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Article

Palladium(II), Platinum(II), and Iridium(I) Complexes of 2-Phosphino-1-dimethylaminoferrocenes: A Survey of Structure and Catalysis

Costa Metallinos,* Josh Zaifman, Lori Van Belle, Laura Dodge, and Melanie Pilkington

Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario L2S 3A1, Canada

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A series of $PdCl_2$, $PtCl_2$, and Ir(COD)BAr_F complexes bearing a rare class of racemic bidentate 2-phosphino-1-dimethylaminoferrocene ligands were prepared and characterized by NMR spectroscopy and X-ray crystallography. The new complexes displayed a structural trend relating a decrease in heteroatom-metal bond length with an increase in ligand bite angle on going from Ir to Pd and Pt. The $PdCl_2$ and $PtCl_2$ complexes were almost isostructural and featured MCl_2 moieties in the plane of the substituted Cp ring of the ligand. In contrast, the $Ir(COD)^+$ complex was distinguished by a bend of the Ir(COD) moiety toward the unsubstituted (Cp′) ring. The latter gave rise to a steric interaction that placed the Cp rings in almost eclipsed conformations. Ligand **8a** (2-diphenylphosphino-1-dimethylaminoferrocene) was able to promote Pd-catalyzed Suzuki−Miyaura and Buchwald−Hartwig coupling of aryl chlorides in addition to Ir-catalyzed hydrogenation of electron-deficient and unactivated alkenes. A preliminary intramolecular hydroamination of a terminal alkene using **8a** in conjunction with Ir(I) afforded the cyclized product in 64% yield.

Introduction

Ligands containing both nitrogen and phosphorus donor groups figure prominently in many synthetically important transformations mediated by transition metals. These catalytic reactions range from achiral processes such as arylation and amination of aryl chlorides with biaryls such a **1**,[1,2] to enantioselective processes such as hydrogenation of prochiral alkenes,[3] for which PHOX ligands[4,5] of general structure **2** are among the most effective (Figure 1). Among ferrocenes, countless *P*,*N* ligands derived from Ugi's chiral (dimethylaminomethyl)ferrocenes[6] (e.g., **3**[7]), oxazolines[8] (**4**), and sulfoxides[9] (e.g., **5**) have been investigated, but these often feature ligating heteroatoms in pendant groups and/or heterocyclic rings and usually contain additional stereogenic centers. Only recently have there been reports of exclusively planar chiral ferrocenyl *P*,*N* ligands in which both heteroatoms are directly attached to the cyclopentadienyl (Cp) ring. These include the racemic indenyl derivative **6** by Stradiotto[10] and the C_2-symmetric diphosphine **7** by Alonso et al.[11] The lack of examples of these types of *P*,*N* ligands may partially reflect limitations of established synthetic routes to aminoferrocenes, although some creative efforts have been aimed at solving these problems.[12]

*Corresponding author. E-mail: cmetallinos@brocku.ca.

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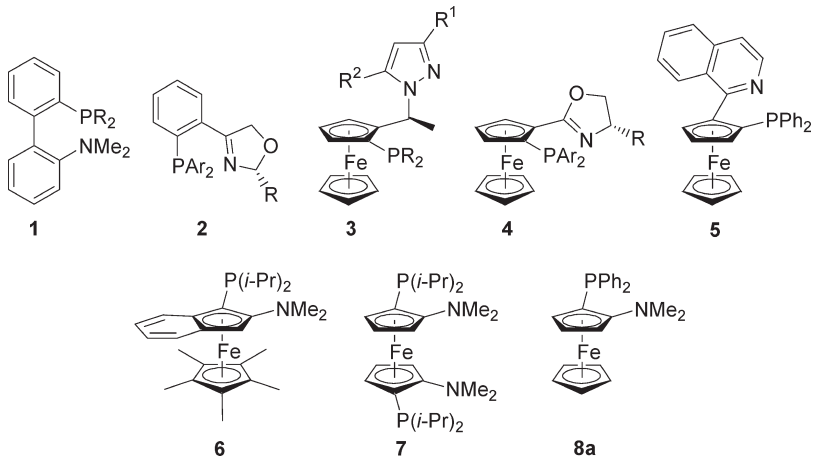
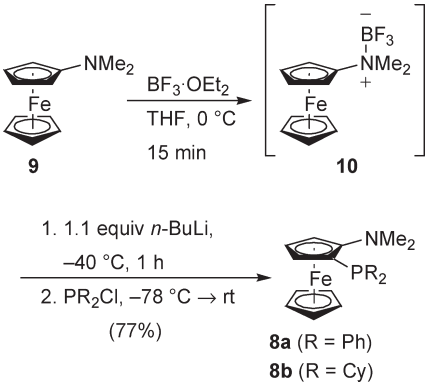


Figure 1. *P*,*N* ligands with applications in cross-coupling (**1**, **7**), aryl amination (**1**), hydroamination (**1**), hydrogenation (**2**, **4**), hydrosilylation (**3**), allylic substitution (**5**), and hydroboration (**6**).

Recently we reported an alternate and potentially more direct synthesis of planar chiral 1,2-*P*,*N*-ferrocenes (e.g., **8a**) by boron trifluoride activated lithiation of dimethylaminoferrocene.[13] An enantioselective variant of this process is currently under investigation in our laboratories and will be reported in due course.[14] In the meantime, we were interested in examining in more detail the coordination behavior of these ligands with catalytically important transition metals. In this paper we investigate the coordination chemistry of racemic ligands of this series toward the square-planar metals Pd(II), Pt(II), and Ir(I), determine their structures by X-ray crystallography, and study their catalytic potential in a number of transformations including Suzuki−Miyaura or Buchwald−Hartwig coupling of aryl chlorides, hydrogenation or hydroamination of alkenes.

Scheme 1. Preparation of Aminophosphines 8a and 8b

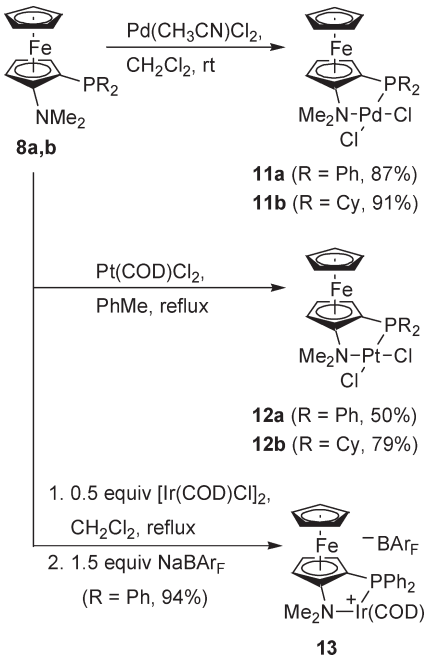


Results and Discussion

Synthesis of Ligands and Complexes. Following our published procedure,[13] dimethylaminoferrocene (**9**) was reacted with boron trifluoride etherate in tetrahydrofuran to give a yellow zwitterion (**10**) that was cooled to −40 °C and treated with *n*-BuLi (Scheme 1). The resulting red-orange 2-lithioferrocene was quenched with two different chlorophosphines to afford diphenyl phosphine **8a** and dicyclohexyl phosphine **8b** in identical yields (77%). Although **8a** was an air-stable solid, compound **8b** was a moderately air-sensitive oil that was best stored under inert atmosphere.

The ability of **8a** and **8b** to behave as chelating ligands toward square-planar transition metals was tested initially with Pd(II). Addition of **8a** or **8b** to a solution of Pd$(CH_3CN)_2Cl_2$ in dichloromethane at room temperature afforded the coordination complexes **11a**,**b** in excellent yields as orange or rust-colored solids, respectively (Scheme 2). Evidence of bidentate coordination was provided by ^{31}P and ^{1}H NMR analysis. Coordination of the phosphine moiety was inferred by the significant downfield shift of the ^{31}P NMR signals of **11a** (δ 25.3) and **11b** (δ 51.1) compared to the phosphorus resonances of the free ligands (**8a**, δ −20.4; **8b**, δ −12.3). Simultaneous coordination of nitrogen would render the amino methyl groups diastereotopic in the

Scheme 2. Synthesis of Pd, Pt, and Ir Complexes



complexes. This nonequivalence is indeed observed in the ^{1}H NMR spectra as two methyl singlets for **11a** (δ 3.46, 3.09) and **11b** (δ 3.47, 3.12). Only one methyl singlet is present in

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Table 1. Diagnostic ^{31}P and ^{1}H NMR Signals for 8a,b, 11a,b, 12a,b, and 13

	8a	8b	11a	11b	12a	12b	13
^{31}P NMR (δ)	−20.4	−12.3	25.3	51.1	2.0	21.7	15.0
^{1}H NMR (NMe_2, δ)	2.69	2.75	3.46, 3.09	3.47, 3.12	3.65, 3.24	3.64, 3.26	3.13, 2.69
solvent	$CDCl_3$	acetone-d_6	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$

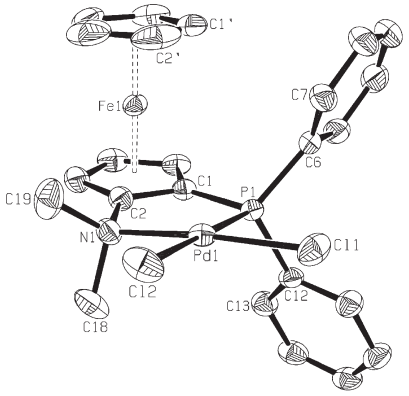

Figure 2. ORTEP plot of **11a** at 50% probability. Hydrogen atoms are omitted for clarity.

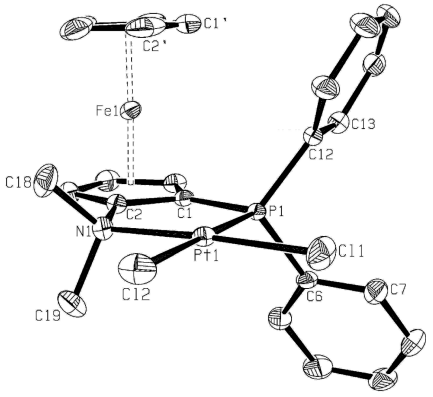

Figure 3. ORTEP plot of **12a** at 50% probability. Hydrogen atoms are omitted for clarity.

the ^{1}H NMR spectra of the noncoordinated ligands (**8a**, δ 2.69; **8b**, δ 2.75).

In a similar manner, Pt(II) complexes of **8a** and **8b** were made by addition of either ligand to a solution of Pt(COD)Cl_2 in toluene at reflux to give **12a** and **12b**. An Ir(I) complex of **8a** was prepared from $[Ir(COD)Cl]_2$ in refluxing dichloromethane and isolated after *in situ* exchange of the chloride ion with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaBAr_F$) to give the BAr_F salt of **13** as an air-stable orange solid. The preceding platinum and iridium complexes displayed analogous downfield shifts of their ^{31}P NMR signals and diastereotopic amino methyl groups by ^{1}H NMR, as observed for **11a**,**b**, suggesting chelation of the ligands to the metals. The key ^{31}P and ^{1}H NMR signals for all ligands and complexes are summarized in Table 1.

Structural Studies. The apparent bidentate coordination behavior of the new ligands was verified by X-ray crystallographic analysis of **11a**, **12a**, and **13**. Suitable crystals of these compounds were grown from acetonitrile, acetone, and benzene, respectively. Diffraction studies established that the palladium and platinum complexes were almost isostructural (Figures 2 and 3), despite the fact that they crystallized in two different crystal systems and space groups (**11a**, orthorhombic *Pbca*; **12a**, monoclinic $P2_1/n$). Both

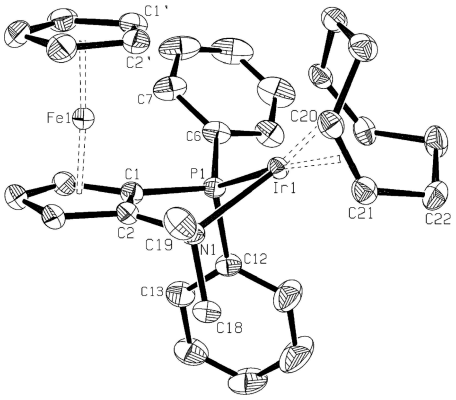

Figure 4. ORTEP plot of **13** at 50% probability. Hydrogen atoms and the BAr_F counterion are omitted for clarity.

complexes featured staggered conformations of their respective Cp rings, with dihedral angles defined by H4−C4−C4′−H4′ of 32.27(14)° for **11a** and 28.59(13)° for **12a**. As expected for square-planar metals, the ligand displayed nearly orthogonal bite angles (P1−Pd1−N2 and P1−Pt1−N2) of 87.87(6)° in **11a** and 88.78(5)° in **12a**. The smaller bite angle for **11a** may be a consequence of the longer N1−Pd1 and P1−Pd1 bond lengths (2.135(2) and 2.2185(7) Å, respectively) versus the N1−Pt and P1−Pt distances in **12a** (2.114 (2) and 2.2066(6) Å, respectively), although the differences are small. Complex **11a** is also distinguished by a slight conformational twist of the NMe_2 group, which causes the N1 atom to be slightly puckered and below the mean plane defined by the P1, Cl1, and Cl2 atoms (deviation from plane = 0.251(5) Å). For comparison, the N1 atom of **12a** is nearly coplanar with the P1, Cl1, and Cl2 atoms (deviation from plane = 0.091(4) Å).

Unlike **11a** and **12a**, where the $PdCl_2$ and $PtCl_2$ moieties are in the same plane as the substituted Cp ring of the ligand, the Ir(COD) portion of complex **13** is bent upward toward the unsubstituted (Cp′) ring (Figure 4). This spatial preference is most likely a result of the steric demands of the COD ligand and results in relatively close contact distances between H1′ or H2′ and H26B of COD (H1′···H26B = 2.68 (1) Å; H2′···H26B = 2.56(1) Å). The proximity of H26B to H1′ and H2′ may also be responsible for the near eclipsed conformation of the Cp rings in **13** (H4−C4−C4′−H4′ dihedral angle = 4.53(8)°). Another factor affecting the shape of **13** may be the pseudoaxial/pseudoequatorial arrangement of the P-Ph groups. In the preferred conformation of the chelate ring, the pseudoequatorial phenyl group (C6−C11) is pointing away from the Cp′ ring. The same phenyl group would become pseudoaxial in the alternate conformer in which Ir(COD) is bent downward, resulting in an unfavorable interaction with the Cp′ ring. Beyond these interactions, bond length and bite angle metrics of **13** continued the trend observed with **11a** and **12a**. In this respect, the iridium complex possesses the longest heteroatom−metal bonds of the series (N1−Ir1 and P1−Ir1 bond lengths = 2.225(3) and 2.2951(9) Å, respectively) in addition to the smallest bite angle (N1−Ir−P1 angle = 82.84(8)°). The shape of **13** in the

Table 2. Selected X-ray Crystallographic Data for 11a, 12a, and 13

	11a	12a	13
formula	$C_{24}H_{24}Cl_2FeNPPd$	$C_{24}H_{24}Cl_2FeNPPt$	$C_{64}H_{48}BF_{24}FeNPIr$
mol weight (g/mol)	590.56	679.22	1576.88
color	orange	orange	orange
cryst size (mm)	0.24 × 0.22 × 0.18	0.34 × 0.27 × 0.12	0.30 × 0.26 × 0.04
temp (K)	173(2)	150(2)	150(2)
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbca*	$P2_1/n$	$P\bar{1}$
a (Å)	17.378(3)	9.9906(18)	12.7697(6)
b (Å)	14.1396(18)	14.365(3)	12.8455(6)
c (Å)	18.736(3)	16.145(3)	19.8377(10)
α (deg)	90	90	74.724(2)
β (deg)	90	90.946(6)	76.026(3)
γ (deg)	90	90	87.188(2)
V (Å^3)	4603.8(11)	2316.7(8)	3045.8(3)
Z	8	4	2
D_c (g/cm^3)	1.704	1.947	1.719
radiation	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	1.725	6.970	2.563
θ range (deg)	2.15 to 29.00	2.84 to 28.21	2.19 to 28.48
unique data	6126 [*R*(int) = 0.0398]	5807 [*R*(int) = 0.0237]	15 144 [*R*(int) = 0.0341]
maximum, minimum transmn	0.7465, 0.6823	0.432, 0.110	0.9043, 0.5133
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0324$, $wR_2 = 0.0831$	$R_1 = 0.0148$, $wR_2 = 0.0331$	$R_1 = 0.0352$, $wR_2 = 0.0985$
R indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.0888$	$R_1 = 0.0187$, $wR_2 = 0.0347$	$R_1 = 0.0413$, $wR_2 = 0.1041$
goodness-of-fit on F^2	1.055	1.068	1.133
peak/hole (e Å^{-3})	1.583/−0.468	0.523/−0.741	6.129/−0.790

solid state bears some resemblance to the crystallographically determined structure of complex **6**·Rh(COD)BF_4 reported recently by Stradiotto[10] and co-workers, although the latter has less bend of the Rh(COD) moiety due to the presence of the bulkier pentamethylcyclopentadienyl (Cp*) ring. A summary of other key crystallographic data for **11a**, **12a**, and **13** is shown in Table 2.

Catalytic Studies. The use of ligands of general structure **1** (e.g., R = Cy) in palladium-catalyzed Suzuki−Miyaura and Buchwald−Hartwig cross-coupling of aryl chlorides is well established.[1,2] While **1** and its congeners have the potential to act as bidentate donors, for the most part such ligands are thought to be primarily bulky monodentate phosphines, although evidence exists for *π*-interactions between the 2′-aryl ring and Pd in some cases.[15] Interest in ligands such as **1** (R = *t*-Bu or Cy) received a boost recently by the reports of Widenhoefer[16] and Hartwig[17] that they promote intramolecular hydroamination in excellent yields with catalytic platinum(II)[16] or rhodium(I).[17] Hollis[18] and Stradiotto[19] have reported intramolecular hydroamination of similar substrates catalyzed by iridium(I) complexes bearing pincer-type or bidentate COD ligands, respectively. In addition, chiral bidentate PHOX-type *P*,*N* ligands (**2**) have been shown by Pfaltz, Andersson, and others to be excellent for iridium-catalyzed enantioselective hydrogenation of unactivated alkenes.[3,4]

The penchant of racemic ligands **8a** and **8b** to chelate palladium, platinum, and iridium presented an opportunity to survey their catalytic potential in non-stereoselective transformations of both achiral and prochiral substrates. Successful results with prochiral substrates, in particular, would provide the impetus to investigate asymmetric versions of some of these reactions with enantiomerically enriched ligands **8a**,**b** in the future.[14] Initial catalytic studies using **8a**,**b** focused on achiral palladium-mediated cross-coupling reactions of aryl chlorides. The first test involved Suzuki−Miyaura coupling of 4-trifluoromethylchlorobenzene (**14a**) with phenylboronic acid (2 mol % **11a**, 3 equiv of CsF, dioxane, reflux), which afforded **15a** in 65% yield. Better results were realized by *in situ* generation of the catalyst (2 mol % $Pd(OAc)_2$, 4 mol % **8a**, 3 equiv of CsF, dioxane, reflux), which gave **15a** in excellent 94% yield (Scheme 3). Under these conditions, good yields were also obtained with 4-acetyl and 4-cyano chlorobenzenes (**15b**, 88%; **15c**, 92%). The sterically hindered 2-nitro derivative (**14d**) gave **15d** in 73% yield. Chlorobenzenes with electron-donating substituents such as 4-methoxy (**14e**) and 4-methyl (**14f**) were less reactive, resulting in lower yields of biphenyls (**15e**, 70%; **15f**, 56%). Replacing ligand **8a** with **8b** did not improve the yields of **15e** or **15f**. However, the double phenylation of quinolinyl dibromide **14g** proceeded smoothly under the standard reaction conditions to give **15g** in 88% yield, which was significantly better than what was obtained using $Pd(PPh_3)_4$ as the catalyst (42% yield).

Buchwald−Hartwig amination of aryl halides with morpholine proved to be more challenging. While satisfactory results were obtained with chlorides **14a** and **14b**, the low reactivity of electron-rich and electron-neutral substrates necessitated the use of the corresponding bromides (**14e**,**h**). The latter afforded products **16e** and **16h** in 67% and 82% yields, respectively. Chlorides with *ortho* substituents were also sluggish to react (**14d** → **16d**: 43%). Unlike the Suzuki−Miyaura couplings, which worked best with a 2:1 ratio of ligand to palladium, the Buchwald−Hartwig aminations gave better results with a 1:1 ratio of ligand to palladium, suggesting chelation of the ligand in the catalytically active species. The use of a 2:1 ratio of ligand to palladium in the aryl amination experiments resulted in very low (< 5%) yields.

In contrast to palladium-catalyzed aryl aminations, hydrogenation of unactivated and electron-deficient alkenes

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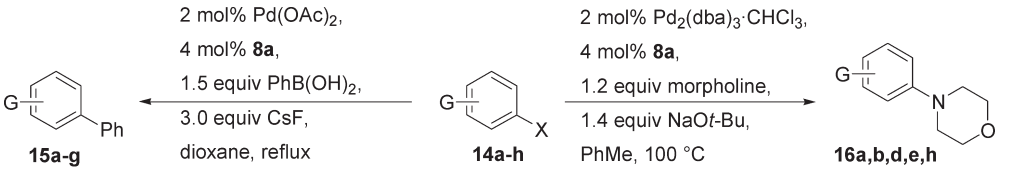
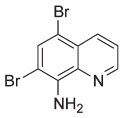
Scheme 3. Palladium-Catalyzed Suzuki−Miyaura and Buchwald−Hartwig Coupling Promoted by 8a



14a-g	G	X	yield, %, 15a-g
a	4-CF_3	Cl	94
b	4-COMe	Cl	88
c	4-CN	Cl	92
d	2-NO_2	Cl	73
e	4-MeO	Cl	70
f	4-Me	Cl	56
g		-	88

14a,b,d,e,h	G	X	yield, % 16a,b,d,e,h
a	4-CF_3	Cl	77
b	4-COMe	Cl	74
d	2-NO_2	Cl	43
e	4-MeO	Br	67
h	H	Br	82

with iridium complex **13** gave excellent results with a broad range of substrates. Thus, stilbenes **17a**,**b** afforded the saturated products **18a**,**b** (Scheme 4) in high yields under standard conditions (2 mol % **13**, 62 bar of H_2, CH_2Cl_2, rt). A number of cinnamate esters (**17c**−**e**) were also hydrogenated under the same conditions in yields ranging from 94% to 96%. Hydrogenation of chalcone (**17f**) resulted in chemoselective reduction of the alkene in 99% yield. Good results were also obtained with imines[20] (**17g**,**h**) and geraniol (**17i**), the latter to give product **18i** in 99% yield after reduction of both double bonds. Hydrogenations of cyclic substrates such as maleimide (**17j**), cyclohexenone (**17k**), and naphthoquinone (**17l**) also proceeded smoothly. More challenging substrates such as chromone (**17m**) required addition of Hünig's base to the reaction mixture,[21] while hydrogenation of carvone (**17n**) under standard conditions resulted in chemoselective reduction of the exocyclic double bond.

Finally, ligands **8a**,**b** were utilized in Pt- and Ir-catalyzed hydroamination of aminoalkene **19** (Scheme 5). For the platinum-catalyzed reactions, a modification of Widenhoefer's procedure[16] (5 mol % $PtCl_2$, 10 mol % **8a**, diethylene glycol, 100 °C) gave low yields (27%) of the desired pyrrolidine (**20**), which could not be improved by changing ligands or solvents or by varying the ligand/metal ratio. The preformed complexes **12a**,**b** did not promote this reaction, implying that chelation of **8a**,**b** to platinum is detrimental to its catalytic activity. In contrast, hydroamination of **19** with iridium complex **13** (2.5 mol % **13**, dioxane, reflux) gave **20** in improved yield (64%) along with an intractable mixture of byproduct of isomerization or reduction of the substrate.[17] This transformation may be improved by small alterations to the ligand structure or by the use of Rh(I).[17]

Conclusion

A series of coordination complexes of racemic 2-phosphino-1-dimethylaminoferrocenes (**8a**,**b**) were readily prepared from the square-planar metals Pd(II), Pt(II), and Ir(I). Spectroscopic data indicated the likelihood that the ligands formed *N*,*P*-chelates with all metals, a fact that was confirmed by X-ray crystallographic analysis. Comparison of the solid-state structures revealed a trend relating a decrease in heteroatom-metal bond length with an increase in ligand bite angle on going from Ir(I) to Pd(II) and Pt(II). The Pd(II) and Pt(II) complexes were almost isostructural and featured MCl_2 moieties in the plane of the substituted Cp ring. In contrast, the Ir(I) complex was distinguished by a bend of the Ir(COD) moiety toward the Cp′ ring. The latter gave rise to a steric interaction that placed the Cp rings in almost eclipsed conformations.

Of the two ligands, **8a** proved to be effective at promoting Pd-mediated Suzuki−Miyaura and Buchwald−Hartwig coupling of aryl chlorides in addition to Ir-catalyzed hydrogenation of structurally diverse alkenes. Preliminary intramolecular hydroamination of terminal alkene **19** using **8a** in conjunction with Ir(I) afforded pyrrolidine **20** in 64% yield, although the corresponding Pt(II)-mediated reaction was poor (27%). Improvements to the hydroamination process along with an investigation of asymmetric transformations mediated by enantiomerically enriched ligands **8a**,**b** are under study in our laboratories and will be reported in due course.[14]

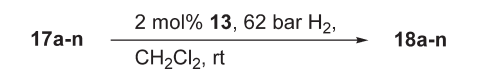
Experimental Section

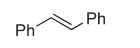
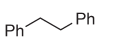
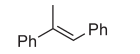
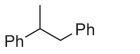
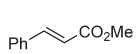
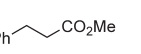
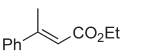
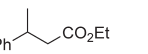
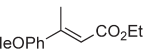
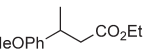
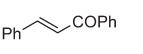
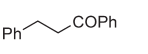
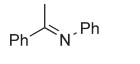
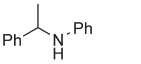
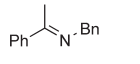
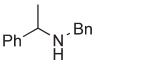
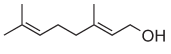
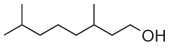
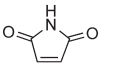
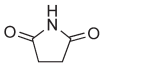
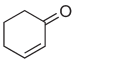
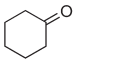
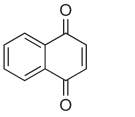
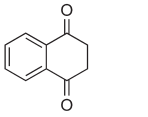
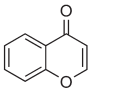
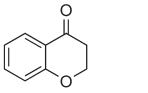
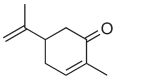
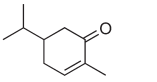
General Procedures. All reagents were purchased from commercial sources and used as received unless otherwise indicated. Tetrahydrofuran (THF) was freshly dried and distilled over sodium/benzophenone ketyl under an atmosphere of nitrogen. Toluene was distilled from sodium under N_2. Dichloromethane and hexane were distilled over CaH_2 under an atmosphere of nitrogen. Dioxane was distilled from $LiAlH_4$ under argon. All reactions were performed under argon in flame- or oven-dried glassware using syringe-septum cap techniques or Schlenk conditions unless otherwise indicated. Column chromatography was performed on silica gel 60 (70−230 mesh) or neutral alumina. NMR spectra were obtained on a Bruker Avance 300 or 600 MHz instrument and are referenced to TMS or to the residual proton signal of the deuterated solvent for ^1H spectra and to the carbon multiplet of the deuterated solvent for ^{13}C spectra according to published values. Pressurized reactions were performed with a Parr 4760 bomb. FT-IR spectra were obtained on an ATI Mattson Research Series spectrometer as KBr pellets for solids or on KBr discs for liquids. Mass

(20) For iridium-catalyzed hydrogenation of imines with a ferrocenyl *P,N* ligand featuring a pendant pyridyl donor, see: Cheemala, M. N.; Knochel, P. *Org. Lett.* **2007**, *9*, 3089.

(21) Semeniuchenko, V.; Khilya, V.; Groth, U. *Synlett* **2009**, 271.

Scheme 4. Hydrogenation of Alkenes and Imines Catalyzed by 13



17a-n	substrate, **17**	product, **18**	yield, %, **18a-n**
a			97
b			86
c			95
d			94
e			96
f			99
g			81
h			88
i			98
j			82
k			84
l			89[a]
m			66[b]
n			96

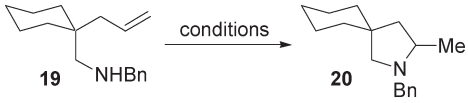
[a] Mixture of keto and phenol tautomers.

[b] Reaction performed in PhMe at 100 bar in the presence of Hünig's base.

spectra were obtained on an MSI/Kratos Concept 1S mass spectrometer. Combustion analyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. X-ray data were collected on a Bruker APEX II CCD area detector equipped with a Kappa goniometer and using Mo Kα graphite-monochromated radiation, $\lambda = 0.71073$ Å. The structure was solved by direct methods using SHELXTL software. The refinement and all further calculations were carried out using SHELXTL. The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. A multiscan absorption correction was applied using the SADABS routine.

2-Dicyclohexylphosphino-1-dimethylaminoferrocene (8b). In a dry round-bottom flask under argon, an ice-cold solution of dimethylaminoferrocene **9** (229 mg, 1.00 mmol) in THF (10 mL) was treated with $BF_3 \cdot OEt_2$ (0.13 mL, 1.05 mmol). After 15 min, the yellow solution was cooled to −40 °C, and *n*-BuLi (0.46 mL of a 2.40 M solution in hexanes, 1.10 mmol) was added by syringe to give an orange-red solution, which was stirred for 1 h before $ClPCy_2$ (0.24 mL, 1.10 mmol) was added and the mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (10 mL) and worked up with saturated aqueous $NaHCO_3$ solution (10 mL). The organic layer was washed with H_2O (1 × 10 mL) and brine (1 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was redissolved in pentane and chromatographed on silica gel (25 mL), eluting with 95:5 pentane/Et_2O to give 397 mg (77%) of the desired aminophosphine **8b** as a moderately air-sensitive viscous orange oil: R_f 0.50 (silica gel, 9:1 hexane/EtOAc); IR ($CHCl_3$) ν_{max} 2920, 2848, 1489, 1446 cm^{-1}; ^{31}P NMR (121 MHz, acetone-d_6) δ −12.3; ^1H NMR (300 MHz, acetone-d_6) δ 4.22 (s, 5H), 4.15 (t, 1H, $J = 1.1$ Hz), 4.04 (t, 1H, $J = 2.3$ Hz), 3.92 (t, 1H, $J = 1.7$ Hz), 2.75 (s, 6H), 2.49−2.41 (m, 1H), 2.00−1.93 (m, 1H), 1.92−1.81 (m, 3H), 1.77−1.67 (m, 2H), 1.67−1.61 (m, 1H), 1.61−1.52 (m, 3H), 1.50−1.20 (m, 7H), 1.20−1.06 (m, 2H), 1.06−0.97 (m, 1H), 0.90−0.79 (m, 1H); ^{13}C NMR (75.5 MHz, acetone-d_6) δ 118.0 (d, $J^{13}_{C-^{31}P} = 14.0$ Hz), 67.5, 66.6 (d, $J^{13}_{C-^{31}P} = 3.4$ Hz), 63.3 (d, $J^{13}_{C-^{31}P} = 25.3$ Hz), 63.2, 61.3 (d, $J^{13}_{C-^{31}P} = 1.5$ Hz), 43.9 (d, $J^{13}_{C-^{31}P} = 13.2$ Hz), 35.0 (d, $J^{13}_{C-^{31}P} = 15.9$ Hz), 33.2 (d, $J^{13}_{C-^{31}P} = 13.2$ Hz), 32.2 (d, $J^{13}_{C-^{31}P} = 20.6$ Hz), 30.2 (d, $J^{13}_{C-^{31}P} = 15.9$ Hz), 29.5 (d, $J^{13}_{C-^{31}P} = 10.8$ Hz), 29.0, 27.3 (d, $J^{13}_{C-^{31}P} = 11.8$ Hz), 27.2 (d, $J^{13}_{C-^{31}P} = 6.5$ Hz), 27.0 (d, $J^{13}_{C-^{31}P} = 12.8$ Hz), 26.8 (d, $J^{13}_{C-^{31}P} = 8.3$ Hz), 26.3 (d, $J^{13}_{C-^{31}P} = 15.5$ Hz); EIMS (m/z (%)) 425 (M^+, 87), 130 (62), 55 (100), 41 (94); HRMS (EI; m/z) calcd for $C_{24}H_{36}NP^{56}Fe$ 425.1936, found 425.1934.

Scheme 5. Intramolecular Hydroamination of 19



conditions	yield, %, **20**
5 mol% $PtCl_2$, 10 mol% **8a**, diethylene glycol, 100 °C, 48 h	27
2.5 mol% **13**, dioxane, reflux, 22 h	64

2-Diphenylphosphino-1-dimethylaminoferrocene (8a). 8a was prepared in a manner analogous to **8b**: A solution of **9** (229 mg, 1.00 mmol) in THF (10 mL) was sequentially treated with $BF_3 \cdot OEt_2$ (0.13 mL, 1.05 mmol), *n*-BuLi (0.45 mL, 2.45 M, 1.10 mmol), and Ph_2PCl (0.22 mL, 1.20 mmol). Standard workup followed by column chromatography of the preadsorbed product (silica gel, Et_2O) gave an orange solid. Recrystallization from Et_2O afforded **8a** (317 mg, 77%) as orange needles in two crops: mp 146−148 °C (Et_2O); IR (KBr) ν_{max} 3090, 3050, 2952, 2840, 2780, 1494 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −20.4; ^1H NMR (600 MHz, $CDCl_3$) δ 7.55−7.52 (m, 2H), 7.39 (m, 3H), 7.28 (m, 5H), 4.20 (s, 1H), 4.13 (s, 5H), 4.10 (t, 1H, $J = 2.4$ Hz), 3.50 (s, 1H), 2.69 (s, 6H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 139.8 (d, $J^{13}_{C-^{31}P} = 11.0$ Hz), 137.9 (d, $J^{13}_{C-^{31}P} = 10.6$ Hz), 135.3 (d, $J^{13}_{C-^{31}P} = 22.6$ Hz), 132.4 (d, $J^{13}_{C-^{31}P} = 18.1$ Hz), 129.0, 128.1 (d), 128.0 (d), 127.8, 119.0 (d, $J^{13}_{C-^{31}P} = 18.1$ Hz), 68.7, 68.5 (d, $J^{13}_{C-^{31}P} = 3.0$ Hz), 65.9 (d, $J^{13}_{C-^{31}P} = 10.6$ Hz), 65.2, 60.1, 45.5; EIMS [m/z (%)] 413 (M^+, 100); HRMS (EI) calcd for $C_{24}H_{24}NP^{56}Fe$ 413.0995, found 413.0991. Anal. Calcd for $C_{24}H_{24}NPFe$: C, 69.75; H, 5.85. Found: C, 69.87; H, 5.94.

2-Diphenylphosphino-1-dimethylaminoferrocenepalladium Dichloride (11a). Representative Procedure. A solution of aminophosphine

8a (94 mg, 0.30 mmol) and $Pd(MeCN)_2Cl_2$ (58 mg, 0.30 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature in a dry flask under argon until TLC indicated consumption of the aminophosphine (75 min). The reaction mixture was then filtered through a pad of silica gel, eluting with 97:3 CH_2Cl_2/MeOH, and concentrated. Recrystallization from acetonitrile at −20 °C gave **11a** (154 mg, 87%) as a light orange powder in two crops: mp > 225 °C (dec at 210 °C); IR (KBr) ν_{max} 3448, 1460, 1434 cm^{-1}; ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.3; ^1H NMR (600 MHz, $CDCl_3$) δ 8.11−8.05 (m, 2H), 7.63−7.58 (m, 1H), 7.58−7.52 (m, 4H), 7.51−7.46 (m, 1H), 7.39−7.34 (m, 2H), 4.74 (t, 1H J = 2.3 Hz), 4.53 (s, 1H), 4.21 (s, 1H), 4.00 (s, 5H), 3.46 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.6 Hz), 132.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 2.2 Hz), 131.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 10.1 Hz), 131.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 57.8 Hz), 131.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 3.1 Hz), 129.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 67.7 Hz), 128.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.6 Hz), 128.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 12.1 Hz), 126.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 24.6 Hz), 75.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.1 Hz), 72.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 56.1 Hz), 63.9, 60.3 (d, $J^{13}_{C-}{}^{31}_{P}$ = 12.3 Hz), 58.2, 54.5. FABMS (m/z (%)) 591 (M^+, 14), 554 (90), 518 (84), 413 (77), 292 (73), 229 (85), 214 (81), 108 (100). Anal. Calcd for $C_{24}H_{24}NPCl_2FePd$: C, 48.81; H, 4.10. Found: C, 49.04; H, 4.09.

2-Dicyclohexylphosphino-1-dimethylaminoferrocenepalladium Dichloride (11b). This was prepared on a 0.22 mmol scale in a manner analogous to **11a** to give 121 mg (91%) of rust-colored crystals after recrystallization from acetonitrile at −20 °C: mp > 225 °C (dec at 195 °C); IR (KBr) ν_{max} 2931, 2850, 1446 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 51.1; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71 (s, 1H), 4.59 (s, 1H), 4.46 (s, 5H), 4.00 (s, 1H), 3.47 (s, 3H), 3.12 (s, 3H), 2.72−2.54 (m, 1H), 2.52−2.33 (m, 1H), 2.33−2.16 (m, 2H), 2.16−1.88 (m, 5H), 1.87−1.31 (m, 10H), 1.31−1.05 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 128.0 (d, $J^{13}_{C-}{}^{31}_{P}$ = 20.9 Hz), 74.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 5.6 Hz), 73.8, 73.3, 63.1, 60.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 10.6 Hz), 58.5, 56.7, 37.7 (d, $J^{13}_{C-}{}^{31}_{P}$ = 30.2 Hz), 35.1 (d, $J^{13}_{C-}{}^{31}_{P}$ = 30.2 Hz), 29.0 (d, $J^{13}_{C-}{}^{31}_{P}$ = 2.0 Hz), 28.7, 28.1, 28.0, 26.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 2.0 Hz), 26.7, 26.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 2.9 Hz), 26.5, 26.4, 25.8, 25.4; FABMS (m/z (%)) 603 (M^+, 8), 566 (81), 229 (100). Anal. Calcd for $C_{24}H_{36}NPCl_2FePd$: C, 47.83; H, 6.02. Found: C, 47.77; H, 6.20.

2-Diphenylphosphino-1-dimethylaminoferroceneplatinum Dichloride (12a). Representative Procedure. A suspension of aminophosphine **8a** (100 mg, 0.24 mmol) and $Pt(COD)Cl_2$ (90 mg, 0.24 mmol) in PhMe (2.5 mL) was heated at reflux until TLC indicated consumption of the aminophosphine (1.5 h). The solvent was removed on a rotary evaporator, and the residue was redissolved in CH_2Cl_2, filtered through a pad of silica gel eluting with 97:3 CH_2Cl_2/MeOH, and concentrated again under reduced pressure. Recrystallization from acetone at −20 °C gave **12a** (82 mg, 50%) as fine orange crystals: mp > 225 °C (dec at 210 °C); IR (KBr) ν_{max} 3469, 3421, 3048, 2925, 1435 cm^{-1}; ^{31}P NMR (243 MHz, $CDCl_3$) δ 2.01 (t, $J^{31}_{P-}{}^{195}_{Pt}$ = 1982 Hz); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18−8.06 (m, 2H), 7.63−7.40 (m, 6H), 7.39−7.30 (m, 2H), 4.92 (t, 1H, J = 2.6 Hz), 4.53 (s, 1H), 4.29 (t, 1H, J = 1.0 Hz), 3.94 (s, 5H), 3.65 (t, 3H, J = 16.6 Hz), 3.24 (t, 3H, J = 15.1 Hz); ^1H NMR (600 MHz, acetone-d_6) δ 8.24−8.17 (m, 2H), 7.70−7.60 (m, 3H), 7.59−7.53 (m, 2H), 7.53−7.48 (m, 1H), 7.45−7.39 (m, 2H), 5.08 (t, 1H, J = 2.3 Hz), 4.94 (s, 1H), 4.62 (t, 1H, J = 1.1 Hz), 4.01 (s, 5H), 3.66 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.5 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.9 Hz), 132.1 (d, $J^{13}_{C-}{}^{31}_{P}$ = 2.2 Hz), 131.5 (d, $J^{13}_{C-}{}^{31}_{P}$ = 10.3 Hz), 131.1 (d, $J^{13}_{C-}{}^{31}_{P}$ = 68.8 Hz), 130.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 2.7 Hz), 129.1 (d, $J^{13}_{C-}{}^{31}_{P}$ = 21.6 Hz), 128.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 73.8 Hz), 128.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.4 Hz), 128.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 12.3 Hz), 74.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.4 Hz), 74.0 (d, $J^{13}_{C-}{}^{31}_{P}$ = 66.7 Hz), 63.2, 59.7, 59.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 10.6 Hz), 55.6; FABMS (m/z (%)) 679 (M^+, 6), 643 (100), 605 (30), 486 (22). Anal. Calcd for $C_{24}H_{24}NPCl_2FePt$: C, 42.44; H, 3.56. Found: C, 42.67; H, 3.56.

2-Dicyclohexylphosphino-1-dimethylaminoferroceneplatinum Dichloride (12b). 12b was prepared on a 0.19 mmol scale in a manner analogous to **12a** to give 101 mg (79%) as orange crystals after recrystallization from CH_2Cl_2/EtOAc at −20 °C: mp > 225 °C (dec at 210 °C); IR (KBr) ν_{max} 3448, 1460, 1434 cm^{-1}; ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.7 (t, $J^{31}_{P-}{}^{195}_{Pt}$ = 1898 Hz); ^1H NMR (600 MHz, $CDCl_3$) δ 4.86 (t, 1H, J = 2.5 Hz), 4.57 (s, 1H), 4.46 (s, 5H), 4.00 (s, 1H), 3.65 (t, 3H, J = 14.8 Hz), 3.26 (t, 3H, J = 14.3 Hz), 2.77−2.61 (m, 1H), 2.57−2.39 (m, 1H), 2.31−2.17 (m, 1H), 2.14−1.75 (m, 8H), 1.74−1.53 (m, 4H), 1.50−1.30 (m, 3H), 1.30−1.05 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 129.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 17.8 Hz), 74.5 (d, $J^{13}_{C-}{}^{31}_{P}$ = 52.6 Hz), 74.3 (d, $J^{13}_{C-}{}^{31}_{P}$ = 4.8 Hz), 71.5, 62.44, 59.4, 59.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 8.9 Hz), 58.0, 36.1 (d, $J^{13}_{C-}{}^{31}_{P}$ = 36.9 Hz), 33.0 (d, $J^{13}_{C-}{}^{31}_{P}$ = 37.6 Hz), 28.9, 28.0, 27.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 4.4 Hz), 27.0 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.6 Hz), 26.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 8.0 Hz), 26.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.1 Hz), 26.5 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.9 Hz), 26.1, 25.5; FABMS (m/z (%)) 691 (M^+, 8), 655 (100), 616 (59), 55 (76). Anal. Calcd for $C_{24}H_{24}NPCl_2FePd$: C, 48.81; H, 4.10. Found: C, 49.04; H, 4.09.

2-Diphenylphosphino-1-dimethylaminoferroceneiridium(COD) BAr_F (13). A mixture of ligand **8a** (82 mg, 0.20 mmol) and $[Ir(COD)Cl]_2$ (67 mg, 0.10 mmol) in CH_2Cl_2 (2.1 mL) was stirred under argon at reflux for 2 h. Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaBAr_F$, 266 mg, 0.30 mmol) and water (2.1 mL) were then added, at which time the color changed from orange to red. The solution was allowed to stir for 15 min, after which the layers were separated. The aqueous layer was washed with CH_2Cl_2 (3 × 5 mL), and the combined organic phase was washed with water. The solution was concentrated almost to dryness on a rotary evaporator and then passed through a plug of silica gel, eluting with additional CH_2Cl_2. Removal of the solvent *in vacuo* afforded **13** as orange flakes (296 mg, 94%). A portion of the product was recrystallized from benzene to give analytically pure crystals that were suitable for X-ray analysis: mp 197−198 °C (dec, benzene); IR (KBr) ν_{max} 2958, 2925, 2891, 1610, 1439, 1356, 1279, 1169, 1126 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 14.95; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −62.34; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (m, 10H), 7.55−7.42 (m, 12H), 5.04 (m, 1H), 4.90 (t, 1H, J = 2.7 Hz), 4.56 (m, 1H), 4.41 (m, 1H), 4.31 (m, 1H), 4.08 (s, 5H), 4.05 (m, 1H), 3.51 (m, 1H), 3.13 (s, 3H), 2.69 (s, 3H), 2.39−2.24 (m, 4H), 2.05 (m, 1H), 1.90 (d, 2H, J = 9.3 Hz), 1.75 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 161.9 (q, $J^{13}_{C-}{}^{11}_{B}$ = 49.8 Hz), 135.0, 133.1, 132.7 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.3 Hz), 132.4, 132.3 (d, J = 2.3 Hz), 131.9 (d, J = 1.5 Hz), 130.1, 129.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 11.3 Hz), 129.5 (d, $J^{13}_{C-}{}^{31}_{P}$ = 10.6 Hz), 129.0 (q, $J^{13}_{C-}{}^{19}_{F}$ = 29.4 Hz), 127.2, 124.7 (q, $J^{13}_{C-}{}^{19}_{F}$ = 272.4 Hz), 124.3 (d, $J^{13}_{C-}{}^{31}_{P}$ = 22.7 Hz), 117.6, 92.9, 92.7, 91.5, 91.3, 74.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.0 Hz), 72.2, 70.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 57.4 Hz), 65.7, 61.0, 60.7, 58.6, 58.5, 57.8, 50.7, 32.44, 32.40, 29.7, 29.54, 29.51; FABMS (m/z, (%)) 714 (M-BAr_F, (100)); HRMS (FAB; m/z) calcd for $C_{32}H_{36}NPFe^{193}Ir$ 714.1564, found 714.1502. Anal. Calcd for $C_{64}H_{48}BF_{24}FeNPIr$: C, 48.75; H, 3.07. Found: C, 48.79; H, 2.98.

General Procedure A (Suzuki−Miyaura Couplings). An oven-dried reaction tube under argon containing a mixture of phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in dioxane (2.5 mL) was treated with an aryl halide **14a−g** (0.50 mmol) and stirred at room temperature for 5 min before heating to reflux for 22 h. After cooling to room temperature and diluting with Et_2O (7 mL), the mixture was filtered through a pipet containing a plug of silica gel and eluted with additional Et_2O. Evaporation of the solvent under reduced pressure and recrystallization or column chromatography gave the purified products **15a−g**.

4-Trifluoromethylbiphenyl (15a). According to general procedure A, a mixture of 4-chlorotrifluoromethylbenzene (0.07 mL, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. Column chromatography (2% EtOAc in hexane, silica gel) gave **15a** (104 mg, 94%) as a colorless crystalline solid: mp 66−69 °C (95% EtOH) (lit.[22] 66−68 °C). Spectroscopic

(22) Najman, R.; Cho, J.; Coffey, A.; Davies, J.; Bradley, M. *Chem. Commun.* **2007**, 5031.

data matched literature reports:[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.60 (d, 2H, $J = 7.2$ Hz), 7.50−7.41 (m, 3H).

4-Phenylacetophenone (15b). According to general procedure A, a mixture of 4-chloroacetophenone (65 μL, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and ligand **8a** (8 mg, 0.02 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. After evaporation of the solvent, recrystallization from hexane containing a small amount of EtOAc gave **15b** (86 mg, 88%) as colorless crystals. Spectroscopic data matched literature reports:[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 2H, $J = 8.4$ Hz), 7.69 (d, 2H, $J = 8.4$ Hz), 7.63 (d, 2H, $J = 7.2$ Hz), 7.50−7.40 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 197.7, 145.8, 139.8, 135.8, 128.93, 128.89, 128.2, 127.24, 127.20, 26.6.

4-Cyanobiphenyl (15c). According to general procedure A, a mixture 4-chlorobenzonitrile (69 mg, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (5% Et_2O in hexanes, silica gel) gave **15c** (83 mg, 92%) as a colorless solid. Spectroscopic data matched literature reports:[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (q, 4H, $J = 6$ Hz), 7.61−7.57 (m, 2H), 7.52−7.40 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.1, 118.8, 110.8.

2-Nitrobiphenyl (15d). According to general procedure A, a mixture of *o*-chloronitrobenzene (79 mg, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (1% Et_2O in hexane, silica gel) gave **15d** (73 mg, 73%) as a bright yellow oil. Spectroscopic data matched data literature reports:[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 1H, $J = 8.0$ Hz), 7.62 (t, 1H, $J = 7.5$ Hz), 7.51−7.40 (m, 5H), 7.34−7.31 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 149.3, 137.4, 136.3, 132.2, 131.9, 128.7, 128.2, 128.1, 127.9, 124.0.

4-Methoxybiphenyl (15e). According to general procedure A, a mixture of 4-chloroanisole (0.06 mL, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (0.5−1.0% isopropanol/hexane, silica gel) gave **15e** (64 mg, 70%) as a colorless solid. Spectroscopic data matched literature reports:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (t, 4H, $J = 6.8$ Hz), 7.42 (t, 2H, $J = 6.8$ Hz), 7.32−7.26 (m, 1H), 6.99 (d, 2H, $J = 8.7$ Hz), 3.86 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Methylbiphenyl (15f). According to general procedure A, a mixture of 4-chlorotoluene (59 μL, 0.50 mmol), phenylboronic acid (91 mg, 0.75 mmol), CsF (228 mg, 1.50 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (1% Et_2O in hexane silica gel) gave **15f** (47 mg, 56%) as a colorless solid. Spectroscopic data matched literature reports:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, 2H, $J = 7.8$ Hz), 7.51 (d, 2H, $J = 7.8$ Hz), 7.44 (d, 2H, $J = 7.8$ Hz), 7.35−7.24 (m, 3H), 2.41 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 126.9, 21.1.

5,7-Diphenyl-8-aminoquinoline (15g). According to general procedure A, a mixture of 5,7-dibromo-8-aminoquinoline (**14g**, 100 mg, 0.33 mmol), phenylboronic acid (60 mg, 0.50 mmol), CsF (150 mg, 0.99 mmol), $Pd(OAc)_2$ (1.3 mg, 0.007 mmol), and ligand **8a** (5.3 mg, 0.013 mmol) in 1,4-dioxane (2.5 mL) was heated to reflux, cooled, and filtered. After evaporation of the solvent, recrystallization from Et_2O/hexane gave **15g** (86 mg, 88%) as colorless crystals: mp 100−102 °C (Et_2O/hexane); IR (KBr) ν_{max} 3450, 3347, 3050, 3023, 1583 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85−8.80 (m, 1H), 8.28 (dd, 1H, $J = 8.4$, 1.5 Hz), 7.66−7.63 (m, 2H), 7.54−7.44 (m, 6H), 7.42−7.34 (m, 4H), 5.32 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.5, 140.2, 139.9, 138.3, 134.2, 130.2, 130.0, 129.2, 129.0, 128.4, 128.2, 127.2, 126.8, 126.1, 121.7, 121.2; EIMS (*m*/*z*, (%)) 296 (72), 219 (24), 86 (100), 47 (85); HRMS (EI; *m*/*z*) calcd for $C_{21}H_{16}N_2$ 296.1314, found 296.1312.

General Procedure B (Buchwald−Hartwig Couplings). An oven-dried reaction tube under argon containing a mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg, 0.01 mmol), **18a** (8 mg, 0.02 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in PhMe (2.5 mL) was treated with an aryl halide (**14a**,**b**,**d**,**e**,**h**) (0.50 mmol) and morpholine (52 μL, 0.60 mmol). The resulting green-brown mixture was heated at 100 °C for 22 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (5 mL) and filtered through a pipet containing a plug of silica gel while eluting with additional Et_2O. Evaporation of the solvent under reduced pressure and recrystallization or column chromatography of crude material gave products **16a**,**b**,**d**,**e**,**h**.

***N*-(4-Trifluoromethylphenyl)morpholine (16a).** According to general procedure B, a mixture of 4-chlorotrifluoromethylbenzene (67 μL, 0.50 mmol), morpholine (52 μL, 0.60 mmol), NaO*t*-Bu (67 mg, 0.70 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in PhMe (2.5 mL) was heated, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (20% Et_2O in hexane, silica gel) gave **16a** (89 mg, 77%) as off-white crystals. Spectroscopic data matched literature reports:[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, 2H, $J = 8.7$ Hz), 6.92 (d, 2H, $J = 8.7$ Hz), 3.87 (t, 4H, $J = 4.8$ Hz), 3.24 (t, 4H, $J = 5.1$ Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.3, 126.4 (q, $J^{13}_{C-31}_{P} = 3$ Hz), 124.6 (q, $J^{13}_{C-31}_{P} = 271$ Hz), 120.9 (q, $J^{13}_{C-31}_{P} = 33$ Hz) 114.3, 66.6, 48.1.

***N*-(4-Acetylphenyl)morpholine (16b).** According to general procedure B, a mixture of 4-chloroacetophenone (65 μL, 0.50 mmol), morpholine (52 μL, 0.60 mmol), NaO*t*-Bu (67 mg, 0.70 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in PhMe (2.5 mL) was heated, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (83:2:15 to 78:2:20 hexane/Et_3N/EtOAc, silica gel) gave **16b** (76 mg, 74%) as a pale yellow solid. Spectroscopic data matched literature reports:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2H, $J = 9.0$ Hz), 6.87 (d, 2H, $J = 9.0$ Hz), 3.86 (t, 4H, $J = 4.8$ Hz), 3.31 (t, 4H, $J = 5.1$ Hz), 2.53 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 196.4, 154.2, 130.3, 128.1, 113.2, 66.5, 47.5, 26.1.

***N*-(2-Nitrophenyl)morpholine (16d).** According to general procedure B, a mixture of 2-nitrochlorobenzene (79 mg, 0.50 mmol), morpholine (52 μL, 0.60 mmol), NaO*t*-Bu (67 mg, 0.70 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg, 0.01 mmol), and **8b** (0.4 mL of a 0.05 M solution in PhMe) in PhMe (2.5 mL) was heated, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (40% Et_2O in hexane, silica gel) gave **16d** (45 mg, 43%) as a yellow oil. Spectroscopic data matched literature reports:[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, 1H, $J = 8.1$ Hz), 7.52−7.47 (m, 1H), 7.15 (d, 1H, $J = 8.3$ Hz), 7.10−7.06 (m, 1H), 3.85−3.83 (m, 4H), 3.07−3.04 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.8, 143.7, 133.5, 125.9, 122.3, 120.9, 66.8, 52.1.

***N*-(4-Methoxyphenyl)morpholine (16e).** According to general procedure B, a mixture of 4-bromoanisole (63 μL, 0.50 mmol),

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morpholine (52 μL, 0.60 mmol), NaO*t*-Bu (67 mg, 0.70 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in PhMe (2.5 mL) was heated, cooled, and filtered. Evaporation of the solvent under reduced pressure and column chromatography of the preadsorbed crude material (2:50:48 Et_3N/Et_2O/hexane, silica gel) gave **16e** (64 mg, 67%) as an off-white solid. Spectroscopic data matched literature reports:[28] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92−6.84 (m, 4H), 3.86 (t, 4H, J = 4.8 Hz), 3.77 (s, 3H), 3.06 (t, 4H, J = 4.8 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.9, 145.5, 117.7, 114.4, 66.9, 55.5, 50.7.

***N*-Phenylmorpholine (16h).** According to general procedure B, a mixture of bromobenzene (53 μL, 0.50 mmol), morpholine (52 μL, 0.60 mmol), NaO*t*-Bu (67 mg, 0.70 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg, 0.01 mmol), and **8a** (8 mg, 0.02 mmol) in PhMe (2.5 mL), was heated, cooled, and filtered. Column chromatography (6:1:93 Et_2O/Et_3N/hexane, silica gel) gave **16h** (67 mg, 82%) as a colorless solid. Spectroscopic data matched literature reports:[27] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, 2H, J = 4.2 Hz), 6.97−6.91 (m, 3H), 3.90 (t, 4H, J = 2.4 Hz), 3.19 (t, 4H, J = 2.4 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 151.3, 129.2, 120.1, 115.7, 67.0, 49.4.

General Procedure C (Hydrogenation). A solution of substrate (∼0.2−0.3 mmol) and iridium catalyst **13** (2 mol %) in CH_2Cl_2 (3 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and backfilled with H_2 three times, pressurized to 62 bar, and stirred at room temperature for the indicated time. After the pressure was released, the reaction mixture was passed through a plug of silica gel, eluting with Et_2O to remove catalyst residue. Products obtained in this manner were sufficiently pure, as determined by melting point and/or spectroscopic analysis.

1,2-Diphenylethane (18a). According to general procedure C, a solution of *trans*-stilbene (50 mg, 0.28 mmol) and **13** (8.8 mg, 0.0056 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 48 h. Filtration of the reaction mixture and evaporation of the solvent gave **18a** (50 mg, 97%): mp 48−50 °C (lit.[29] 47−49 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.25 (m, 10H), 3.01 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 141.9, 128.6, 128.5, 126.0, 38.1.

1,2-Diphenylpropane (18b). According to general procedure C, a solution of methyl stilbene (40 mg, 0.21 mmol) and **13** (6.4 mg, 0.0041 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 24 h. Filtration of the reaction mixture and evaporation of the solvent gave **18b** as a clear oil (35 mg, 86%): ^{1}H NMR[30] (300 MHz, $CDCl_3$) δ 7.35−7.12 (m, 10H), 3.10−2.98 (m, 2H), 2.88−2.79 (m, 1H), 1.30 (d, 3H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.1, 140.9, 129.3, 128.4, 128.2, 127.2, 126.1, 126.0, 45.1, 42.0, 21.3.

Methyl 3-Phenylpropanoate (18c). According to general procedure C, a solution of methyl *trans*-cinnamate (49 mg, 0.30 mmol) and **13** (9.8 mg, 0.0062 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 48 h. Filtration of the reaction mixture and evaporation of the solvent gave **18c** as a clear oil (48 mg, 95%): ^{1}H NMR[29] (300 MHz, $CDCl_3$) δ 7.33−7.19 (m, 5H), 3.68 (s, 3H), 2.97 (t, 2H, J = 8.1 Hz), 2.65 (t, 2H, J = 7.8 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 173.4, 140.6, 128.6, 128.4, 126.4, 51.7, 35.8, 31.0.

Ethyl 3-Phenylbutanoate (18d). According to general procedure C, a solution of ethyl 3-phenylbut-2-enoate (54 mg, 0.28 mmol) and **13** (9.0 mg, 0.0057 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 48 h. Filtration of the reaction mixture and evaporation of the solvent gave **18d** as a clear oil (52 mg, 94%): ^{1}H NMR[31] (300 MHz, $CDCl_3$) δ 7.34−7.18 (m, 5H), 4.10 (q, 2H, J = 7.2 Hz), 3.28 (sextet, 1H, J = 7.2 Hz), 2.67−2.51 (m, 2H), 1.32 (d, 3H, J = 6.9 Hz), 1.19 (t, 3H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.5, 145.9, 128.6, 126.9, 126.5, 60.3, 43.1, 36.6, 21.9, 14.3.

Ethyl 3-(4-Methoxyphenyl)butanoate (18e). According to general procedure C, a solution of ethyl 3-(4-methoxyphenyl)but-2-enoate (60 mg, 0.27 mmol) and **13** (8.7 mg, 0.0055 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 72 h. Filtration of the reaction mixture and evaporation of the solvent gave **18e** as a clear oil (59 mg, 96%): ^{1}H NMR[32] (300 MHz, $CDCl_3$) δ 7.14 (d, 2H, J = 8.7 Hz), 6.84 (d, 2H J = 6.9 Hz), 4.07 (q, 2H, J = 7.2 Hz), 3.78 (s, 3H), 3.23 (sextet, 1H, J = 7.2 Hz), 2.61−2.47 (m, 2H), 1.28 (d, 3H, J = 6.9 Hz), 1.19 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.6, 158.2, 138.0, 127.8, 113.9, 60.3, 55.4, 43.4, 35.9, 22.1, 14.3.

1,3-Diphenylpropan-1-one (18f). According to general procedure C, a solution of chalcone (**17f**, 50 mg, 0.24 mmol) and **13** (7.4 mg, 0.0047 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 96 h. Filtration of the reaction mixture and evaporation of the solvent gave **18f** as a colorless solid (50 mg, 99%): mp 69−70 °C (lit.[33] 70−72 °C); ^{1}H NMR[33] (300 MHz, $CDCl_3$) δ 7.98 (d, 2H, J = 7.2 Hz), 7.6−7.2 (m, 8H), 3.33 (t, 2H, J = 7.8 Hz), 3.10 (t, 2H, J = 7.2 Hz); ^{13}C NMR[32] (75.5 MHz, $CDCl_3$) δ 199.3, 141.4, 136.9, 133.2, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.

***N*-(1-Phenylethyl)aniline (18g).** According to general procedure C, a solution of *N*-(1-phenylethylidene)aniline (50 mg, 0.26 mmol) and **13** (7.8 mg, 0.0050 mmol, 1.9 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 72 h. Filtration of the reaction mixture and evaporation of the solvent gave **18g** as a clear oil (41 mg, 81%): ^{1}H NMR[34] (300 MHz, $CDCl_3$) δ 7.50−7.35 (m, 4H), 7.30−7.25 (m, 1H), 7.15 (t, 2H, J = 7.5 Hz), 6.70 (t, 1H, J = 7.5 Hz), 6.59 (d, 2H, J = 7.5 Hz), 4.56 (quin, 1H, J = 6.6 Hz), 4.08 (bs, 1H), 1.56 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.4, 145.4, 129.3, 128.8, 127.0, 126.0, 117.4, 113.4, 53.6, 25.2.

***N*-Benzyl-1-phenylethanamine (18h).** According to general procedure C, a solution of 1-phenyl-*N*-(1-phenylethylidene) methanamine (50 mg, 0.24 mmol) and **13** (7.5 mg, 0.0048 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 72 h. Filtration of the reaction mixture and evaporation of the solvent gave **18h** as a clear oil (45 mg, 88%): ^{1}H NMR[35] (300 MHz, $CDCl_3$) δ 7.35−7.27 (m, 10H), 3.85 (q, 1H, J = 6.6 Hz), 3.66 (ABq, 2H, J = 13.2 Hz), 1.59 (bs, 1H), 1.39 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.7, 140.8, 128.6, 128.5, 128.3, 127.0, 126.95, 126.8, 57.6, 51.8, 24.7.

3,7-Dimethyloctan-1-ol (18i). According to general procedure C, a solution of geraniol (52 μL, 0.29 mmol) and **13** (9.0 mg, 0.0057 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 24 h. Filtration of the reaction mixture and evaporation of the solvent gave **18i** as a clear liquid (47 mg, 98%): ^{1}H NMR[36] (300 MHz, $CDCl_3$) δ 3.68 (m, 2H), 1.61−1.17 (m, 10 H), 0.90 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 61.4, 30.1, 39.4, 37.5, 29.7, 28.1, 24.8, 22.8, 22.7, 19.8.

Pyrrolidine-2,5-dione (18j). According to general procedure C, a solution of maleimide (32 mg, 0.33 mmol) and **13** (10.4 mg, 0.0066 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 96 h. Filtration of the reaction mixture and evaporation of the solvent gave **18j** as a colorless solid (27 mg, 82%): mp 125−127 °C (lit.[37] 125−127 °C); ^{1}H NMR[38] (300 MHz,

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acetone-d_6) δ 2.68 (s, 4H), 9.88 (bs, 1H); ^{13}C NMR[38] (75.5 MHz, acetone-d_6) δ 178.9, 30.2.

Cyclohexanone (18k). According to general procedure C, a solution of cyclohexenone (30 μL, 0.31 mmol) and **13** (9.8 mg, 0.0062 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 48 h. Filtration of the reaction mixture and evaporation of the solvent gave **18k** as a clear liquid (26 mg, 84%): ^{1}H NMR[38] (300 MHz, $CDCl_3$) δ 2.31 (t, 4H, J = 6.9 Hz), 1.85−1.81 (m, 4H), 1.70−1.69 (m, H); ^{13}C NMR[38] (75.5 MHz, $CDCl_3$) δ 212.2, 40.1, 27.1, 25.1.

2,3-Dihydronaphthalene-1,4-dione (18l). According to general procedure C, a solution of naphthoquinone (50 mg, 0.31 mmol) and **13** (10.0 mg, 0.0063 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 72 h. Filtration of the reaction mixture and evaporation of the solvent gave the crude product, which was purified by column chromatography (30% EtOAc in hexane, silica gel) to give **18l** (45 mg, 89%) as a 2:1 mixture of 2,3-dihydronaphthalene-1,4-dione and 1,4-dihydronaphthalene-1,4-diol: ^{1}H NMR (300 MHz, acetone-d_6, 2,3-dihydronaphthalene-1,4-dione[39]) δ 8.00−7.97 (m, 2H), 7.83−7.81 (m, 2H), 3.11 (s, 4H); 1,4-(dihydronaphthalene-1,4-diol[40]) δ 8.32 (bs, 2H), 8.18−8.15 (m, 2H), 7.47−7.43 (m, 2H), 6.73 (s, 2H).

Chroman-4-one (18m). Prepared according to a modification of general procedure C. A solution of chromone (45 mg, 0.31 mmol), Hünig's base (540 μL), and **13** (9.8 mg, 0.0062 mmol, 2.0 mol %) in PhMe (3 mL) was pressurized with H_2 to 100 bar and stirred for 48 h. Filtration of the reaction mixture and evaporation of the solvent gave the crude product, which was purified by column chromatography (30% EtOAc in hexane, silica gel) to give **18m** (30 mg, 66%) as a colorless oil: ^{1}H NMR[41] (300 MHz, $CDCl_3$) δ 7.90 (dd, 1H, J = 7.8, 1.5 Hz), 7.50−7.45 (m, 1H), 7.05−6.96 (m, 2H), 4.54 (t, 2H, J = 6.6 Hz), 2.82 (t, 2H, J = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.0, 162.0, 136.1, 127.3, 121.5, 118.0, 67.1, 37.9.

5-Isopropyl-2-methylcyclohex-2-enone (18n). According to general procedure C, a solution of carvone (45 μL, 0.29 mmol) and **13** (8.0 mg, 0.0051 mmol, 1.8 mol %) in CH_2Cl_2 (3 mL) was pressurized with H_2 to 62 bar and stirred for 48 h. Filtration of the reaction mixture and evaporation of the solvent gave **18n** as a colorless oil (43 mg, 96%): ^{1}H NMR[42] (300 MHz, $CDCl_3$) δ 6.72−6.69 (m, 1H), 2.53−2.47 (m, 1H), 2.37−2.27 (m, 1H), 2.13−1.99 (m, 2H), 1.85−1.78 (m, 1H), 1.73−1.72 (m, 3H), 1.54 (quin, 1H, J = 6.6 Hz), 0.87 (dd, 6H, J = 6.9 Hz, 0.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 200.6, 145.2, 135.2, 42.0, 41.9, 31.9, 29.8, 19.5, 19.4 15.6.

2-Benzyl-3-methyl-2-aza-spiro[4.5]decane (20). A solution of aminoalkene **19** (135 mg, 0.55 mmol) and **13** (22 mg, 2.5 mol %) in dioxane (2 mL) under argon was heated to reflux for 22 h. After cooling to room temperature, the solvent was removed on a rotary evaporator. The residue was taken up in Et_2O and filtered through a pipet of silica gel and concentrated again *in vacuo*. The crude product mixture was dissolved in THF (2 mL), treated with Ac_2O (63 μL, 1.2 equiv), Et_3N (0.23 mL, 3.0 equiv) and DMAP (3 mg, 0.05 equiv), and heated at 45 °C for 16 h to acylate any remaining secondary amines. The reaction mixture was then diluted with Et_2O and extracted with 1 M aqueous HCl (3 × 5 mL), and the combined acidic extracts were made alkaline (pH 12) by addition of 6 M aqueous NaOH. The aqueous phase was back-extracted with Et_2O (3 × 5 mL), washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give **20** (87 mg, 64%) as a pale yellow oil. Spectroscopic data were in agreement with literature reports:[43] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.22 (m, 5H), 4.04 (d, 1H, J = 13.2 Hz), 3.12 (d, 1H, J = 13.2 Hz), 2.81 (d, 1H, J = 9.3 Hz), 2.58−2.46 (m, 1H), 1.90 (d, 1H, J = 9.3 Hz), 1.78 (ABq, 1H, J = 12.6, 6.9 Hz), 1.50−1.25 (m, 11H), 1.17 (d, 3H, J = 6.0 Hz).

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Supporting Information Available: Crystallographic information files (CIF) for **11a**, **12a**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 732234, 732235, and 732236 also contain crystallographic data for compounds **13**, **11a**, and **12a**, respectively. This material can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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