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Synthesis of Stable Phosphomide Ligands and their Use in Ru-Catalyzed Hydrogenations of Bicarbonate and Related Substrates

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New benzoyl- and naphthoyl-substituted phosphines have been synthesized, which are stable to air and moisture. Testing these so-called phosphomide ligands in the presence of different ruthenium precursors, the hydrogenation of sodium bicarbonate ($NaHCO_3$) to sodium formate ($NaHCO_2$) proceeded with good catalyst turnover numbers in the range of 1300–1600 at 80 °C and a total pressure of hydrogen of 60 bar in the absence of amines or other additives. Similarly, catalytic hydrogenations of carbon dioxide, cinnam-, and benzaldehyde were possible with these new ruthenium complexes. As an intermediate of the catalytic cycle the defined ruthenium complex [(η^6-C_6H_6)-$RuCl_2$(Cy_2P(1-naphthoyl)] (Cy = cyclohexyl) was prepared and characterized by X-ray crystallography.

Introduction

Organometallic complexes with phosphine ligands represent the most important catalysts for the homogeneous hydrogenation of unsaturated compounds, such as olefins, alkynes, ketones, etc.[1] More recently, these catalysts became also of interest for hydrogen storage and the utilization of C_1 building blocks. In this respect, especially molecular-defined complexes of ruthenium and iridium have been investigated for the catalytic hydrogenation of carbon dioxide and bicarbonate.[2] In general, well-known triaryl- or trialkylphosphines (R_3P, **I**) are used to modify and control the activity and selectivity of the respective active metal centers.

Based on our continuing interest in the refinement of carbon dioxide,[3] we became attracted to investigate the catalytic potential of less common phosphorous ligands for the reduction of bicarbonate and CO_2. More specifically, we had the idea to use acyl-substituted phosphorus ligands (R_2PCOR, **II**), which have been largely neglected in homogeneous catalysis.[4] These so-called phosphomide ligands (Figure 1) are characterized by decreased σ-donor and increased π-acceptor abilities relative to traditional triaryl- or trialkylphosphines. Because of the assumed labile P–CO bond, only few studies on the electronic properties of phosphomide ligands and the catalytic behavior of corresponding complexes have been reported so far.[4] Additionally, such ligands might be conveniently prepared relative to traditional phosphines by direct reaction of secondary phosphines with carboxylic acid derivatives and should be less prone towards P-oxidation.

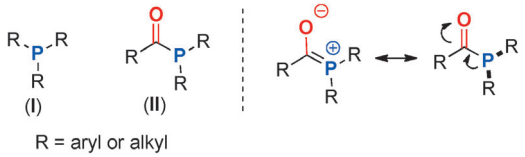

Figure 1. Comparison between phosphines and phosphomide ligands.

Herein, we describe the preparation of several new phosphomide ligands, which are surprisingly stable to air and moisture. For the first time the catalytic potential of this class of ligands is demonstrated in the hydrogenation of carbon dioxide to formic acid derivatives, sodium bicarbonate to sodium formate, and cinnamaldehyde and benzaldehyde to the corresponding alcohols.

Results and Discussion

Synthesis of phosphomide ligands

Previous reports suggested that phosphomide ligands are effectively prepared from alkylsilylphosphines, dialkylphosphines, and metalated phosphides by reaction with ketene, benzoyl chloride, or other acid chlorides, respectively.[5] However, a variety of sterically hindered phosphomides can be conveniently synthesized from commercially available acid chlorides and secondary phosphines (Scheme 1). Notably, this method gives easy access to new phosphomides (**L8**–**L20**) from aromatic, heteroaromatic, and aliphatic carboxylic acids. As an example, the reaction of benzoyl chloride with diadamantylphosphine in the presence of triethylamine immediately gives a bright

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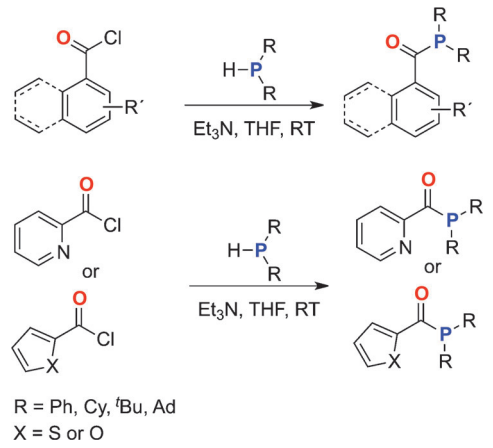


Scheme 1. General synthesis of phosphomide ligands.

orange solution of diadamantyl benzoyl phosphine (**L8**) as the only phosphorus-containing product. In general, the new phosphomides are obtained in good yield (>70%) and high purity (>90%) simply by filtration and removal of the solvent. Notably, most of the prepared ligands are remarkably stable to air and moisture. Hence, even after several days in THF/H_2O only a negligible amount of hydrolysis and impurities was detected by ^{31}P NMR spectroscopy (see the Supporting Information).[6]

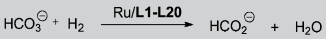
The unusual stability of different ligands stems from the increased steric protection of bulky cyclohexyl, *tert*-butyl, or adamantyl substituents on the phosphorous atom. This may also prevent the coplanar orientation between the carbonyl group and the lone electron pair of the phosphorus atom, which is required for the conjugation/delocalization of phosphomide ligands.

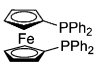
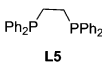
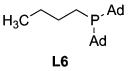
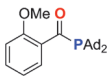
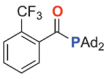
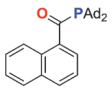
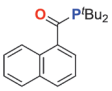
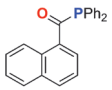
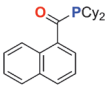
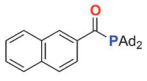
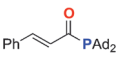
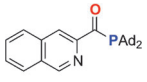
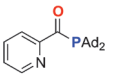
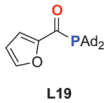
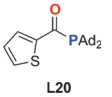
Catalytic tests: Hydrogenation of $NaHCO_3$, CO_2, cinnamaldehyde, and benzaldehyde

In the past two decades a variety of rhodium-, iridium-, and ruthenium-based complexes have been developed for the hydrogenation of CO_2 to formic acid derivatives.[7] The insertion of CO_2 into ruthenium hydride complexes was intensively studied with water-soluble phosphine ligands, such as triphenylphosphine monosulfonate (TPPMS), triphenylphosphine trisulfonate (TPPTS), $P(CH_2OH)_3$, $P(CH_2CH_2CH_2OH)_3$, $P(CH_2CH_2CN)_3$, $P(CH_2)_6N_3$, and 1,3,5-triaza-7-phosphaadamantane.[8] However, much less work is known[9] on the related reduction of bicarbonates and the reported catalyst activities are significantly lower[9a,e] relative to the reduction of CO_2.

To compare the activity of P-containing catalysts appropriately, initially different commercially available ruthenium complexes such as $[RuCl_2(C_6H_5)]_2$, [Ru(Me-allyl)$_2$(cod)] (cod = 1,5-cyclooctadiene), and [$RuCl_2$(cod)] were tested for the hydrogenation of sodium bicarbonate at a H_2 pressure of 60 bar and a temperature of 80 °C in methanol without any phosphine ligand present. As expected, no desired reduction was observed. However, in combination with **L8**, both $[RuCl_2(C_6H_6)]_2$ and [Ru(Me-allyl)$_2$(cod)] generated active hydrogenation catalysts. Interestingly, our new ligands gave rise to also more active catalysts relative to [Ru(Me-allyl)$_2$(cod)] in the presence of commercially available ligands, such as triphenylphosphine (PPh_3), tricyclohexylphosphine (PCy_3), dicyclohexylphosphine ($PHCy_2$), 1,1′-bis(diphenylphosphino)-ferrocene (dppf), 1,2,-bis-(diphenylphosphino)ethane (dppe), di(1-adamantyl)-*n*-butylphosphine ($BuPAd_2$), and di(1-adamantyl)-benzylphosphine ($BzPAd_2$). With all these ligands, only a low yield of the desired sodium formate (<18%) was obtained (Table 1, entry 1–7). Conversely, experiments performed in the presence of **L8** provided formate in 36% yield with a catalyst turnover number (TON) of 875. Due to this promising result, we tested ligands **L9**–**L20** under similar reaction conditions in the same model reaction (Table 1). Applying **L14** gave rise to a yield in formate

Table 1. Catalytic hydrogenation of bicarbonate to formate: Variation of ligands (**L1**–**L20**).[a]



Ligand	Yield [%]	TON	Ligand	Yield [%]	TON
 **L1**	3	73	 **L2**	16	389
 **L3**	7	170	 **L4**	–	–
 **L5**	7	170	 **L6**	3	73
 **L7**	18	437	 **L8**	36	872
 **L9**	13	316	 **L10**	14	340
 **L11**	30	729	 **L12**	23	559
 **L13**	20	486	 **L14**	65 60 53	1575 1454[b] 1284[c]
 **L15**	13	316	 **L16**	12	292
 **L17**	15	364	 **L18**	16	389
 **L19**	21	510	 **L20**	12	292

[a] Reaction conditions: $NaHCO_3$ (1.6 g, 0.0190 mol), [Ru(Me-allyl)$_2$(cod)] (2.5 mg, 7.84×10^{-6} mol), **L1**–**L20** (2.0 equiv), 80 °C, H_2 (60 bar), 20 h. Yield based on ^1H NMR signals of sodium formate with THF used as an internal standard. TON = mol of sodium formate/per mol of catalyst. [b] $[RuCl_2(C_6H_5)]_2$ and **L14** (2.0 equiv). [c] [$RuCl_2$(cod)].

Table 2. Ru/**L14**-catalyzed hydrogenation of sodium bicarbonate, carbon dioxide, and carbonyl compounds.

Entry	Product	*T* [°C]	$P(H_2/CO_2)$[a]	Yield [%]	TON
1[b]	sodium formate	80	60:0	15	7188
2[c]	methyl formate	100	30:30	20	4126
3[d]	benzyl alcohol	80	50:0	64	1600
4[e]	(*E*)-3-phenylprop-2-en-1-ol	80	50:0	87	1764

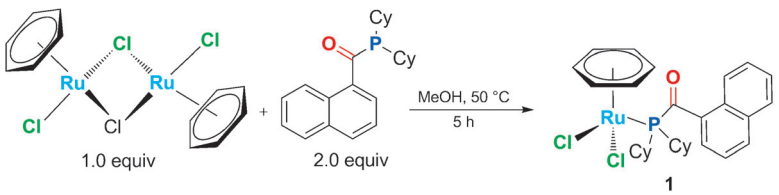
[a] Pressures are in bar. [b] $NaHCO_3$ (1.26 g, 0.015 mol), $[Ru(Me\text{-}allyl)_2(cod)]$ (0.313×10^{-6} mol), 20 h, **L14** (2.0 equiv). [c] NEt_3 (2 mL), MeOH (40 mL). [d] Benzaldehyde (2.0 g, 0.0196 mol), *t*BuOK (0.45 mmol), catalyst (7.84×10^{-6} mol). [e] Cinnamaldehyde (0.0159 mol), *t*BuOK (0.45 mmol), catalyst (7.84×10^{-6} mol).

of 65% and a TON of 1575 after 20 h. By lowering the catalyst amount, a remarkable TON of 7188 was achieved (Table 2, entry 1). To the best of our knowledge, this is the highest TON so far reported for the hydrogenation of bicarbonates using purely hydrogen pressure without any additives. Notably, also **L14** was air-stable and could be conveniently handled in air.[10]

Subsequently, we set out to see whether the catalytic system comprising $[Ru(Me\text{-}allyl)_2(cod)]$/**L14** could be applied more generally for the hydrogenation of carbonyl compounds and CO_2. Methyl formate was produced from CO_2 hydrogenation with a TON of 4126 (Table 2, entry 2), whereas benzyl alcohol was produced from benzaldehyde without optimization in 64% yield and with a TON of 1600 (Table 2, entry 3). In addition, the hydrogenation of ethyl cinnamate to (*E*)-3-phenylprop-2-en-1-ol was achieved in 87% yield and a TON of 1764 (Table 2, entry 4).

Synthesis of a defined Ru phosphomide complex

The active catalyst species in the hydrogenations above are likely to be monomeric ruthenium phosphomide complexes. In this respect, the ability of ruthenium dimers, such as $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, to convert into monomeric ruthenium(II) complexes of the general formula $[RuCl_2(\eta^6\text{-}C_6H_6)L]$ (L = phosphine donor ligand) through cleavage of the chloride bridges is well documented. Under our conditions, the optimum ratio of ruthenium dimer and ligand was found to be 1:2. Isolation of the resulting complex $[(\eta^6\text{-}C_6H_6)RuCl_2(Cy_2P(1\text{-naphthoyl})]$ (**1**) was achieved in 86% yield by mixing $[RuCl_2(C_6H_5)]_2$ with two equivalents of **L14** in MeOH at 50 °C for 5 h (Scheme 2).



Scheme 2. Reaction conditions for the formation of **1**: $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (1.0 equiv), $Cy_2P(1\text{-naphthoyl})$ (2.0 equiv), MeOH, 50 °C, 5 h.

We failed to obtain crystals of other ruthenium precursors, such as $[Ru(Me\text{-}allyl)_2(cod)]$ and $[RuCl_2(cod)]$ suitable for X-ray analysis. We also failed to obtain crystals of the defined ruthenium carbonato complex **2**[11] and the corresponding dihydride complex **3**[12] under different reaction conditions. These were important intermediates in the catalytic cycle for the hydrogenation of bicarbonate.

As shown in Figure 2, in complex **1** the ruthenium atom is coordinated to the benzene ring, two chloride atoms, and the

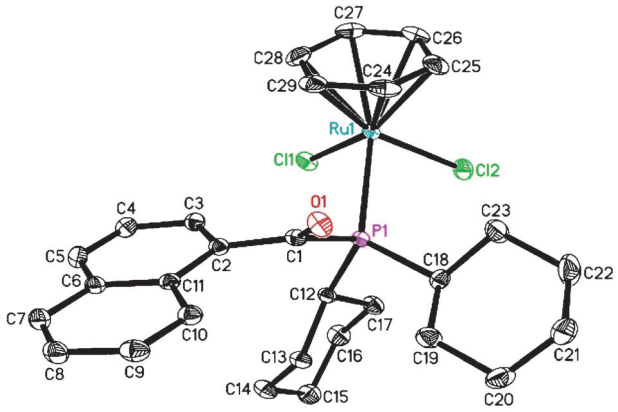


Figure 2. ORTEP representation of $[(\eta^6\text{-}C_6H_6)RuCl_2(Cy_2P(1\text{-naphthoyl})]$. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru1–P1 2.3764(6), Ru1–Cl1 2.4033(6), Ru1–Cl2 2.3985(7), C1–O1 1.219(3), P1–Ru1–Cl1 89.29(2), P1–Ru1–Cl2 86.62(2), Cl1–Ru1–Cl2 88.21(2), C1–P1–Ru1 105.95(7).

P-bonded phosphomide ligand.[10] The coordination geometry at the ruthenium center can be described as a piano-stool geometry.

Conclusions

We have demonstrated that new phosphomides can be readily prepared from carboxylic acid chlorides and secondary phosphines. This class of ligands has been largely neglected in catalysis; however, with appropriate substituents they are remarkably stable to air and moisture. Combinations of phosphomides with commercially available ruthenium precursors generate active catalysts for the hydrogenation of carbonyl compounds, carbon dioxide, and bicarbonate. In the case of bicarbonate, improved catalyst TONs relative to previously known catalyst systems have been achieved.

Experimental Section

General procedure for the formation of sodium formate: Dissolving $[Ru(Me\text{-}allyl)_2(cod)]$ (2.5 mg, 7.84×10^{-6} mol) and **L14** (2.0 equiv) in MeOH (40 mL) led to the immediate formation of a light yellow solution. $NaHCO_3$ (1.6 g, 0.0190 mol) was placed in an auto-

clave (100 mL) and the preformed catalyst solution was then added. The autoclave was deoxygenated and then filled with H_2 (60 bar) at room temperature. The reaction mixture was stirred (400 rpm) for 20 h at 80 °C. Subsequently, the autoclave was cooled with ice water and the pressure was slowly released. The solution was fully evaporated in a rotary evaporator and the formate content (white powder) was determined by ^{1}H NMR spectroscopy in D_2O with THF as an internal standard and a relaxation time of 20 s.

Formation of methyl formate: The synthesis of methyl formate was performed in a similar way as the synthesis of sodium formate. MeOH (40 mL) was used and NEt_3 (2 mL) was added to the catalyst solution. CO_2 (30 bar) and H_2 (30 bar) were added at room temperature to the solution and the reaction mixture was stirred at 100 °C for 20 h. The product was analyzed by GC (HP 6890N) with a HP5 column (30 m) with an internal diameter of 0.32 mm; film thickness of 0.25 mm; N_2 as carrier gas; inlet temperature of 270 °C; injection volume of 1 μL; split ratio of 50:1; flow rate of 0.6 mL min^{-1} (up to 20 min), then increasing by 0.5 mL min^{-1} steps up to 2.1 mL min^{-1}, temperature of 35 °C (up to 20 min), then increasing by 20 °C min^{-1} steps up to 295 °C (17 min), detector temperature of 300 °C, H_2 flow of 30 mL min^{-1}, air flow of 300 mL min^{-1}, and makeup flow of 25 mL min^{-1}, with diglyme used as an internal standard. The yields are expressed as the ratio of mols of product per mol of NEt_3 used.

Synthesis of [(η^6-C_6H_6)$RuCl_2$(Cy_2P(1-naphthoyl)] (1): MeOH (3 mL) was added to a Schlenk tube containing [(η^6-C_6H_6)$RuCl_2$]$_2$ (100 mg, 0.20 mmol, 1.0 equiv) and Cy_2P(1-naphthoyl) (154 mg, 0.44 mmol, 2.0 equiv). The resulting solution was stirred for 5–6 h at 50 °C under argon, and then the solvent was removed. The crude material was washed three times with heptane. Removal of solvent and drying in vacuum produced **1** (108 mg) in 86% yield as an air-stable orange powder. Crystals suitable for X-ray analysis were obtained from recrystallization in $CHCl_3$/heptane. The crude product was analyzed by NMR spectroscopy. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71–8.66 (m, 1H), 8.61–8.54 (m, 1H), 8.02–7.96 (m, 1H), 7.91–7.84 (m, 1H), 7.57–7.44 (m, 2H), 5.48 (s, 6H), 2.80–2.58 (m, 2H), 2.40–2.25 (m, 2H), 1.80–0.83 ppm (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.54, 215.46, 134.81, 134.49, 134.37, 134.31, 130.07, 129.02, 128.91, 126.93, 124.88, 124.57, 88.83, 88.80, 35.48, 35.25, 31.20, 31.13, 29.73, 29.07, 28.27, 28.13, 27.23, 27.12, 26.07 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 47.98 ppm; IR (neat): $\tilde{\nu}$ = 2923 cm^{-1} (C=O); high resolution (HR) MS (ESI): *m/z* calcd for $C_{29}H_{35}Cl_2NaOPRu^+$: 625.07403 [*M*+Na^+]; found: 625.07453.
Crystal data for [(η^6-C_6H_6)$RuCl_2$(Cy_2P(1-naphthoyl)]·2$CHCl_3$: $C_{31}H_{37}Cl_8OPRu$, M = 841.25; triclinic; space group $P\bar{1}$; a = 11.5804(4), b = 11.7775(4), c = 13.1399(5) Å; α = 94.561(3), β = 97.392(3), γ = 97.949(3)°; V = 1751.5(1) Å^3; T = 150(2) K; Z = 2; μ = 1.129 mm^{-1}; 30258 reflections measured; 8374 independent reflections (R_{int} = 0.0317); final R values ($I > 2\sigma(I)$): R_1 = 0.0312, wR_2 = 0.0661; final R values (all data): R_1 = 0.0478, wR_2 = 0.0684; 379 refined parameters. Data were collected on a STOE IPDS II diffractometer using graphite monochromatic MoK_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[13]

Diadamantyl benzoyl phosphine (L8): Benzoyl chloride (1.0 g, 7.1 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (2.16 g, 7.1 mmol) and triethylamine (0.87 g, 8.5 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L8** as an orange solid (2.15 g, 74%). The crude product was recrystallized from MeOH. This synthesis produced the desired product in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.03 (m, 2H), 7.51–7.43 (m, 1H), 7.40–7.32 (m, 2H), 2.05–1.93 (m, 6H), 1.92–1.77 (m, 12H), 1.68–1.54 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 218.53, 217.84, 144.35, 143.90, 133.20, 128.91, 128.75, 128.39, 128.37, 43.51, 43.37, 41.54, 41.41, 38.60, 38.30, 36.86, 36.79, 28.92, 28.81 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 39.43 ppm; IR (neat): $\tilde{\nu}$ = 2896, 2844, 1632, 1196, 1171, 797, 689 cm^{-1}; MS (EI): *m/z* (%): 406 (84) [*M*]$^+$, 407 (34), 135 (100).

Diadamantyl *o*-anisoyl phosphine (L9): *o*-Anisoyl chloride (1.0 g, 5.88 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (1.77 g, 5.88 mmol) and triethylamine (0.72 g, 7.0 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L9** as a yellow solid (2.0 g, 78%). The crude product was recrystallized from MeOH. This synthesis always gave rise to the desired product in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01–7.93 (m, 1H), 7.47–7.37 (m, 1H), 7.02–6.91 (m, 2H), 3.88 (s, 3H), 2.19–2.05 (m, 6H), 2.05–1.84 (m, 12H), 1.80–1.63 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 219.3, 218.6, 156.37, 156.33, 135.05, 134.59, 132.91, 132.54, 132.28, 119.71, 111.88, 111.86, 55.74, 41.38, 41.26, 39.18, 38.88, 36.93, 28.99, 28.89 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 51.93 ppm.

Diadamantyl 2-(trifluoromethyl)benzoyl phosphine (L10): 2-(Trifluoromethyl)benzoyl chloride (1.0 g, 7.1 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (2.16 g, 7.1 mmol) and triethylamine (0.87 g, 8.5 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L10** as an orange solid (2.15 g, 74%). The crude product was recrystallized from MeOH. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45–8.37 (m, 1H), 7.73–7.64 (m, 1H), 7.62–7.45 (m, 2H), 1.86–1.70 (m, 18H), 1.73–1.53 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 219.1, 218.4, 143.93, 143.47, 133.43, 133.10, 131.44, 131.30, 127.78, 127.72, 126.55, 125.48, 121.84, 41.40, 41.27, 39.70, 39.39, 36.77, 28.91, 28.80 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 52.90 ppm; IR (neat): $\tilde{\nu}$ = 2897, 2846, 1638, 1310, 1141, 766, 652 cm^{-1}; MS (EI): *m/z* (%): 474 (13) [*M*]$^+$, 135 (100), 173 (34); HRMS (ESI): *m/z* calcd for $C_{28}H_{35}F_3OP$+H^+: 475.23721 [*M*+H^+]; found: 475.23811.

Diadamantyl 1-naphthoyl phosphine (L11): 1-Naphthoyl chloride (1.0 g, 5.26 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (1.6 g, 5.26 mmol) and triethylamine (0.64 g, 6.3 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L11** as an orange solid (1.91 g, 80%). The crude product was recrystallized from MeOH. This synthesis always produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69–8.60 (m, 1H), 8.57–8.49 (m, 1H), 7.93–7.86 (m, 1H), 7.83–7.75 (m, 1H), 7.56–7.36 (m, 3H), 2.14–1.99 (m, 6H), 1.98–1.75 (m, 6H), 1.85–1.75 (m, 6H), 1.68–1.54 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 221.9, 221.2, 141.55, 141.2, 134.11, 134.08,133.24, 132.85, 128.91, 128.86, 128.49, 128.21,

126.44, 125.58, 124.26, 124.24, 41.59, 41.46, 39.37, 39.07, 36.89, 28.96, 28.85 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 49.80$ ppm; IR (neat): $\tilde{\nu} = 2887$, 2842, 1621, 1165, 1057, 772 cm^{-1}; MS (EI): *m/z* (%): 456 (48) $[M]^+$, 155 (100), 457 (17); HRMS (ESI): *m/z* calcd for $C_{31}H_{38}OP+H^+$: 457.26548 $[M+H^+]$; found: 457.26450.

Di-*tert*-butyl 1-naphthoyl phosphine (L12): 1-Napthoyl chloride (1.0 g, 5.26 mmol) was added dropwise over about 20 min to a solution of di-*tert*-butylphosphine (0.76 g, 5.26 mmol) and triethylamine (0.64 g, 6.3 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L12** as an orange solid (1.4 g, 89%). Purification of the crude product by flash column chromatography (silica gel) using initially hexane and finally ethyl acetate/hexane (5:95) as eluent gave rise to the title compound as a yellow oil. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.57$–8.48 (m, 1H), 8.48–8.41 (m, 1H), 7.91–7.83 (m, 1H), 7.79–7.71 (m, 1H), 7.54–7.33 (m, 3H), 1.18 (s, 9H), 1.14 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 222.15$, 221.50, 140.98, 140.55, 134.14, 134.11, 132.12, 132.16, 131.83, 129.06, 129.06, 129.01, 128.52, 128.16, 128.50, 125.53, 124.23, 124.21, 34.22, 33.93, 30.56, 30.40 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 53.33$ ppm; IR (neat): $\tilde{\nu} = 2943$, 2894, 2860, 1626, 1166, 1056, 793 cm^{-1}; MS (EI): *m/z* (%): 155 (100) $[M]^+$, 300 (56); HRMS (ESI): *m/z* calcd for $C_{19}H_{26}OP+H^+$: 301.17158 $[M+H^+]$; found: 301.17192.

Diphenyl 1-naphthoyl phosphine (L13): 1-Naphthoyl chloride (1.0 g, 5.26 mmol) was added dropwise over about 20 min to a solution of diphenylphosphine (0.98 g, 5.26 mmol) and triethylamine (0.64 g, 6.31 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L13** as an orange solid (1.45 g, 80%). The crude product was recrystallized or filtered through a small column. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.58$–8.49 (m, 1H), 8.31–8.22 (m, 1H), 7.81–7.75 (m, 1H), 7.74–7.68 (m, 1H), 7.41–7.31 (m, 5H), 7.26–7.16 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.49$, 215.55, 137.45, 137.03, 134.92, 134.68, 133.92, 132.95, 132.89, 131.95, 130.03, 129.76, 129.46, 128.90, 128.71, 128.61, 128.35, 128.14, 126.85, 126.53, 125.73, 125.46, 124.35 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 18.81$ ppm; IR (neat): $\tilde{\nu} = 3050$, 2922, 1632, 1058, 781, 740, 693 cm^{-1}; MS (EI): *m/z* (%): 340 (6) $[M]^+$, 155 (100), 156 (20), 201 (10); HRMS (ESI): *m/z* calcd for $C_{23}H_{18}OP+H^+$: 341.10898 $[M+H^+]$; found: 341.10857.

Dicyclohexyl 1-naphthoyl phosphine (L14): 1-Naphthoyl chloride (1.0 g, 5.26 mmol) was added dropwise over about 20 min to a solution of dicyclohexylphosphine (1.04 g, 5.26 mmol) and triethylamine (0.64 g, 6.31 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L14** as an orange solid (1.45 g, 78%). The crude product was recrystallized from MeOH. This synthesis produced the desired material in high purity as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.53$–8.44 (m, 1H), 8.27–8.20 (m, 1H), 7.94–7.85 (m, 1H), 7.82–7.75 (m, 1H), 7.53–7.37 (m, 3H), 1.88–1.74 (m, 2H), 1.74–1.43 (m, 8H), 1.29–0.86 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 222.2$, 221.7, 139.89, 139.50, 134.06, 134.03, 132.84, 130.61, 130.32, 129.03, 129.98, 128.43, 127.99, 126.51, 125.48, 124.34, 124.33, 33.04, 32.87, 31.17, 31.04, 29.84, 29.72, 27.49, 27.36, 27.30, 27.18, 26.29 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 28.79$ ppm; IR (neat): $\tilde{\nu} = 2924$, 2850, 1627, 1447, 1234, 1133, 779, 495 cm^{-1}; MS (EI): *m/z* (%): 352 (14) $[M]^+$, 155 (100), 156 (13); HRMS (ESI): *m/z* calcd for $C_{23}H_{30}OP+H^+$: 353.20288 $[M+H^+]$; found: 353.20213.

Diadamantyl 2-naphthoyl phosphine (L15): 1-Naphthoyl chloride (1.0 g, 5.26 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (1.6 g, 5.26 mmol) and triethylamine (0.64 g, 6.3 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L15** as an orange solid (1.59 g, 67%). The crude product was recrystallized from MeOH. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.69$–8.60 (m, 1H), 8.57–8.49 (m, 1H), 8.91–8.85 (m, 1H), 7.98–7.89 (m, 2H), 7.83–7.75 (m, 2H), 7.56–7.41 (m, 2H), 2.10–1.98 (m, 6H), 1.96–1.86 (m, 6H), 1.86–1.78 (m, 6H), 1.64–1.56 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 217.30$, 216.55, 141.73, 141.27, 135.82, 132.79, 132.53, 130.04, 128.54, 128.45, 127.79, 126.68, 123.19, 123.1043.52, 43.39, 41.63, 41.50, 38.66, 38.37, 36.87, 28.93, 28.82 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 38.46$ ppm; IR (neat): $\tilde{\nu} = 2895$, 2845, 1614, 1117, 747 cm^{-1}; MS (EI): *m/z* (%): 456 (22) $[M]^+$, 135 (100), 155 (72); HRMS (ESI): *m/z* calcd for $C_{31}H_{38}OP+H^+$: 457.26548 $[M+H^+]$; found: 457.2645.

(*E*)-1-(Diadamantylphosphino)-3-phenylprop-2-en-1-one (L16): Cinnamoyl chloride (1 g, 6.0 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (1.82 g, 7.1 mmol) and triethylamine (1.0 g, 7.2 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L16** as an orange solid (1.95 g, 75%). The crude product was recrystallized from MeOH. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.91$ (dd, $J = 4.8$ Hz, 1H), 7.55–7.46 (m, 2H), 7.36–7.29 (m, 3H), 6.83–6.71 (m, 1H), 2.06–1.81 (m, 18H), 1.67–1.59 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 216.34$, 145.16, 144.90, 134.83, 134.69, 134.15, 130.60, 128.98, 128.65, 41.58, 41.45, 38.46, 36.89, 28.94, 28.83 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 42.44$ ppm; IR (neat): $\tilde{\nu} = 2896$, 2844, 1603, 1135, 754, 689 cm^{-1}; MS (EI): *m/z* (%): 432 (14) $[M]^+$, 131 (65), 135 (100); HRMS (ESI): *m/z* calcd for $C_{29}H_{38}OP+H^+$: 433.26548 $[M+H^+]$; found: 433.26638.

(Diadamantylphosphino)(quinolin-2-yl)methanone (L17): Quinoline-2-carbonyl chloride (1.0 g, 5.21 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (1.57 g, 5.21 mmol) and triethylamine (0.63 g, 8.5 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L17** as a dark violet solid (1.96 g, 82%). The crude product was recrystallized from MeOH. This synthesis gave rise to the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.21$ (d, $J = 8.5$ Hz, 1H), 8. 61 (d, $J = 8.9$ Hz, 1H), 7.88 (d, $J = 8.5$ Hz, 1H), 7.78–7.25 (m, 1H), 7.70–7.62 (m, 1H), 7.56–7.49 (m, 1H), 2.12–1.89 (m, 12H), 1.85–1.75 (m, 6H), 1.65–1.54 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 219$, 157.1, 157.4, 141.1, 137.1, 131.1, 129.9, 129.5, 128.5, 127.5, 117.7, 41.6, 41.4, 39.2, 38.8, 36.9, 29.1, 28.9 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 45.75$ ppm; IR (neat): $\tilde{\nu} =$

2899, 2846, 1732, 1634, 902, 828, 750 cm^{-1}; MS (EI): *m/z* (%): 457 (22) $[M]^+$, 322 (100), 135 (86); HRMS (ESI): *m/z* calcd for $C_{30}H_{37}NOP+H^+$: 458.26073 $[M+H^+]$; found: 458.26148.

(Dimethylphosphino)(pyridin-2-yl)methanone (L18): Picolinoyl chloride·HCl (1.0 g, 5.6 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (1.7 g, 5.6 mmol) and triethylamine (0.68 g, 6.7 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L18** as a dark violet solid (1.59 g, 70%). The crude product was recrystallized or filtered through a small column. This synthesis produced the desired material in 90% purity as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72–8.65 (m, 1H), 7.83–7.69 (m, 2H), 7.39–7.33 (m, 1H), 2.05–1.84 (m, 12H), 1.84–1.78 (m, 6H), 1.63–1.54 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 220.19, 219.52, 158.31, 157.89, 149.16, 136.89, 136.88, 126.77, 120.92, 120.87, 41.45, 41.31, 38.84, 38.52, 36.82, 28.92, 28.82 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 43.18 ppm; IR (neat): $\tilde{\nu}$ = 3391, 2901, 2847, 1721, 1449, 1138 cm^{-1}; MS (EI): *m/z* (%): 409 (1) $[M]^+$, 135 (100), 155 (63), 352 (5).

(Diadamantylphosphino)(furan-2-yl)methanone (L19): Furan-2-carbonyl chloride (1.0 g, 7.7 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (2.2 g, 7.7 mmol) and triethylamine (0.922 g, 8.5 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L19** as an orange solid (2.5 g, 82%). The crude product was recrystallized from MeOH. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.51 (m, 1H), 7.47–7.43 (m, 1H), 6.46–6.39 (m, 1H), 2.07–1.94 (m, 6H), 1.94–1.78 (m, 12H), 1.70–1.55 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.48, 201.88, 158.25, 157.51, 147.24, 121.94, 121.79, 112.04, 112.02, 41.58, 41.44, 38.55, 38.25, 36.83, 28.88, 28.77 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 41.99 ppm; IR (neat): $\tilde{\nu}$ = 2899, 2883, 2845, 1612, 1244, 765 cm^{-1}; MS (EI): *m/z* (%): 397 (8) $[M]^+$, 135 (100). HRMS (ESI): *m/z* calcd for $C_{25}H_{34}O_2P+H^+$: 397.22909 $[M+H^+]$; found: 397.22969.

(Diadamantylphosphino)(thiophen-2-yl)methanone (L20): Benzoyl chloride (1.0 g, 6.8 mmol) was added dropwise over about 20 min to a solution of diadamantylphosphine (2.05 g, 6.8 mmol) and triethylamine (0.82 g, 8.1 mmol) in THF (10 mL) and stirred for 5 h. The mixture was quenched with H_2O (10 mL) and the product was extracted with CH_2Cl_2 (2×50 mL). The combined CH_2Cl_2 extracts were washed with water (20 mL), dried over Na_2SO_4, and evaporated to give **L20** as an orange solid (2.02 g, 72%). The crude product was recrystallized from MeOH. This synthesis produced the desired material in high purity (>95%) as determined spectroscopically. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–7.96 (m, 1H), 7.61–7.56 (m, 1H), 7.09–7.02 (m, 1H), 2.07–1.94 (m, 6H), 1.94–1.79 (m, 12H), 1.68–1.57 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.34, 152.37, 151.75, 134.52, 134.47, 134.37, 128.09, 41.57, 41.44, 38.60, 38.29, 36.84, 28.90, 28.79 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 44.38 ppm; IR (neat): $\tilde{\nu}$ = 2903, 2885, 2845, 1610, 1197, 798, 727 cm^{-1}; MS (EI): *m/z* (%): 412 (36) $[M]^+$, 135 (100). HRMS (ESI): *m/z* calcd for $C_{25}H_{34}OPS+H^+$: 413.20625 $[M+H^+]$; found: 413.20692.

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of Ad-BellGiPhos-Bz (**L8:** Sigma–Aldrich Catalog No.: 744816), Ad-BellGiPhos-1-Nap (**L11:** Sigma–Aldrich Catalog No.: 744913), and Cy-BellGiPhos-1-Nap (**L14:** Sigma–Aldrich Catalog No.: 744700).

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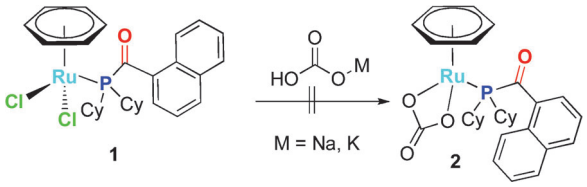

Reaction conditions for the preparation of **2**: a mixture of **1** (100 mg, 0.165 mmol, 1.0 equiv), carbonate ($NaHCO_3$ or K_2CO_3, 5.0 equiv), and solvent (acetone, THF, MeOH) was stirred for 20 h at 25 – 40 °C. Unfortunately, we failed to obtain **2** under different reaction conditions.

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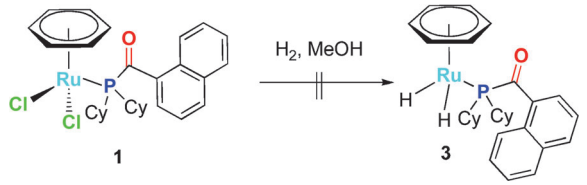

Reaction conditions for the preparation of **3**: complex **1** (100 mg, 0.165 mmol, 1.0 equiv) was dissolved in MeOH ($CHCl_3$, THF). The autoclave was deoxygenated and then filled with H_2 (10 bar) at room temperature. The reaction mixture was stirred (400 rpm) for 10 h at 40 °C. We could not find any up-field shifts characteristic of hydrides in the respective ^1H NMR spectra.

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