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Synthesis of New Late Transition Metal P,P-, P,N-, and P,O-Complexes Using Phosphonium Dimers as Convenient Ligand Precursors

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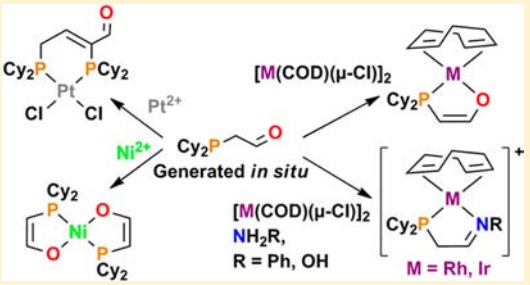
Supporting Information

ABSTRACT: The phosphonium dimer $[\text{-}Cy_2PCH(OH)CH_2\text{-}]_2(X)_2$, X = Cl^-, Br^- was used to synthesize and characterize a variety of late transition metal complexes containing chelating phosphino-enolate ($PCy_2CH{=}CHO^-$), imine ($PCy_2CH_2CH{=}NR$, R = Ph, (*S*)-CHMePh), and oxime ($PCy_2CH_2CH{=}NOH$) ligands. The phosphonium dimer, when deprotected with base, generates the phosphine aldehyde PCy_2CH_2CHO in situ, which, in the presence of $[M(COD)Cl]_2$, M = Rh, Ir, and a PF_6^- salt, or $[Ni(H_2O)_6][BF_4]_2$, facilitates a condensation reaction with an amine or hydroxylamine to form phosphino-imine or phosphino-oxime metal complexes $[M(COD)(P{-}N)][PF_6]$ or $[Ni(P{-}N)_2][X]_2$, X = ClO_4^-, BF_4^-, respectively. In the absence of an amine, phosphino-enolate containing complexes are formed. A neutral Ni(II) complex $Ni(PCy_2CH{=}CHO)_2$ with *trans*-bis(phosphino-enolate) ligands which resemble ligands used on nickel for olefin oligomerization, as well as neutral Rh(I) and Ir(I) 1,5-cyclooctadiene complexes $M(COD)(PCy_2CH{=}CHO)$ are characterized. Both the rhodium and iridium complexes are active olefin hydrogenation catalysts. Reaction of the phosphino-aldehyde with $Pt(COD)Cl_2$ results in the formation of *trans*-$PtCl_2(PCy_2CH_2CHO)_2$ with pendant aldehyde groups, and under certain conditions, they undergo an intraligand aldol condensation to form a disphosphine ligand.



INTRODUCTION

As a result the prevalence of chelating phosphine and oxygen/nitrogen ligands in late transition metal catalysts, methods for their facile synthesis are valuable and sought-after. Transition metal complexes containing P−O and P−N ligands can catalyze a variety of reactions, including transfer[1−4] and direct hydrogenation,[5−11] olefin polymerization,[12,13] Michael addition,[14] hydroamination,[15] hydroformylation[16] among others.[17−19] Specific examples include Ni(II) catalysts containing P−O chelating ligands, which are used in the Shell Higher Olefin Process,[20] where the first step is catalytic oligomerization of ethylene. Olefin hydrogenation catalysts based on Crabtree's catalyst often contain a P−N[5,6] or P−O[1,9] ligand. As Crabtree's catalyst has a phosphine and a pyridine ligand,[21] many groups have since successfully used similar complexes based on Ir(I) containing a 1,5-cyclooctadiene ligand and a chelating P−N, or similar, ligand (Figure 1). Addition of chelating ligands is attractive as it may potentially increase catalyst lifetime and assists in enforcing asymmetry in enantioselective processes. In particular, Pfaltz and co-workers have developed a particularly active and enantioselective catalyst for the hydrogenation of unfunctionalized tri- and tetra-substituted olefins.[5] These catalysts contain chiral P−N ligands with an N-bound oxazoline. Stradiotto et al. have also reported similar catalysts that are neutral[9] or zwitterionic,[8] in contrast to the majority of Ir(I) olefin hydrogenation catalysts which are cationic. These show promise in being used in greener hydrocarbon solvents and removing the need for expensive counteranions to improve reactivity.[22]

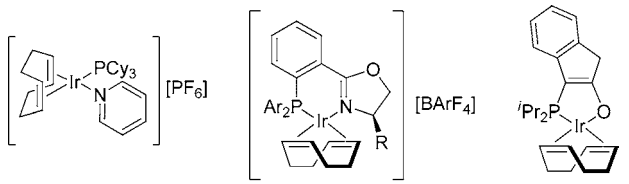


Figure 1. Selected examples of known Ir(I) olefin hydrogenation catalysts: (a) Crabtree's catalyst, (b) Pfaltz's catalyst with a PHOX ligand, (c) Stradiotto's neutral phosphino-enolate catalyst.

A powerful synthetic strategy for generating P−O and P−N ligands is to use phosphine aldehydes.[23−25] Here, the phosphine can be substituted with a variety of aryl and alkyl groups,[26] and the aldehyde can be condensed with various amines to form a wide range of imines. Furthermore, tri- or tetradentate ligands can be generated via the metal-assisted condensation of phosphine aldehydes with amines containing different donor groups, as previously demonstrated in the synthesis of Fe(II) complexes (Scheme 1).[24] This method allows the efficient synthesis of tetradentate [Fe(PNNP)(CO)-

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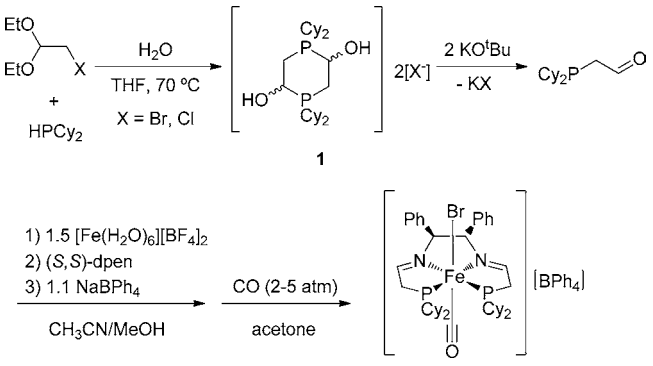
Scheme 1. One-step Synthesis of Dimeric Phosphonium Compound 1, Deprotection of the Aldehyde with Base, and Subsequent Metal-Assisted Template Synthesis of an Fe(II) PNNP Complex



$(Br)]^+$ complexes that are highly active for the enantioselective reduction of polar double bonds.[4] Mechanistic studies have revealed that these complexes are precursors to the active catalysts where reduction of one imine ligand to an amine is required in an activation step.[27]

Phosphine aldehydes are often very air sensitive oils and thus disadvantageous for use in synthesis. Moreover, very few are commercially available, notably the air stable and crystalline 2-(diphenylphosphino)benzaldehyde which has been used for the synthesis of various ligands.[28−30] To circumvent these problems, we have used phosphonium dimers instead. Phosphonium dimers are air stable solids that can be deprotonated with base to release two equivalents of phosphine aldehyde in situ. Our group has previously demonstrated the facile synthesis of numerous alkyl and aryl phosphonium dimers.[26,31] Studies on the effects of sterics and electronics of the ligand on metal catalysis and fine-tuning of catalyst activity are possible because of the phosphonium precursor's modularity.[31,32]

The synthesis of metal complexes using phosphonium dimers is done in a template, one-pot synthesis. The phosphine aldehyde is generated in situ by deprotonation of the phosphonium dimer; then, in conjunction with an amine and a metal precursor it forms the P−N complex. In this reaction, the metal acts both as a Lewis acid facilitating the condensation reaction and as a thermodynamic sink via coordination of the chelating ligand. The direct reaction of the phosphine aldehyde with amines in the absence of the metal has not lead to isolable P−N ligands in our hands.

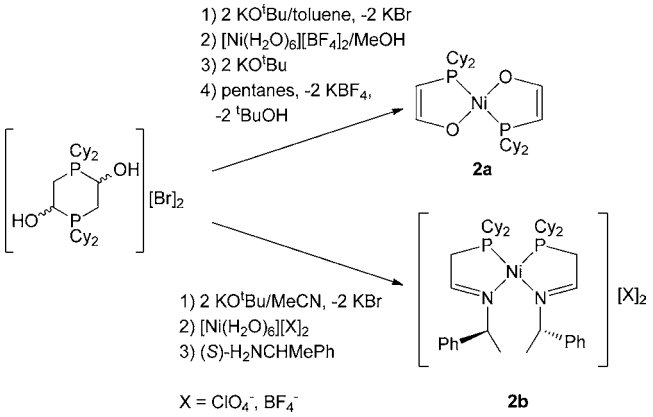
In this paper, we focus mainly on the synthesis of late transition metal complexes that contain bidentate P−O or P−N ligands. The formation of phosphino-enolate, imine, and oxime ligands are presented, as well as phosphine ligands with pendant aldehydes and their intraligand aldol reactivity resulting in a diphosphine ligand. Several metal ions are explored, including Ni(II), Pt(II), Rh(I), and Ir(I), to demonstrate that the template synthesis with our phosphine aldehydes are not limited to Fe(II). The Rh(I) and Ir(I) complexes contain a 1,5-cyclooctadiene ligand, therefore resembling Crabtree's catalyst, and were tested for olefin hydrogenation.

RESULTS AND DISCUSSION

Synthesis of the Neutral Ni(II) Complex 2a Containing Phosphino-Enolate Ligands and Dicationic Ni(II) Complex 2b Containing Phosphino-Imine Ligands.

The synthesis of the *trans*-bis(phosphino-enolato)Ni(II) complex **2a** was carried out by deprotection of phosphonium dimer **1** with 2 equiv of base in toluene followed by filtration to remove KBr salts. Then coordination of the free phosphine aldehyde that was generated in situ was achieved by the addition of 1 equiv of $[Ni(H_2O)_6][BF_4]_2$ and enough methanol to solubilize the Ni(II) salt. The addition of two more equivalents of base caused the light brown reaction mixture to darken instantaneously, indicating the formation of an enolate via deprotonation of the phosphine aldehyde (Scheme 2). The neutral Ni(II)

Scheme 2. Synthesis of Ni(II) Complexes 2a and 2b



complex, **2a**, was easily isolated upon removal of solvent in vacuo as a pale brown solid in 72% yield. Complex **2a** is soluble in most organic solvents, including pentane, hexanes, ethers, toluene, and CH_2Cl_2. Its moderate solubility in pentane allows easy separation from salts generated in the synthesis.

Characteristic resonances of **2a** in the ^1H NMR spectra are the olefinic peaks at 7.08 and 3.43 ppm, with the more downfield signal displaying virtual coupling due to *trans*-phosphine ligands. The X-ray diffraction data shows that the *trans*-phosphine groups were 180.0(1)° to each other, as were the *trans*-enolate groups, displaying complete planarity about the Ni(II) metal center and the atoms that are coordinated to it (Figure 2a). The sum of the internal angles of the 5-membered ring formed by the ligand backbone and the metal center is 540.0(9)°, thus mostly planar. An analogous Ni(II) complex $Ni(OC(Ph)=CHP^iPr_2)_2$ isolated by Braunstein and co-workers, which contain *trans*-bis(di-*iso*-propylphosphino-enolate)

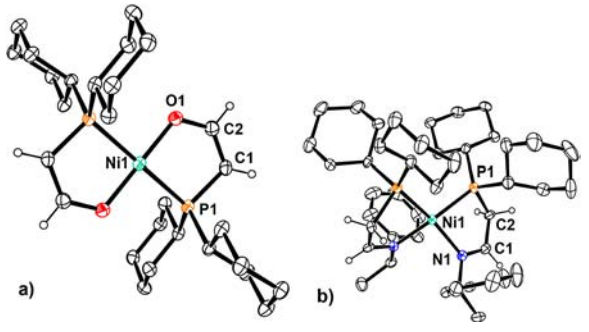


Figure 2. ORTEP representation (thermal ellipsoids at 30% probability; the solvent and most of the hydrogen atoms and ClO_4^- anions of **2b** are omitted for clarity) and atom numbering for (a) **2a** and (b) **2b**.

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ligands derived from a phenyl ketone shows similar planarity displaying an O1−Ni−O2 bond angle of 180.0(1)°, and a sum for the internal angle of its metallacycle of 539.7(3)°.[33] Both complexes display identical P1−Ni−O1 bond angles of 87.0(1)°. The C1−C2 bond length of **2a** is 1.343(4) Å, which is closer to the typical bond length observed for olefins than to that of benzene, 1.34 Å vs 1.40 Å, respectively.

The *cis*-bis(phosphino-imine)Ni(II) complex **2b** was synthesized by a metal-assisted template reaction using phosphine aldehyde and (*S*)-1-phenylethylamine. After deprotection of the phosphonium dimer **1** with 2 equiv of KO^{t}Bu in acetonitrile, $[Ni(H_2O)_6][X]_2$ (X = ClO_4^-, BF_4^-) and (*S*)-(-)-1-phenylethylamine were added, forming an orange solution. After removal of the solvent in vacuo, the residue was taken up with methanol from which an orange precipitate was collected. The precipitate was washed with ether, yielding the *cis*-phosphino-imine complex **2b** as an orange solid in 55% yield. The product is only soluble in polar solvents such as acetonitrile in contrast to the neutral complex **2a** because of its dicationic nature.

The new Ni(II) complex **2b** displays characteristic ^{1}H NMR resonances for the imine proton at 8.79 ppm and diastereotopic CH_2 protons of the ligand backbone at 3.86 and 3.34 ppm. In contrast to the neutral complex **2a**, complex **2b** is not completely square planar, and has a slight tetrahedral distortion (Figure 2b). Furthermore, the 5-membered metallacycle formed by the ligand and the metal center in **2b** has a sum of internal angles of 522(2)°, indicating nonplanarity of the metallacycle because of the lack of the π-conjugation that exists in **2a**.

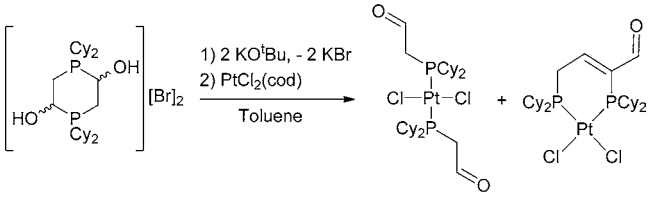
The two phosphino-enolate ligands of **2a** were found to coordinate trans to each other. Braunstein and co-workers have synthesized similar Ni(II) complexes containing two phosphino-enolate ligands, but generated from ketones instead of an aldehyde.[33] They found that the diphenylphosphino-enolate ligands exclusively formed the cis isomer, the di-*tert*-butylphosphino-enolate ligands exclusively formed the trans isomer, and the di-*iso*-propylphosphino-enolate ligands formed a mixture of the trans and cis isomers. This can be rationalized by both the trans influence and steric interactions. Because of the trans influence, the trans-coordination of bidentate P,O-ligands is destabilized and thus cis-coordination is favorable if only electronic factors are considered. However, if steric energies between *cis*-phosphines are great enough, the ligands will then preferentially coordinate trans. Hence, in the case of the di-*tert*-butylphosphino-enolate ligands of Braunstein and the dicyclohexylphosphino-enolate of **2a**, the steric factors outweigh any trans influence/electronic factors. The phosphino-imine ligands of complex **2b** coordinate cis presumably because of the steric bulk being similar on both the phosphine and the imine sides of the ligand, allowing the trans influence to predominate.

Interestingly, when 2 equiv of deprotected phosphine aldehyde and $[Ni(H_2O)_6][BF_4]_2$ are reacted in a toluene and MeOH solution, the phosphino-enolate complex **2a** is the major product formed, even without the addition of two more equivalents of base to deprotonate the two aldehydes to enolates. The formation of the enolate, even in the absence of added base, likely results from the deprotonation of a highly acidic cationic phosphine aldehyde complex by the water from the hydrate salt. The formation of the highly π-conjugated 5-membered metallacycle, along with Ni(II) acting as a Lewis acid, stabilizes the enolate.

Because of the insolubility of Ni(II) salts in toluene, a reaction only began to take place when methanol was added, as the colorless slurry solution slowly turned brown and homogeneous. However, the addition of methanol results in solubilization of the halide salts generated in the deprotection of the phosphonium aldehyde. The halide anions are then capable of forming unwanted byproducts. This was avoided by carefully removing all halide salts by filtration in the deprotection step when done in toluene, and also by using $[Ni(OH_2)_6][BF_4]_2$ or $[Ni(OH_2)_6][ClO_4]_2$ which contain weakly coordinating anions.

Synthesis of Platinum(II) Bis(phosphino-aldehyde) Complexes 3a and 3b. We were interested in applying the synthesis to the other group 10 elements. Addition of the platinum complex, Pt(COD)Cl_2, to the phosphine aldehyde that was generated in situ at room temperature allowed the isolation of a crude product as a white solid. The product was easily separated from salts generated in the synthesis by extraction of the solid crude product with diethyl ether. The product is also soluble in other organic solvents such as toluene, CH_2Cl_2, and tetrahydrofuran (THF), but not hexanes. Analysis by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy revealed that two species were formed in the reaction: the *trans*-phosphinoaldehyde complex, **3a**, was observed as the major product (88%), and the unexpected diphosphine complex, **3b**, was observed as a minor product (12%) (Scheme 3). They are

Scheme 3. Synthesis of Pt(II) Complexes 3a and 3b



	3a	3b
25°:	88%	12%
-78° to 25°:	30%	70%

maintained in solution as indicated by ^{31}P{^{1}H} NMR spectroscopy where **3a** gives a singlet while **3b** shows two doublets with $^2J_{PP}$ = 16.9 Hz. The aldehyde hydrogen for **3a** and **3b** resonates at 9.96 and 9.52 ppm, respectively.

The structures as determined from the X-ray diffraction study are shown in Figure 3. Curiously, the two molecules cocrystallized in 1:1 ratio despite the greater abundance of complex **3a** in solution. The Pt−P (2.315(3) Å) and Pt−Cl (2.310(3) Å) bond lengths measured for **3a** are comparable to the Pt−P bond length of 2.337(2) Å and Pt−Cl bond length of

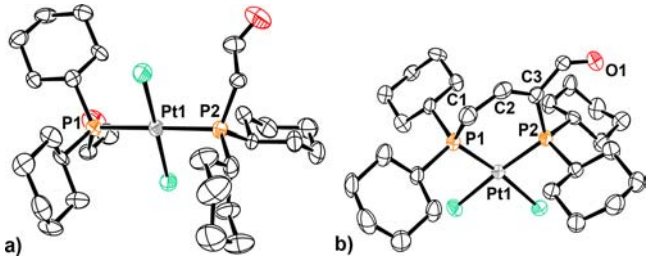


Figure 3. ORTEP representation (thermal ellipsoids at 50% probability; the solvent and most of the hydrogen atoms are omitted for clarity) and atom numbering for (a) **3a** and (b) **3b**.

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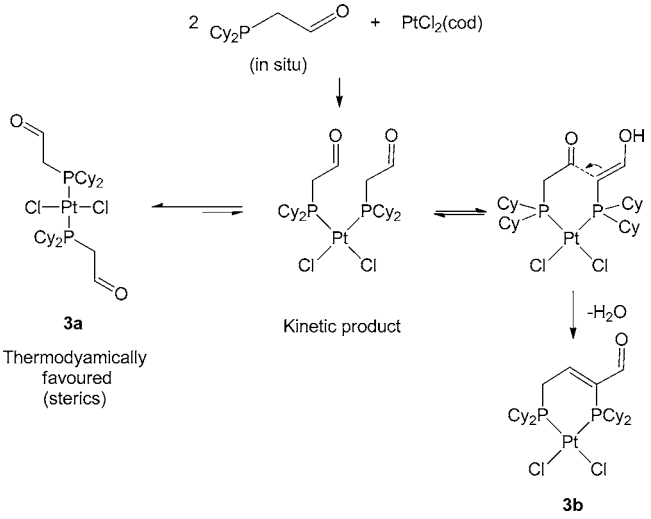
2.317(2) Å of the complex *trans*-$Pt(PCy_3)_2Cl_2$.[34] The Pt−P bonds for the *cis*-aldol complex **3b** are significantly shorter at 2.258(3) Å, while the Pt−Cl bond lengths are longer at 2.367(2) Å and correlate well with the measured bond lengths of the complex $Pt(PCy_2CH_2CH_2CH_2PCy_2)Cl_2$.[35] The differences in bond lengths are due to the high trans influence of phosphine ligands. The P1−Pt−P2 bond angle of **3b** is 96.1(1)°, which is comparable to the $Pt(PCy_2CH_2CH_2CH_2PCy_2)Cl_2$ bond angle of 96.1(3)°. Furthermore, no exchange of the chloro ligand is observed when the bromide salt of **1** is used.

The diphosphine ligand is the product of a novel intraligand aldol condensation reaction in presumably the *cis*-bis(phosphino-aldehyde) complex (Scheme 4). As it was observed from the Ni(II) complex **2a**, the bulky dicyclohexylphosphines preferentially coordinate trans due to steric effects. However, because of the stereochemistry of the displacement of the 1,5-cyclooctadiene ligand and the aldol reactivity of the cis aldehydes, initial coordination of the phosphino-aldehyde ligands is likely cis. A combination of the repulsion between the bulky P-cyclohexyl groups which keeps the aldehyde groups close together and the formation of a proposed six-membered metallocyclic transition state causes the aldol condensation to be favorable. This is another example of a template-assisted ligand synthesis, because if the phosphine aldehydes are reacted under various aldol condensation reaction conditions in the absence of a metal, no diphosphine compound is observed.

Scheme 4. Proposed Mechanism for the Formation of 3b

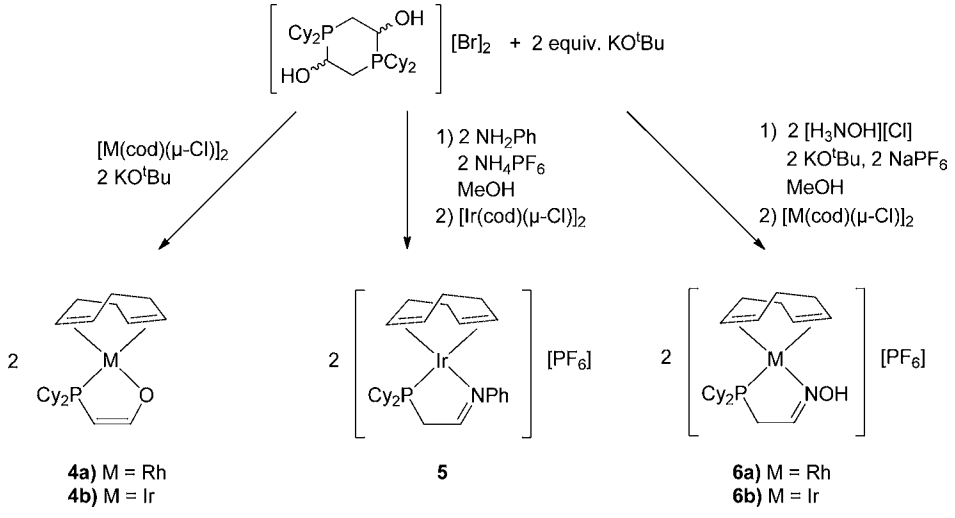


When the reaction was started at −78 °C and then warmed to 25 °C, yields of the diphosphine complex **3b** and **3a** are 70% and 30%, respectively, according to $^{31}P\{^1H\}$ NMR spectra. At lower temperatures isomerization to the trans isomer slows down, allowing the aldol condensation reaction to take place. By contrast, when the synthesis is done with H_2O as the solvent, exclusive formation of **3a** observed, as the aldol condensation reaction is suppressed.

Alternate methods toward the synthesis of the aldol condensation diphosphine ligand were attempted to increase its yield. The focus was to utilize a dianionic bidentate ligand to replace the chloride ligands, restricting the formation of the *trans*-phosphinoaldehyde. A catechol derived Pt(II) complex was synthesized[36] and reacted with phosphine aldehydes, but it did not lead to the formation of an aldol-condensation product. In another attempt, a mixture of complexes **3a** and **3b** was reacted with silver oxalate to force the phosphines to coordinate in a cis fashion; however, the reaction yielded an intractable mixture by NMR spectroscopy. These reactions presumably did not work because the catecholate and oxalate ligands decoordinated from the metal after reacting as an internal base with the enolizable phosphine aldehyde.

Synthesis of Neutral Rh(I) and Ir(I) Phosphino-enolate Complexes 4a and 4b. Neutral rhodium and iridium phosphino-enolate complexes were synthesized (Scheme 5). The phosphine aldehyde was first generated in situ from the phosphonium dimer and base, after which the metal precursor, $[M(COD)(\mu\text{-}Cl)]_2$ (M = Rh, Ir), was added. When additional base was added to enolize the aldehyde functionality, neutral phosphino-enolate complexes were formed. Both the rhodium and the iridium complexes are moderately soluble in hexanes, making them especially easy to isolate from various salts in the mixture. The rhodium complex, **4a**, was isolated in 57% yield as

Scheme 5. Synthesis of Rh(I) and Ir(I) 1,5-Cyclooctadiene Phosphino-Enolate Complexes 4a and 4b, Phosphino-Imine Complex 5, and Phosphino-Oxime Complexes 6a and 6b



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a yellow solid, while the iridium complex, **4b**, as an orange-red solid in 57% yield.

Structures from X-ray diffraction studies of single crystals of **4a** and **4b** (Figure 4) show that both complexes are square

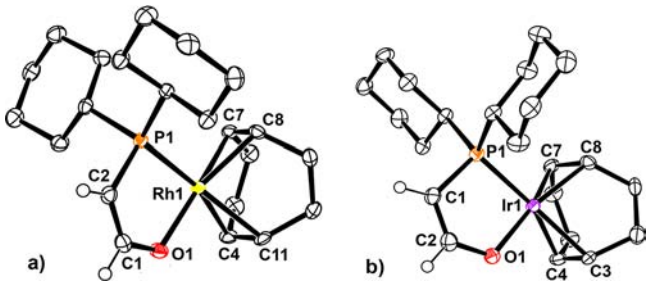

Figure 4. ORTEP representation (thermal ellipsoids at 50% probability; the solvent and most of the hydrogen atoms are omitted for clarity) and atom numbering for (a) **4a** and (b) **4b**.

planar and have comparable bond distances and angles. There is significant lengthening of the M-C bonds trans to the phosphine because of the trans influence which is also observed in Stradiotto and co-workers' neutral Ir(P−O)COD complex.[9] The M-L bond distances for both Rh and Ir complexes are similar as was expected because of their similar covalent radii as deduced from a study of crystallographic data.[37] Comparisons to similar Rh[16] and Ir[9] P−O complexes also show comparable data.

Most cobalt group olefin hydrogenation catalysts with COD precursors are cationic, although some neutral precatalysts have been reported. Stradiotto and co-workers have reported both neutral and zwitterionic Ir(COD)(P−N)[8] and neutral Ir(COD)(P−O)[9] complexes that are active for olefin hydrogenation. These types of catalysts have also been shown to be active for olefin hydroamination[15] and hydroformylation.[16] Although highly active and enantioselective catalysts already exist, investigations into neutral analogues may prove useful. Neutral catalysts are often more soluble in hydrocarbon solvents than in higher dielectric chlorinated solvents and thereby allow greener reaction conditions, as well as avoid the deactivating properties of coordinating solvents. Another advantage of developing neutral olefin hydrogenation catalysts is that there is no potential for counteranion effects, thus precluding the use of expensive counteranions such as $[BArF_4]^-$.[22]

The Rh complex **4a** was tested for catalytic hydrogenation of stilbene and was found to be inactive. The Ir complex **4b** was poorly active for stilbene hydrogenation, but found to be more active for hydrogenation of the olefinic bonds in cyclooctene and (*E*)-4-phenyl-3-buten-2-one (Table 1). When catalysis was conducted in CH_2Cl_2, significantly higher turnover frequencies were obtained than with hexanes as the solvent. This is in contrast to Stradiotto and co-workers' results where hexanes were found to be the best solvent for the hydrogenation of styrene. Changes in catalyst reactivity in different solvents can be ascribed to stabilization or destabilization of catalytic intermediates due to solvent coordination.

Synthesis of Rh(I) and Ir(I)(P−N) Complexes 5, 6a, and 6b. The cationic iridium phosphino-imine complex **5** was synthesized using aniline as the amine source in a condensation reaction with the phosphine aldehyde (Scheme 5). The synthesis of P−N complexes is done in a template fashion, where the addition of the metal precursor is necessary to enable

Table 1. Direct Hydrogenation of Olefins with Catalysts 4−6[a]

entry	catalyst	solvent	substrate	product	time (h)	conv. (%)
1	4a	CH_2Cl_2	cyclooctene	cyclooctane	4	100
2	4a	CH_2Cl_2	4-phenyl-3-buten-2-one	4-phenyl-2-butanone	2	100[b]
3	4a	hexanes	cyclooctene	cyclooctane	2	100
4	4a	hexanes	4-phenyl-3-buten-2-one	4-phenyl-2-butanone	2	100[b]
5	4a	hexanes	stilbene	bibenzyl	10	0
6	4b	CH_2Cl_2	cyclooctene	cyclooctane	0.5	96
7	4b	CH_2Cl_2	4-phenyl-3-buten-2-one	4-phenyl-2-butanone	1	100[b]
8	4b	hexanes	cyclooctene	cyclooctane	2	75
9	4b	CH_2Cl_2	stilbene	bibenzyl	2	26
10	4b	hexanes	stilbene	bibenzyl	10	14
11	5	CH_2Cl_2	cyclooctene	cyclooctane	3	88
					5	99
12	5	CH_2Cl_2	4-phenyl-3-buten-2-one	4-phenyl-2-butanone	3	29[b]
13	6a	CH_2Cl_2	cyclooctene	cyclooctane	1	13
14	6b	CH_2Cl_2	cyclooctene	cyclooctane	2	51

[a]Catalysis run at 35 °C, 35 bar H_2, and 1 mol % catalyst. [b]Selective reduction of olefin.

the reaction to go to completion. The addition of $[NH_4][PF_6]$ yielded the product as the $[PF_6]^-$ salt in 82% yield as air stable red crystals. If $NaPF_6$ or KPF_6 were used instead, a mixture of the cationic imine and the neutral enamido complexes are observed due to the acidic α-proton of the imine and the basicity of the methanol solvent or any moisture present in the reaction mixture.

Changing the amine in the condensation reaction from aniline to hydroxylamine resulted in the formation of phosphino-oxime complexes **6a** and **6b**. The ligand backbones of the oxime complexes **6a** and **6b** are less enolizable than the ligand backbone of imine complex **5**, as evident by $NaPF_6$ being a suitable PF_6^- source. These complexes were formed as the $[PF_6]^-$ salts, where the rhodium complex **6a** was isolated as a yellow solid in 70% yield, and the iridium complex **6b** as an orange solid in 97% yield. They have two potentially acidic hydrogens on the backbone and oxime oxygen. The rhodium complex **6a** was crystallized and examined by X-ray diffraction (Figure 5). The C(1)−C(2) bond distance for the ligand backbone is 1.483(3) Å, which is longer than the bond distances of the enolate complexes, and characteristic of a C−C single bond.

Phosphino-oxime ligands are uncommon in literature, with the closest examples being bidentate phosphino-oxide, oxime ligands. In particular, Wan and co-workers have used chelating phosphine oxide and N-oxime ligands with Cu(I) for N-arylation of alkylamines and N−H containing heterocycles,[38] as well as aryl iodide and thiol coupling.[29] No well-defined metal complexes have been isolated in these studies. These new phosphino-oxime complexes present new possibilities in catalyst design. An example of a catalyst containing an oxime ligand is the bifunctional ketone transfer hydrogenation catalyst by Ikariya and co-workers,[39] which contains a C−N oxime ligand and a Cp* ligand on Ir(III). Preliminary tests on the new Rh(I) and Ir(I) oxime complexes for the transfer hydrogenation of acetophenone showed no activity.

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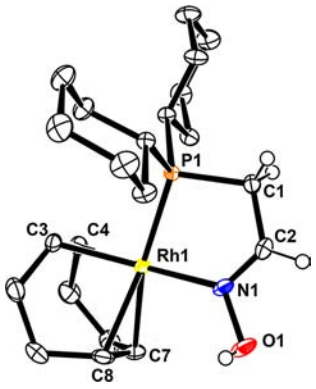

Figure 5. ORTEP representation (thermal ellipsoids at 50% probability; the solvent, most of the hydrogen atoms, and PF_6^- anion are omitted for clarity) and atom numbering for **6a**.

Hydrogenation Catalysis with Rh(I) and Ir(I) Complexes 4−6. The catalytic hydrogenation of olefins was attempted with the neutral complexes **4a** and **4b**, and the cationic complexes **5**, **6a**, and **6b** (Table 1). Stilbene was used as the initial olefin substrate; however, attempted catalysis with complexes **4**−**6** was slow and incomplete. Activity was observed for the hydrogenation of cyclooctene with catalysts **4** and **5**, where both Rh(I) and Ir(I) neutral catalysts were faster than the cationic catalyst **5**. Cationic metal centers are often thought to be optimal for catalytic activity, especially in the case of poorly coordinating unfunctionalized tri- and tetrasubstituted olefins, as they may have greater affinity for the olefins. However, with less substituted olefins such as cyclooctene, it is possible that this is not a major factor. A previous study by Pfaltz and co-workers on counteranions[22] has shown that the use of hexafluorophosphate anions are suboptimal for cationic Ir(I) olefin hydrogenation catalysts and resulted in slower turnover and more rapid catalyst death when compared to the larger and less coordinating $[BAr^F{}_4]^-$ anion. The neutral complexes **4a** and **4b** do not have counteranions and thus have the potential to avoid this problem.

The Rh(I) complex **4a** is more active for the hydrogenation of cyclooctene in hexanes than in CH_2Cl_2, whereas the Ir(I) complex **4b** had the reverse activity. One possible explanation is after the COD ligand dissociates after hydrogenation, the Rh(I) metal center is more Lewis acidic than the Ir(I) metal center. This difference renders Rh(I) to have a higher affinity for CH_2Cl_2 coordination and thereby cause a greater hindering of substrate coordination. It may also be possible that the Ir(I) catalyst is more prone to catalyst deactivation through oligomerization[7] of the active catalyst than the Rh(I) catalyst, and CH_2Cl_2 coordination is able to stabilize and maintain the active catalyst in solution.[21]

Phosphino-oxime complexes **6a** and **6b** were poorly active for the hydrogenation of olefins and acetophenone. This was expected, as they are coordinatively unsaturated hydrogenation catalysts with coordinating alcohol or amine groups on the ligand. Hence, their inactivity is likely due to a deactivation pathway involving the formation of dimers or other oligomers. Catalysts **4** and **5** are selective for olefin hydrogenation over carbonyl groups, as demonstrated by the selective hydrogenation of 4-phenyl-3-buten-2-one to 4-phenyl-2-butanone.

CONCLUSION

Facile, one-pot methods for the synthesis of bidentate P−O, P−P, and P−N complexes, some of which were catalytically active for the hydrogenation of C=C double bonds, were developed based on the utility of the phosphino aldehyde ligand precursor. A Ni(II) complex containing two bidentate phosphino-enolate ligands coordinated trans to each other was synthesized. This complex may be of interest for further investigations toward the synthesis of an ethylene oligomerization catalyst, as Fryzuk and co-workers have published a method of forming active olefin oligomerization catalysts from similar starting materials.[40] Also, a novel method of generating a diphosphine ligand containing a pendant aldehyde in a template method is presented using Pt(II) as the metal precursor. These ligands have potential for tethering metal complexes to heterogeneous materials making them more recyclable, or may be further transformed through functionalization of the alkene or aldehyde in the ligand backbone to generate more interesting ligands. Rh(I) and Ir(I) complexes have been synthesized based on Crabtree's iridium catalyst design. The neutral Ir(I) complex **4b** shows moderate activity for the hydrogenation of disubstituted olefins. However, it is less active with the more sterically hindered stilbene. It was surprising that **4b** was found to be more active than the cationic Ir(I) phosphino-imine complex considering that most catalysts of this design are cationic and contain a P−N ligand. Lastly, novel cationic Rh(I) and Ir(I) phosphino-oxime complexes **6** were synthesized and characterized. These complexes have potential for a variety of catalytic processes which require further investigation.

EXPERIMENTAL SECTION

All of the preparations and manipulations, unless otherwise stated, were carried out under a nitrogen or argon atmosphere using standard Schlenk-line and glovebox techniques. Dry and oxygen-free solvents were used unless otherwise stated. Pentane, hexanes, toluene, and diethyl ether were dried and distilled over sodium and benzophenone under an argon atmosphere. Methanol was dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under an argon atmosphere. Dichloromethane was dried and distilled over CaH_2 under an argon atmosphere. The synthesis of the bromide salt of dicyclohexylphosphonium dimer **1** was synthesized according to literature procedures.[26] The synthesis of the chloride salt of **1** only requires the replacement of bromoacetaldehyde diethyl acetal with chloroacetaldehyde diethyl acetal. All other reagents and solvents were purchased from commercial sources and were used as received. Deuterated solvents were purchased from either Cambridge Isotope Laboratories or Sigma Aldrich, and degassed and dried over molecular sieves prior to use. NMR spectra were recorded on a Varian Mercury 400 MHz or Bruker Avance 400 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced relative to their respective partially deuterated solvent peaks. All ^{31}P chemical shifts were measured relative to 85% phosphoric acid as an external reference. The electrospray ionization mass spectrometry (ESI-MS) data were collected on an AB/Sciex QStar mass spectrometer with an ESI source and the DART-MS data were collected on a JEOL AccuTOF-DART mass spectrometer with a DART-ion source (no solvent is required). Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer at the Department of Chemistry at the University of Toronto. Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structures were solved and refined using SHELXTL V6.1. ***Caution!*** *Perchlorate salts of organic compounds can be explosive.*

Ni(OCHCHPCy$_2$)$_2$ (2a). A vial was charged with dicyclohexylphosphinoaldehyde chloride dimer **1** (26 mg, 0.047 mmol), KO*t*Bu (11 mg,

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0.094 mmol), and toluene (2 mL). The mixture was stirred for 10 min, yielding a white suspension. Solids were filtered off through Celite, and $[Ni(H_2O)_6][BF_4]_2$ (16 mg, 0.047 mmol) and methanol (1 mL) were added to the reaction mixture resulting in a brown solution. Upon addition of additional KO*t*Bu (11 mg, 0.094 mmol), the solution darkened slightly and was stirred overnight. The volatiles were removed in vacuo, and the brown residue extracted with pentane (3 × 2 mL) until only white solids were left. Filtration of the mixture through Celite and removal of pentane in vacuo afforded the product as a brown solid. Yield: 72% (25 mg). Crystals of **2** suitable for X-ray diffraction studies were grown by the slow evaporation of hexanes. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.08 (m, 1H, *H*C−O), 3.43 (d, J_{HH} = 3.13 Hz, 1H, *H*C−P), 2.60 (m, 2H, H_2C_{cy}), 1.97−1.67 (m, 8H, H_2C_{cy}), 1.70−1.60 (m, 2H, HC_{cy}-P), 1.52−1.20 (m, 10H, H_2C_{cy}). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 175.66 (t, J_{CP} = 4.4 Hz, *C*-O), 76.79 (dd, J_{CP} = 25.0 Hz, 27.9 Hz, *C*-P), 35.92 (t, J_{CP} = 12.5 Hz, C_{cy}-P), 29.53 (s, C_{cy}), 27.90 (t, J_{CP} = 2.2 Hz, C_{cy}), 26.82 (m, C_{cy}), 25.85 (s, C_{cy}). ^{31}P {^{1}H} NMR (161 MHz, CD_2Cl_2): δ 47.57 (s). Anal. Calcd for $C_{28}H_{48}O_2P_2Ni$: C, 62.59; H, 9.00. Found: C, 62.11; H, 9.55. MS (ESI, methanol/water; m/z^+): 537.3 ($[C_{28}H_{49}O_2P_2Ni]^+$).

(*S*)-[Ni(Cy$_2$PCH$_2$CHN(CH(Me)(Ph))$_2$][ClO$_4$]$_2$ (2b). A vial was charged with phosphonium dimer, **1**, (70 mg, 0.109 mmol), KOtBu (25 mg, 0.218 mmol) and acetonitrile (10 mL). The solution was allowed to stir for 15 min. To this solution $[Ni(H_2O)_6][ClO_4]_2$ (80 mg, 0.218 mmol) was added followed by (*S*)-(-)-α-methylbenzylamine (27 mg, 0.218 mmol). The reaction turned orange and was allowed to stir overnight. The solvent was removed, and the residue was taken up with MeOH (5 mL). The orange precipitate was isolated and washed with diethyl ether (2 × 5 mL). Yield: 55% (57 mg). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.79 (t, 2H, J_{HH} = 12 Hz, C*H*N), 7.32−7.62 (m, 10H, *H*Ph), 4.41 (m, 2H, C*H*(CH$_3$)(Ph)), 3.86 (d, 2H, J_{HP} = 18 Hz, CH_2), 3.34 (m, 2H, CH_2), 1.88 (CH_3, indirectly determined from ^{1}H-^{1}H COSY), 1.92−0.83 (m, 50H, *H*Cy, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 177.5 (*C*HN), 139.0 (*C*Ph), 130.2 (*C*Ph), 129.9 (*C*Ph), 128.9 (*C*Ph), 128.5 (*C*Ph), 128.4 (*C*Ph), 68.3 (CH_2), 60.9 (*C*H(Me)(Ph)), 30.3−25.1 (*C*Cy), 21.1 (CH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 72.2. MS (ESI, methanol/water; m/z^+): 372.2 $[C_{44}H_{68}N_2NiP_2]^{2+}$. Anal. Calcd for $C_{44}H_{68}Cl_2N_2NiO_8P_2$: C, 55.95; H, 7.26; N, 2.97; Found: C, 52.68; H, 7.10; N, 2.83.

Pt(Cy$_2$PCH$_2$CHO)$_2$Cl$_2$, Pt(Cy$_2$PCH$_2$CHC(CHO)PCy$_2$)Cl$_2$ (3a, 3b). A vial was charged with dicyclohexylphosphinoaldehyde chloride dimer **1** (33 mg, 0.060 mmol), KO*t*Bu (13 mg, 0.12 mmol) and toluene (2 mL). The mixture was stirred for 10 min, yielding a white suspension. 1,5-Cyclooctadiene dichloroplatinum (23 mg, 0.060 mmol) was weighed directly into the vial, and stirred overnight. The resulting pale yellow solution was filtered through Celite to remove salts and dried in vacuo to yield the product as a white solid. Yield: 98% (44 mg).

Through NMR analysis, it was shown that 88% of the recovered product was the *trans*-phosphinoaldehyde complex **3a**, and 12% was the *cis*-aldol condensation product **3b**. When the same reaction was attempted at −78 °C for 1 h, and then slowly warmed to room temperature, the reaction yielded only 30% **3a** and 70% **3b**.

Recrystallization in CH_2Cl_2 and hexanes yielded crystals containing a molecule of **3a** and a molecule of **3b** per unit cell.

3a: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.96 (t, $^3J_{HH}$ = 3.2 Hz, 1H, *H*C═O), 3.20 (m, 2H, H_2C−P), 2.09 (m, 2H, HC_{cy}-P), 1.93−1.15 (m, 20H, H_2C). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 198.74 (s, *C*═O), 32.69 (t, J_{CP} = 10.3 Hz, *C*-PC$_{cy2}$), 32.30 (t, J_{CP} = 14.7 Hz, P-*C*$_{cy}$), 28.80 (s, C_{cy}), 28.42 (s, C_{cy}), 27.32 (m, C_{cy}), 26.64 (s, C_{cy}). ^{31}P {^{1}H} NMR (121 MHz, CD_2Cl_2): δ 15.40 (s). Anal. Calcd for $C_{28}H_{50}Cl_2O_2P_2Pt$: C, 45.04; H, 6.75. Found: C, 45.50; H, 6.84. MS (DART; m/z^+): 710.3 ($[C_{28}H_{50}ClO_2P_2Pt]^+$).

3b: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.52 (m, *H*C═O), 7.94 (m, 1H, *H*C═C), 2.98 (m, 4H, H_2C−P), 1.93−1.15 (m, 20H, H_2C). ^{31}P {^{1}H} NMR (121 MHz, CD_2Cl_2): δ 32.88 (d, J_{PP} = 16.9 Hz), 9.91 (d, J_{PP} = 16.9 Hz).

Rh(COD)(OCHCHPCy$_2$) (4a). A vial was charged with dicyclohexylphosphinoaldehyde chloride dimer **1** (26 mg, 0.047 mmol), KO*t*Bu (10 mg, 0.094 mmol), and toluene (2 mL). The mixture was stirred for 20 min, yielding a white suspension. Cyclooctadiene rhodium chloride dimer (23 mg, 0.047 mmol) was weighed directly into the vial, and stirred briefly, followed by addition of KO*t*Bu (10 mg, 0.094 mmol). The yellow solution was stirred at room temperature for 2.5 h. The yellow solution was filtered through Celite to remove salts and dried in vacuo to yield the product as a yellow solid. The product was recrystallized by slow diffusion of methanol into a CH_2Cl_2 solution of the product. Yield: 97% (46 mg). Bright yellow crystals of **4a** suitable for X-ray diffraction studies were grown from slow diffusion of methanol into a hexane solution of the product. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35 (dt, $^3J_{HH}$ = 3.7 Hz, $^3J_{HP}$ = 39.3 Hz, 1H, *H*C−O), 4.91 (m, 2H, *HC*═C*H*), 3.75 (m, 2H, *HC*═C*H*), 3.49 (dd, $^3J_{RhH}$ = 1.8 Hz, $^3J_{HH}$ = 3.7 Hz, 1 H, *H*C−P), 2.36−2.14 (m, 4H, COD H_2C), 2.06−1.92 (m, 4H, COD H_2C), 1.90−1.79 (m, 2H, HC_{cy}-P), 1.77−1.56 (m, 10H, H_2C), 1.38−1.03 (m, 10H, H_2C). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 177.35 (d, $^2J_{CP}$ = 15.4 Hz, *C*-O), 101.64 (dd, *J* = 8.1 Hz, 10.3 Hz, COD *C*═*C trans*-P), 78.55 (d, $^1J_{CP}$ = 41.8 Hz, C=C-P), 66.85 (d, $^1J_{RhC}$ = 13.2 Hz, COD *C*═*C cis*-P), 34.01 (dd, $^2J_{RhC}$ = 1.5 Hz, $^3J_{CP}$ = 24.9 Hz COD CH_2), 33.63 (d, $^2J_{RhC}$ = 2.9 Hz, COD CH_2), 28.69 (d, J_{CP} = 3.67 Hz, C_{Cy}), 28.47 (d, J_{CP} = 1.47 Hz, C_{Cy}), 28.35 (s, C_{Cy}), 27.46 (d, J_{CP} = 16.1 Hz, C_{Cy}), 27.35 (d, J_{CP} = 13.20 Hz, C_{Cy}), 26.80 (d, J_{CP} = 1.47 Hz, C_{Cy}). ^{31}P {^{1}H} NMR (161 MHz, CD_2Cl_2): δ 44.92 (d, $^1J_{RhP}$ = 155.0 Hz). Anal. Calcd for $C_{22}H_{36}OPRh$: C, 58.67; H, 8.06. Found: C, 57.64; H, 8.10. MS (ESI, methanol/water; m/z^+): 451.2 ($[C_{22}H_{37}OPRh]^+$).

Ir(COD)(OCHCHPCy$_2$) (4b). A vial was charged with dicyclohexylphosphinoaldehyde chloride dimer **1** (26 mg, 0.047 mmol), KO*t*Bu (10 mg, 0.094 mmol), and toluene (2 mL). The mixture was stirred for 20 min, yielding a white suspension. Cyclooctadiene iridium chloride dimer (32 mg, 0.047 mmol) was weighed directly into the vial, and stirred briefly, followed by addition of KO*t*Bu (10 mg, 0.094 mmol). The dark red solution was stirred at room temperature overnight. The red solution was filtered through Celite to remove salts and dried in vacuo to obtain the crude product as a dark red sticky solid. The solid was washed with a few drops of Et_2O several times to yield an orange solid. The product was recrystallized by slow diffusion of methanol into a CH_2Cl_2 solution of the product. Yield: 45% (23 mg). Red crystals of **4b** suitable for X-ray diffraction studies were grown from slow diffusion of methanol into a hexane solution of the product. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (dd, $^3J_{HH}$ = 4.1 Hz, $^3J_{HP}$ = 34.0 Hz, 1H, *H*C−O), 4.60 (m, 2H, COD *HC*═C*H*), 3.80 (t, $^3J_{HH}$ = 4.1 Hz, 1H, *H*C−P), 3.58 (m, 2H, COD *HC*═C*H*), 2.31−2.16 (m, 2H, HC_{cy}-P), 2.15−1.13 (m, 28H, H_2C). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 180.21 (d, $^2J_{CP}$ = 13.2 Hz, *C*-O), 89.14 (d, $^2J_{CP}$ = 11.7 Hz, COD *C*═*C trans*-P), 82.64 (d, $^1J_{CP}$ = 48.4 Hz, C═C-P), 50.65 (s, COD *C*═*C cis*-P), 34.44 (d, $^3J_{CP}$ = 13.2 Hz, COD CH_2), 34.58 (s, COD CH_2), 34.02 (s, HC_{cy}-P), 27.36 (d, J_{CP} = 12.5 Hz, C_{cy}), 27.28 (d, J_{CP} = 11.0 Hz, C_{cy}), 26.73 (d, J_{CP} = 1.5 Hz, C_{cy}). ^{31}P {^{1}H} NMR (161 MHz, CD_2Cl_2): δ 37.42 (s). Anal. Calcd for $C_{22}H_{36}OPIr$: C, 48.96; H, 6.72. Found: C, 48.62; H, 6.94. MS (ESI, methanol/water; m/z^+): 541.2 ($[C_{22}H_{37}OPIr]^+$).

[Ir(COD)(PhNCHCH$_2$PCy$_2$)][PF$_6$] (5). A vial was charged with dicyclohexylphosphinoaldehyde bromide dimer (38 mg, 0.060 mmol), KO*t*Bu (13 mg, 0.116 mmol), aniline (12 mg, 0.129 mmol), and toluene (2 mL). The mixture was stirred for 30 min, yielding a yellow solution. Cyclooctadiene iridium chloride dimer (40 mg, 0.060 mmol), NH_4PF_6 (20 mg, 0.120 mmol), and methanol (1 mL) were then added directly into the vial to form a bright red/orange solution. The solution was stirred at room temperature overnight, and the solvent removed in vacuo. The resulting red solid was dissolved in cold CH_2Cl_2 and filtered through Celite to remove any insoluble salts. The solvent was removed and washed several times with pentane. The filtrate was dried in vacuo to yield the product as a red solid. Yield: 82% (75 mg). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (dt, $^3J_{HH}$ = 2.3 Hz, $^3J_{HP}$ = 22.7 Hz, 1H, *H*C═N), 7.43−7.09 (m, 5H, H_{Ph}), 3.83 (br s, 4H, COD CH_2), 3.11 (dd, $^3J_{HH}$ = 2.3 Hz, $^2J_{HP}$ = 8.2 Hz, 1H, H_2C−P), 2.28−1.23 (m, aliphatic H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 149.76 (s, HC═N), 129.03 (s, C_{Ph}), 128.06 (s, C_{Ph}), 122.82 (s, C_{Ph}), 68.95 (bs, COD C═C), 35.59 (d, $^1J_{CP}$ = 23.5 Hz, *C*-P), 35.48 (d, $^1J_{CP}$ = 22.7 Hz, *C*-P), 31.89 (s, CH_2), 29.30 (s, CH_2), 28.82 (s, CH_2), 27.26

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(d, J_{CP} = 10.3 Hz, CH_2), 26.49 (d, J_{CP} = 1.5 Hz, CH_2). ^{31}P {^1H} NMR (161 MHz, CD_2Cl_2): δ 47.81 (s), −144.38 (septet, J = 711 Hz, PF_6). Anal. Calcd for $C_{28}H_{42}F_6NP_2Ir$: C, 44.20; H, 5.56; N, 1.84. Found: C, 41.88; H, 5.57; N, 1.85. (ESI, methanol/water; m/z^+): 616.3 ($[C_{28}H_{42}NPIr]^+$).

[Rh(COD)(HONCHCH$_2$PCy$_2$)][PF$_6$] (6a). A vial was charged with dicyclohexylphosphinoacetaldehyde chloride dimer (33 mg, 0.060 mmol), KO*t*Bu (13 mg, 0.120 mmol), and toluene (2 mL). The mixture was stirred for 10 min, yielding a white suspension. Hydroxylammonium chloride (6 mg, 0.080 mmol), KO*t*Bu (9 mg, 0.080 mmol), and methanol (2 mL) were added and stirred for 20 min. Cyclooctadiene rhodium chloride dimer (20 mg, 0.040 mmol) and $NaPF_6$ (16 mg, 0.094 mmol) were then weighed directly into the vial forming a yellow solution. The solution was stirred at room temperature overnight, and the solvent removed in vacuo. The resulting red solid was dissolved in CH_2Cl_2 and filtered through Celite to remove any insoluble salts. The filtrate was dried in vacuo to yield the product as a yellow solid. Yellow crystals of **6a** suitable for X-ray diffraction studies were grown from slow diffusion of pentane into a CH_2Cl_2 solution of the product. Yield: 70% (36 mg). ^1H NMR (400 MHz, CD_2Cl_2): δ 9.17 (bs, 1H, N−O*H*), 8.00 (m, 1H, *H*C═N), 5.57 (br s, 2H, COD C*H*$_2$), 4.45 (m, 2H, COD C*H*$_2$), 2.65 (dd, $^3J_{HH}$ = 2.7 Hz, $^2J_{HP}$ = 8.8 Hz, 1H, H_2C−P), 2.47−1.10 (m, aliphatic H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 164.73 (t, J = 5.1 Hz, *C*═N), 106.38 (dd, J = 7.3 Hz, 8.8 Hz, COD *C*═*C*), 79.08 (d, $^1J_{RhC}$ = 11.7 Hz, COD *C*═*C*), 34.30 (dd, $^2J_{RhC}$ = 1.8 Hz, $^1J_{CP}$ = 21.3 Hz, C_{cy}-P), 32.55 (d, J = 2.9 Hz, COD *C*H$_2$), 29.07 (d, J = 2.2 Hz, *C*H$_2$), 28.80 (d, J = 1.5 Hz, COD *C*H$_2$), 28.49 (s, *C*H$_2$), 27.34 (d, $^1J_{CP}$ = 21.3 Hz, H_2*C*-P), 26.90 (d, J = 11.0 Hz, *C*H$_2$), 26.28 (d, J = 1.5 Hz, *C*H$_2$). ^{31}P {^1H} NMR (161 MHz, CD_2Cl_2): δ 50.90 (d, $^1J_{RhP}$ = 149.4 Hz), −144.20 (p, $^1J_{PP}$ = 711 Hz, $[PF_6]^-$). Anal. Calcd. for $C_{22}H_{38}FNOP_2Rh$: C, 43.22; H, 6.26; N, 2.29. Found: C, 44.31; H, 5.97; N, 2.43. MS (ESI, methanol/water; m/z^+): 466.2 ($[C_{22}H_{38}NOPRh]^+$).

[Ir(COD)(HONCHCH$_2$PCy$_2$)][PF$_6$] (6b). A vial was charged with dicyclohexylphosphinoaldehyde chloride dimer (26 mg, 0.047 mmol), KO*t*Bu (10 mg, 0.094 mmol), and toluene (2 mL). The mixture was stirred for 10 min, yielding a white suspension. Hydroxylammonium chloride (7 mg, 0.094 mmol), KO*t*Bu (10 mg, 0.094 mmol), and methanol (2 mL) were added and stirred for 20 min. Cyclooctadiene iridium chloride dimer (31 mg, 0.047 mmol) and $NaPF_6$ (16 mg, 0.094 mmol) were then weighed directly into the vial forming a bright red/orange solution. The solution was stirred at room temperature overnight, and the solvent removed in vacuo. The resulting red solid was dissolved in CH_2Cl_2 and filtered through Celite to remove any insoluble salts. The filtrate was dried in vacuo to yield the product as a red solid. Yield: 97% (46 mg)

^1H NMR (400 MHz, CD_2Cl_2): δ 11.07 (bs, 1H, N−O*H*), 8.71 (broad d, $^3J_{HP}$ = 23.9 Hz, 1H, *H*C═N), 4.97 (broad s, 2H, COD *H*C═C*H*), 4.29 (broad s, 2H, COD *H*C═C*H*), 2.78 (d, $^3J_{HH}$ = 8.0, 2H, H_2C−P), 2.31−1.08 (m, aliphatic H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 188.39 (d, $^2J_{CP}$ = 6.6 Hz, *C*═N), 90.16 (s, COD *C*═*C*), 60.31 (s, COD *C*═*C*), 34.92 (d, $^1J_{CP}$ = 26.4 Hz *C*-P), 34.57 (d, J_{CP} = 26.4 Hz, *C*-P), 32.31 (s, *C*H$_2$), 28.79 (d, J_{CP} = 2.2 Hz, *C*H$_2$), 28.74 (s, *C*H$_2$), 27.00 (d, J_{CP} = 12.5 Hz, *C*H$_2$), 26.86 (d, J_{CP} = 11.0 Hz, *C*H$_2$), 26.26 (d, J_{CP} = 1.5 Hz, *C*H$_2$). ^{31}P {^1H} NMR (161 MHz, CD_2Cl_2): δ 45.34 (s), −144.41 (p, J = 711 Hz). Anal. Calcd for $C_{22}H_{38}FNOP_2Ir$: C, 37.71; H, 5.47; N, 2.00. Found: C, 38.94; H, 5.50; N, 2.35. MS (ESI, methanol/water; m/z^+): 556.2 ($[C_{22}H_{38}NOPIr]^+$).

Catalysis. Hexanes and CH_2Cl_2 were dried and degassed following standard procedures. All of the substrates were vacuum-distilled, dried over activated molecular sieves, and stored under argon prior to use. All of the hydrogenation runs were performed at constant pressures using a stainless steel 50 mL Parr hydrogenation reactor. The temperature was maintained at 35 °C using a constant temperature water bath. The reactor was flushed several times with hydrogen gas at 2−4 bar prior to the addition of catalyst/substrate and base solutions.

In a typical run (Table 1, Entry 1), the catalyst **4a** (6 mg, 13.3 μmol) and cyclooctene (146 mg, 1.33 mmol) were dissolved in CH_2Cl_2 (16 g) (or 10 g hexanes) under an argon atmosphere. The catalyst/substrate solution was taken up by a syringe and needle in the glovebox. The needles were stoppered, and the syringes were taken to the reactor. The solutions were then injected into the reactor against a flow of hydrogen gas. The hydrogen gas was adjusted to the desired pressure (35 bar). Small aliquots of the reaction mixture were quickly withdrawn with a syringe and needle under a flow of hydrogen at timed intervals by venting the Parr reactor at reduced pressure. Alternatively, small aliquots of the reaction mixture were sampled from a stainless steel sampling dip tube attached to a modified Parr reactor. The dip tube was 30 cm in length with an inner diameter of 0.01 in., and a swing valve was attached to the end of the sampling tube. Three small aliquots of sample were thereby withdrawn quickly at timed intervals by opening the swing valve, and the first two aliquots were discarded. All samples were diluted to a total volume of approximately 2 mL using oxygenated THF prior to GC analyses.

A Perkin-Elmer Clarus 400 chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m × 2.5 mm) and an autosampling capability was used for gas chromatography (GC) analyses. Hydrogen was used as a mobile phase at a column pressure of 5 psi with a split flow rate of 50 mL/min. The injector temperature was 250 °C, and the FID temperature was 275 °C. All of the conversions are reported as an average of two GC runs. The reported conversions were reproducible.

The substrate, product, oven temperature (T), and the retention times for the substrate (t_s) and product (t_p) are as follows:

Cyclooctene, cyclooctane, T = 105 °C, t_s = 5.15 min, t_p = 5.38 min.

trans-4-Phenyl-3-buten-2-one, 4-phenyl-2-butanone, T = 125 °C, t_s = 21.95 min, t_p = 11.42 min.

Stilbene, bibenzyl, T = 200 °C, t_s = 5.08 min, t_p = 3.73 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete crystallographic data in CIF format for complexes **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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