-C6	1.392 (7)	C20-C21	1.515 (7)
Bond Angles			
Cl1-Ir-P1	94.56 (5)	P2-Ir-N2	81.2 (1)
Cl1-Ir-P2	95.31 (5)	N1-Ir-N2	92.8 (2)
Cl1-Ir-N1	83.5 (1)	Ir-P1-C1	101.6 (2)
Cl1-Ir-N2	86.2 (1)	Ir-P2-C14	100.9 (2)
P1-Ir-P2	104.00 (5)	Ir-N1-C6	111.1 (3)
P1-Ir-N1	82.0 (1)	Ir-N1-C7	111.7 (3)
Ir-N2-C19	111.5 (3)	P1-C1-C6	115.2 (4)
Ir-N2-C20	111.8 (3)	N1-C6-C1	118.5 (4)
N1-C7-C8	113.1 (4)	P2-C14-C19	116.3 (4)
N2-C20-C21	115.9 (4)	N2-C19-C14	118.5 (5)

Table IV. Characteristic Spectroscopic Data for the Substituted *o*-(Diphenylphosphino)anilines and Their Rhodium and Iridium Chelate Complexes

compound	ν(NH), cm^{-1}	$\delta(CH_2)$	δ(P)
$o\text{-}Ph_2PC_6H_4NHCH_2Ph$	3405	4.30	-27.2
$o\text{-}Ph_2PC_6H_4NHEt$	3356	3.13	-20.3
RhCl(1,5-COD)-($o\text{-}Ph_2PC_6H_4NHCH_2Ph$) (**1**)	3163	4.50	21.7
RhCl(1,5-COD)($o\text{-}Ph_2PC_6H_4NHEt$) (**2**)	3150	3.24	25.3
IrCl(1,5-COD)($o\text{-}Ph_2PC_6H_4NHCH_2Ph$) (**3**)	3120	4.50	14.9
IrCl(1,5-COD)($o\text{-}Ph_2PC_6H_4NHEt$) (**4**)	*a*	3.36	12.0
[Ir(1,5-COD)($o\text{-}Ph_2PC_6H_4NHCH_2Ph$)]-$ClO_4$ (**5**)	3168	4.69, 4.21	27.7
[Ir(1,5-COD)($o\text{-}Ph_2PC_6H_4NHEt$)]ClO_4 (**6**)	3191	3.53, 3.32	29.4
[Ir(1,5-COD)py($o\text{-}Ph_2PC_6H_4NHEt$)]-ClO_4 (**7**)	*a*	3.41	*a*
[Ir(1,5-COD)MeCN($o\text{-}Ph_2PC_6H_4NHEt$)]-ClO_4 (**8**)	*a*	3.40	30.1
[IrH(1,5-COD)($o\text{-}Ph_2PC_6H_4NHCH_2C_6H_4$)]-$ClO_4$ (**9**)	3216	5.22, 4.45	26.7
IrHCl($o\text{-}Ph_2PC_6H_4NCH_2Ph$)-($o\text{-}Ph_2PC_6H_4NHCH_2Ph$) (**10**)	3182	*a*	7.2, 9.0
IrHCl($o\text{-}Ph_2PC_6H_4NEt$)-($o\text{-}Ph_2PC_6H_4NHEt$) (**11**)	3221	3.59	10.6
[IrHCl($o\text{-}Ph_2PC_6H_4NHCH_2Ph$)$_2$]Cl (**12**)	3345	5.17, 4.08	7.4
[IrHCl($o\text{-}Ph_2PC_6H_4NHEt$)$_2$]Cl (**13**)	*a*	3.76, 3.14	8.1
[IrH($o\text{-}Ph_2PC_6H_4NCH_2Ph$)CO-($o\text{-}Ph_2PC_6H_4NHCH_2Ph$)]Cl (**14A**)	*a*	*a*	16.3
(**14B**)	*a*	4.75, 4.22 4.24, 3.57	24.9, 5.65
[IrH($o\text{-}Ph_2PC_6H_4NCH_2Et$)CO-($o\text{-}Ph_2PC_6H_4NHCH_2Et$)]Cl (**15A**)	*a*	*a*	16.7
(**15B**)	*a*	4.21, 3.0 3.0, 2.52	24.7, 6.15

[a] Not measured.

Rhodium(I) and Iridium(I) Complexes. The compounds $[M(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (M = Rh, Ir) react with $o\text{-}Ph_2PC_6H_4NHR$ (R = CH_2Ph, Et) to give the new d^8 complexes $MCl(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHR)$ (eq 2). The product complex results from cleavage of the chloro bridge by the tertiary phosphine. Coordination to the metal via phosphorus is confirmed by the downfield ^{31}P chemical

$$\tfrac{1}{2}[M(\mu\text{-}Cl)(1,5\text{-}COD)]_2 + o\text{-}Ph_2PC_6H_4NHR \longrightarrow (1,5\text{-}COD)M(Cl)(PC_6H_4NHR\,Ph_2) \quad (2)$$

M = Rh, R = CH_2Ph (**1**), Et (**2**); M = Ir, R = CH_2Ph (**3**), Et (**4**)

shift in the complexes as compared to the free ligands. The complexes are all air-sensitive, especially complex **4** which is too unstable to be isolated in a pure state. The methylene hydrogens for both the benzyl and ethyl groups in complexes **1**–**4** show only small downfield NMR chemical shifts from their free ligand positions and also remain chemically equivalent. These NMR spectral data support the formulation of these complexes as having a planar four-coordinate geometry with the amine moiety uncomplexed.

Complexation of the amine nitrogen to iridium(I) has been achieved by creating a vacant coordination site by removing the chloride ligand with silver ion. Thus treating complexes **3** and **4** with silver perchlorate in THF solvent results in the precipitation of silver chloride and formation of bis chelate cationic complexes **5** and **6** (eq 3). The

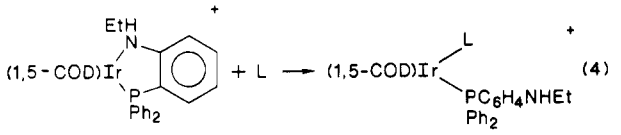
$$(1,5\text{-}COD)Ir(Cl)(PC_6H_4NHR\,Ph_2) + AgClO_4 \longrightarrow [(1,5\text{-}COD)Ir(RHN,P\text{-}Ph_2)]ClO_4 + AgCl \quad (3)$$

R = CH_2Ph (**5**), Et (**6**)

P,N-chelation is supported by the observation of downfield ring shifts in the ^{31}P NMR resonances for complexes **5** and **6**, as compared to those of complexes **3** and **4**.[11] Stronger support for chelation comes from observations that the diastereotopic methylene resonances for the benzyl and ethyl groups in the ^1H NMR spectra are magnetically inequivalent. Free ligand is also diastereotopic, but pyramidal inversion causes the two diastereomers to coalesce into one resonance. Inspection of the spectral data reveals that changes in ν(NH) or $\delta(CH_2)$ cannot be used as reliable indicators of amine coordination (Table I). These coordinately unsaturated 16-electron iridium(I) complexes show no tendency to undergo oxidative addition of the N–H bond. This failure of iridium(I) to insert into the N–H bond is due to the π-acceptor ability of the chelated 1,5-cyclooctadiene, a ligand which sufficiently withdraws electron density from iridium(I) such that this metal center is stabilized in its low oxidation state.

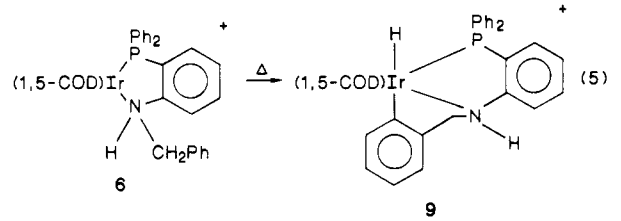
Increasing the electron density at iridium(I) will likely favor N–H addition. We have therefore attempted to destabilize the iridium(I) center by adding the donor ligands pyridine and acetonitrile to a solution of the ethyl complex **6**. This approach has, however, failed to result in the formation of an iridium hydride product; instead we observe a substitution reaction whereby the coordinated amine arm of the chelate ligand is displaced by either complexed pyridine or acetonitrile to give the four-coordinate complexes $[Ir(1,5\text{-}COD)L(o\text{-}Ph_2PC_6H_4NHEt)]ClO_4$ (L = py (**7**), MeCN (**8**)) (eq 4). This replacement reaction in solution can be followed by ^1H NMR spectroscopy because the displacement of the coordinated amine results in the methylene hydrogens of the substituent ethyl group becoming a single chemical shift.

(11) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.



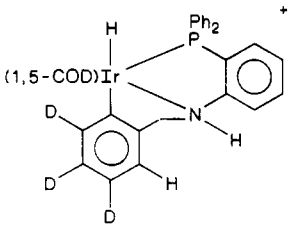
L = py (7), MeCN (8)

Iridium(III) Hydride Complexes. When $CDCl_3$ solutions of complex **5** are allowed to remain under a nitrogen atmosphere for 3 days, the compound converts into a new iridium(III) hydride complex, **9**. This conversion time can be reduced to 3 h by refluxing the solution. By contrast, $CDCl_3$ solutions of the ethyl analogue complex **6** are stable at ambient temperature for a period exceeding 10 days. Complex **9** arises from cyclometalation at the ortho position of the phenyl ring of the dangling benzyl substituent giving $[IrH(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHCH_2C_6H_4)]ClO_4$ (eq 5). This new complex **9** is characterized by an IR band



6 9

due to ν(NH) at 3216 cm^{-1}, along with ν(IrH) at 2183 cm^{-1}. The doublet hydride ^1H NMR resonance is centered at δ −15.1 (^2J(PH) = 11 Hz). This reaction is particularly favored because of the formation of a five-membered ring. The cyclometalation of benzylamines has long been recognized as a facile reaction.[12] In order to further verify the structure of **9** and also to probe the mechanism of this reaction, we have synthesized the deuterated ligand $o\text{-}Ph_2PC_6H_4NHCH_2C_6D_5$. With this deuterated compound we have prepared complex **6** and subsequently converted in into **9** by thermolysis in $CDCl_3$ solution. By ^1H NMR spectroscopy we identify the product as $[IrH(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHCH_2C_6HD_3)]ClO_4$, which has deuterium substituents at the positions shown in complex **9**-d_3.[13] We

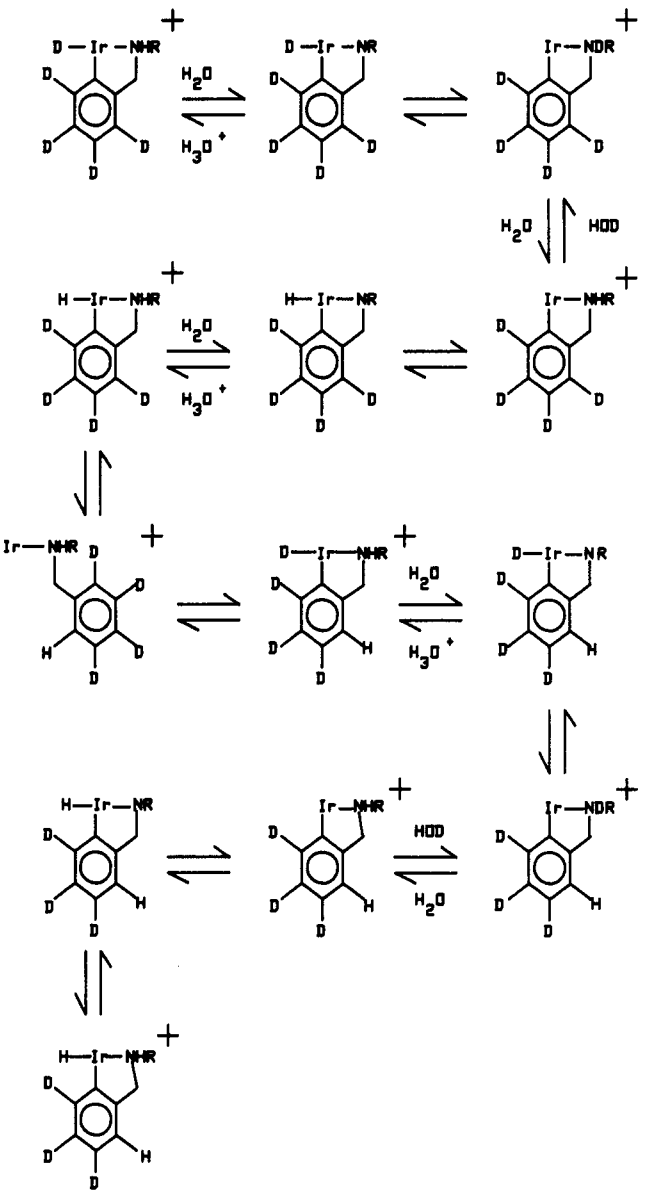


9-d_3

propose that proton/deuterium exchange occurs in the initial product because of the presence of water in the $CDCl_3$ solvent (detectable by ^1H NMR). We propose that this exchange involves a sequence of hydrogen atom transfer reactions between iridium and nitrogen, in concert with H/D exchange between NH and H_2O. The proposed pathway is outlined in Scheme I.

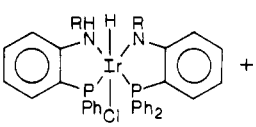
On the basis of the assumption that the chelated 1,5-cyclooctadiene ligand is a sufficiently good π-acceptor to preclude N–H addition, we have modified our synthetic

Scheme I. Proposed H/D Exchange Pathway between Water and N–H, C–H, and Ir–H Bonds



approach to make the addition more favorable by replacing the complexed 1,5-COD ligand with an alkene that can be readily substituted by a strong donor ligand such as a phosphine or an amine. When the complex $[Ir(\mu\text{-}Cl)(cyclooctene)_2]_2$ is treated with 4 equiv of $o\text{-}Ph_2PC_6H_4NHR$ (R = CH_2Ph, Et), an iridium(III) hydride complex, $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$ (R = CH_2Ph (**10**), Et (**11**), is formed (eq 6).[14] The presence of a hydride

$$\tfrac{1}{2}[Ir(\mu\text{-}Cl)(C_8H_{14})_2]_2 + 2o\text{-}Ph_2PC_6H_4NHR \longrightarrow$$



$+ 2C_8H_{14}$ (6)

R = CH_2Ph (**10**), Et (**11**)

ligand is confirmed by IR and ^1H NMR spectroscopy: ν(IrH) 2192 cm^{-1} and δ −22.2 (dd, ^2J(PH) ~ ^2J(P′H) = 20 Hz) for **10** and ν(IrH) 2217 cm^{-1} and δ −22.4 (t, ^2J(PH) = 20 Hz) for **11**. When the same reaction is carried out with

(12) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In Comprehensive *Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 6, p 321.

(13) In complex **9** the hydrogens of the cyclometalated ring are upfield shifted from the other phenyl hydrogens. The following four resonances are observed: δ 6.25 (t, $^3J(HH)$ = 7.5 Hz), 6.51 (t, $^3J(HH)$ = 7.4 Hz), 6.55 (d, $^3J(HH)$ = 7.4 Hz), 6.68 (d, $^3J(HH)$ = 7.3 Hz). For the deuterated compound **9**-d_3, the doublet at δ 6.68 is observed as a singlet at δ 6.67.

(14) The assignment of stereochemistry is based on the close similarity between the ^{31}P NMR spectra of complexes **10** and **12**.

the N-deuterated ligand *o*-$Ph_2PC_6H_4NDR$, the product is the iridium deuteride complex $IrDCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NDR)$. The deuteride complex is characterized by IR spectroscopy: ν(IrD) ca. 1600 cm^{-1} (overlapped with C=C aromatic), ν(ND) 2373 cm^{-1} for **10**-*d*; and ν(IrD) 1614 cm^{-1}, ν(ND) 2395 cm^{-1} for **11**-*d*. These kinetically inert iridium(III) complexes do not undergo H/D exchange at the iridium deuteride bond with added water, which is in direct contrast with the exchange chemistry observed with **9**. This difference in chemistry between the two complexes results from **10** and **11** having N,P donor ligands coordinated to iridium(III) rather than the π-acceptor 1,5-COD chelate ligand in complex **9**. Such N,P donor ligands will disfavor hydrogen atom transfer from iridium to nitrogen (a reductive elimination reaction), which we believe to be a key step in the H/D exchange process. This postulate is supported by our observation that in reaction 6 the first observable product is the iridium(III) hydride, such a complex being formed by an intramolecular N–H addition in an intermediate iridium(I) chelate complex (eq 7).

$$[Ir(o\text{-}Ph_2PC_6H_4NHR)_2]Cl \rightarrow IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR) \quad (7)$$

R = CH_2Ph, Et

The $^{31}P\{^1H\}$ NMR spectra of complexes **10** and **11** show broad resonances for the phosphorus nuclei coordinated to iridium(III) due to the presence of an exchange process. At ambient temperature in CD_2Cl_2 solvent, the spectrum of complex **10** shows two broad resonances at δ 7.2 and 9.02. By contrast, complex **11** shows only a single broad peak centered at δ 10.6. Upon cooling this CD_2Cl_2 solution of **11** from ambient temperature to −60 °C, this peak resolves into two broad resonances centered at δ 9.2 and 13.1. Since the hydride resonance is sharp, topological exchange about the iridium center seems unlikely, especially since the ^1H and $^{31}P\{^1H\}$ NMR line width differences appear to be too great to be accounted for by the different resonant frequencies. The most probable explanation for this line behavior in the $^{31}P\{^1H\}$ NMR spectrum is that a proton transfer exchange occurs between the coordinated nitrogens, resulting in a reversible amide/amine interchange within the complex.

Reaction of the Amide Complexes with Protons and Carbon Monoxide. The iridium(III) amide hydride complexes **10** and **11** react with protonic acids HX to yield cationic complexes that have been protonated at the coordinated amide nitrogen. The reaction is reversible, deprotonation at nitrogen occurring when a strong base such as DABCO is added (eq 8). Addition of a large excess of

$$IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR) \underset{\text{DABCO}}{\overset{\text{HX}}{\rightleftharpoons}} [IrHCl(o\text{-}Ph_2PC_6H_4NHR)_2]X \quad (8)$$

R = CH_2Ph, X = Cl, OH, $MeCO_2$ (**12**); R = Et, X = Cl (**13**)

strong base causes no further change, indicating that the remaining N–H proton has a low kinetic or thermodynamic acidity. The evidence for the formation of $[IrHCl(o\text{-}Ph_2PC_6H_4NHR)_2]X$ comes from ^1H and $^{31}P\{^1H\}$ NMR spectroscopy: δ 10.5 (br, 2 H, N*H*) and 7.4 (s, *P*) for **12**; δ 9.7 (br, 2 H, N*H*) and 8.1 (s, *P*) for **13**. The $^{31}P\{^1H\}$ resonances are now sharp singlets at ambient temperature, indicative of a stereochemically rigid structure.

The structure of $[IrHCl(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl$ shows that the H and Cl groups are in the axial positions and that the chelate ligands have a mutual cis geometry (Figure 1). The hydrogen atom bonded to iridium has been located and refined (Ir–H = 1.60 (4) Å). The long

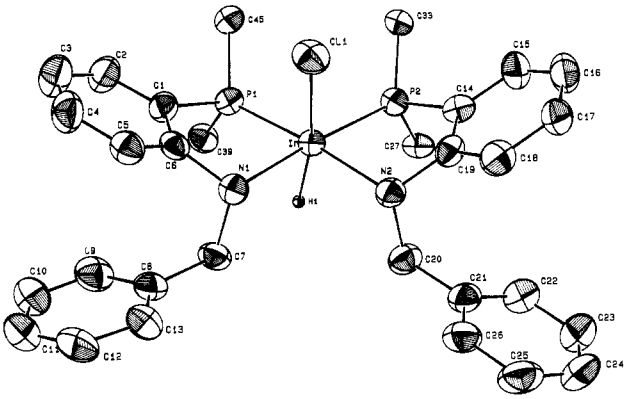


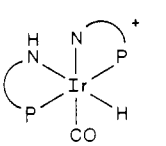
Figure 1. Molecular structure and atom-labeling scheme for $C_{50}P_2N_2Cl_2IrH_{45}\cdot 2CDCl_3$ shown with 50% thermal ellipsoids. The C27–C50 series phenyl rings bonded to P1 and P2 are shown as the ipso atoms only. The hydrogens, other than that bonded to Ir, have also been removed for clarity.

Ir–Cl1 distance (2.477 (1) Å) corresponds to a bond trans to hydride. The Ir–P (Ir–P1 = 2.243 (1), Ir–P2 = 2.253 (1) Å) show that there are no significant distortions in the equatorial plane. The equatorial plane is distorted because of the acute P–Ir–N bite angles in the chelate rings (P1–Ir–N1 = 82.0 (1)°, P2–Ir–N2 = 81.2(1)°). Furthermore the P1–Ir–P2 angle of 104.00 (5)° is larger than the N1–Ir–N2 angle of 92.8 (2)°.

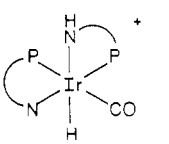
When $CDCl_3$ solutions of $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$ (R = CH_2Ph (**10**), Et (**11**)) are reacted with carbon monoxide, two new products are formed, along with $IrHCl(o\text{-}Ph_2PC_6H_4NHR)_2^+$. This latter complex is likely formed from protonation by water, small quantities of which are introduced along with carbon monoxide. Of the two new compounds the first kinetic product converts to the thermodynamic one within 30 min, with the second product undergoing thermal decomposition after 12 h. Each complex can be isolated from solution by addition of hexane. The IR spectra of all complexes show bands due to ν(IrH) and ν(CO), but no bands indicative of a carbamoyl (IrC(O)NR) moiety resulting from insertion of carbon monoxide into the iridium–amide bond.[15] These complexes are kinetic and thermodynamic isomers of $[IrH(o\text{-}Ph_2PC_6H_4NR)CO(o\text{-}Ph_2PC_6H_4NHR)]Cl$ (R = CH_2Ph (**14**), Et (**15**) (eq 9). On the basis of the spectral

$$IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR) + CO \rightarrow [IrH(o\text{-}Ph_2PC_6H_4NR)CO(o\text{-}Ph_2PC_6H_4NHR)]Cl \quad (9)$$

evidence we propose that the kinetic isomer has stereochemistry A and that the thermodynamic one has stereochemistry B.[16] The replacement of complexed chloride



14A and **15A**



14B and **15B**

ion by carbon monoxide is supported by conductivity measurements; solutions containing either predominantly A or B show large increased conductivities as compared to solutions of $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$. As final proof we observe a marked decrease in the rate of carbonylation (reaction 9) in the presence of added

(15) We expect a carbamoyl moiety to show ν(CO) in the 1600–1700 cm^{-1} region.

(16) These assignments are not unambiguous; however, isomers with hydride trans to phosphorus can be eliminated because of the absence of any large $^2J(PH)$ couplings.

chloride ion. Complex $[IrHCl(o\text{-}Ph_2PC_6H_4NHR)_2]Cl$ (**12**, **13**) does not react with carbon monoxide, an observation which is consistent with its observed formation during the carbonylation reaction of $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$. Indeed, if the carbonylation is carried out in the presence of added DABCO, the quantity of complex **12** or **13** formed is considerably reduced. The reaction of carbon monoxide with the neutral iridium(III) amide complexes **10** and **11**, but not with the cationic iridium(III) amine complexes **12** and **13**, reflects the greater electron density imparted to the iridium center by the anionic amide ligand. Carbon disulfide shows analogous reactivity to carbon monoxide, but these neutral complexes **10** and **11** do not react with ethylene or hydrogen.

Rhodium Complexes. The kinetic lability of rhodium complexes causes them to be less stable than their iridium counterparts. We have, nevertheless, prepared unstable solutions of the rhodium(I) analogues and investigated their reaction chemistry with carbon monoxide. When $[Rh(\mu\text{-}Cl)(C_8H_{14})]_2$ is reacted with 4 equiv of $o\text{-}Ph_2PC_6H_4NHCH_2Ph$ in dichloromethane solvent, a solution containing the air-sensitive complex $[Rh(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl$ (**16**) is formed. No upfield ^1H NMR resonances indicative of a rhodium hydride are observed, and the doublet $^{31}P\{^1H\}$ NMR resonance at δ 53.7 ($^1J(RhP)$ = 176 Hz) supports the formulation as a rhodium(I) complex.[17] Addition of carbon monoxide to the solution yields the rhodium(I) carbonyl complex $RhCl(CO)(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2$ (**17**) (eq 10). Complex **17**

$$\tfrac{1}{2}[Rh(\mu\text{-}Cl)(C_8H_{14})_2]_2 + 2o\text{-}Ph_2PC_6H_4NHCH_2Ph \longrightarrow [Rh(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2]Cl + C_8H_{14} \quad (10)$$

$$\downarrow CO$$

$$RhCl(CO)(o\text{-}Ph_2PC_6H_4NHCH_2Ph)_2$$

17

is characterized by IR and both ^1H and $^{31}P\{^1H\}$ NMR spectroscopy: ν(NH) 3210 cm^{-1}, ν(CO) 1963 cm^{-1}; δ 6.47 (br, 2 H, N*H*), 4.26 (d, 4 H, CH_2), 19.8 (d, $^1J(RhP)$ = 118 Hz). These results show that the intramolecular addition of an N–H bond is more favorable for iridium(I) than it is for rhodium(I), in agreement with previous experimental results on oxidative addition reactions.[18]

Acknowledgment. We thank both the graduate school of Tulane University and the Louisiana Board of Regents for financial support. We thank the Office of Naval Research for funds to purchase the FTIR spectrometer.

Supplementary Material Available: Tables of bond distances, bond angles, general displacement parameter expressions (U's), root-mean-square amplitudes of anisotropic displacement, and torsion angles (17 pages); a listing of values of F_o and F_c (62 pages). Ordering information is given on any current masthead page.

(17) By comparison, ^1J(RhP) = 133 Hz in $[Rh(dppe)_2]Cl$ (Miller, J. S.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97* 1067–1073), and ^1J(RhP) = 124 Hz in *trans*-$RhCl(CO)(PPh_3)_2$ (Tolman, C. A.; Meakin, P. R.; Lindner, D. L.; Jesson, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 2762–2774).

(18) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

Analysis of the π-Facial Preference for Complexation of a Camphor-Derived, Enantiomerically Pure Cyclopentadienyl Ligand to $CpMCl_2$ Fragments (M = Ti and Zr)[1]

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Received November 14, 1988

Optically pure (+)-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]deca-2,5-diene (**3**) has been synthesized and its lithium salt condensed with $TiCl_3$·3THF, $CpTiCl_3$, $ZrCl_4$, $CpZrCl_3$, and $Cp''ZrCl_3$. In each instance, a pair of stereoisomeric complexes was isolated. Relative to the behavior of the parent isodicyclopentadienide anion where exo complexation increases in importance relative to the steric demands of the second ligand, the present camphor-derived anion invariably prefers endo coordination. This change in π-facial response is attributed to the presence of the apical syn-methyl group in **3**, which serves to more closely equalize the available space above- and below-plane. The end result is a synergistic driving force from both electronic and steric contributions to achieve endo coordination to the extent possible.

In the preceding paper,[1] we have established the limits to complexation of the isodicyclopentadienide anion from its two distinctive faces with cyclopentadienyltitanium dichloride reagents. At −78 °C, reaction occurs with $RCpTiCl_3$ under kinetic control to deliver **1** exclusively. When the same process is carried out at room temperature, thermodynamic factors appear to override more subtle electronic influences and exo complexes such as **2** are formed stereoselectively.

Herein, attention is given to preparation of the optically active camphor-derived diene **3** and to elucidation of the

[†] The Ohio State University.
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(1) Paper 44 in the series dealing with isodicyclopentadienes and related molecules. For 43, see: Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. *Organometallics*, in press.

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