Synthesis and Characterization of a Novel Hydrido−Alkyl Complex of Rhodium(III) Formed by Intramolecular Activation of a Benzylic C−H Bond: *trans*-Bis[*N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine]hydridorhodium(III) Hexafluorophosphate

Sven Sjövall, Lars Kloo, Antonios Nikitidis, and Carlaxel Andersson*

Inorganic Chemistry 1, Centre for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

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The phosphine *N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine (**1**), reacting with the precursor complex [Rh(NBD)L][PF_6] (L = **1**, NBD = 2,5-norbornadiene) and molecular hydrogen under ambient conditions, undergoes chelate-assisted C−H bond activation at the benzylic position, quantitatively yielding the five-membered chelate complex *trans*-[RhH(P(C_6H_4-*o*-($CH_2N(CH_3)COCH_2CH_3$))(C_6H_5)$_2$)(P(C_6H_4-*o*-($CHN(CH_3)COCH_2CH_3$))(C_6H_5)$_2$)][PF_6] (**4**). Extensive spectroscopic studies demonstrate that the rhodium is located in the center of a square bipyramid with an apical hydrogen.

Introduction

Alkanes are abundant in nature and are relatively inexpensive, and any chemical synthesis involving utilization of hydrocarbons would be of commercial and environmental importance. Therefore, any possibility to activate unreactive C−H bonds (bond energies in the range of 90−100 kcal/mol and very low basicity/acidity) has been of major interest, but a difficult task, to chemists for the last few decades. Alkanes have long been known to undergo a number of solution and gas-phase reactions involving free radicals as intermediates, such as photochlorination, autoxidation, and combustion. More recently, "super acids" have been developed that are capable of adding protons to alkanes.[1]

A general problem is controlling the selectivity in hydrocarbons possessing different C−H bonds and making sure that the C−H bonds in the product are not more reactive than those in the starting alkane, or low yields will be inevitable.[2] A fruitful way to achieve this in chemical synthesis is to use the versatile reactivity of the carbon−metal bond, and this has been done in homogeneous reactions with transition-metal complexes treated with reactive substrates.[3ab]

The so-called "ortho metalation" reaction and chelate-assisted insertion into C−H bonds are special examples of C−H bond activation. The latter reaction type, also possible in insertion into C−C and Si−H bonds, occurs readily using bifunctional phosphine[4a−c] or 8-quinoline[5ab] ligands in combination with electron-rich late-transition-metal centers. A favorable change in entropy[6] provides the energy for the cyclometalation processes, and therefore the substituent pattern of the reacting ligand is of importance; ligands with the ability to form five- or six-membered cyclometalated products are the ones prone to undergo the insertion reaction. Most examples reported concern phosphine ligands carrying a polar functional group (amide, ether) in proximity to the reacting C−H bond, but insertion of Rh(III) into the C−H bond of the methyl group in tri-*o*-tolylphosphine has also been observed.[7] Part of the current interest in cyclometalated complexes stems from a recent discovery; palladium insertion into the methyl C−H bond of tri-*o*-tolylphosphine gives thermally stable palladacycles, which are highly active as catalysts in C−C bond-forming reactions.[8,9] An ongoing project in our group is to synthesize new metallacyclic complexes by intramolecular C−H activation of suitable phosphine ligands, using late transition metals and different bulky phenyl phosphines. The aim is partly to find general information about how the reactivity and selectivity leading to C−H activation depend on the nature of the side chains in phenylphosphines and partly to determine whether metallacycle formation enhances catalytic activity or causes catalyst deactivation.[9] As an immediate consequence of this we now report a new rhodium-containing complex (**4**) formed by transition-metal insertion into a benzylic C−H bond.

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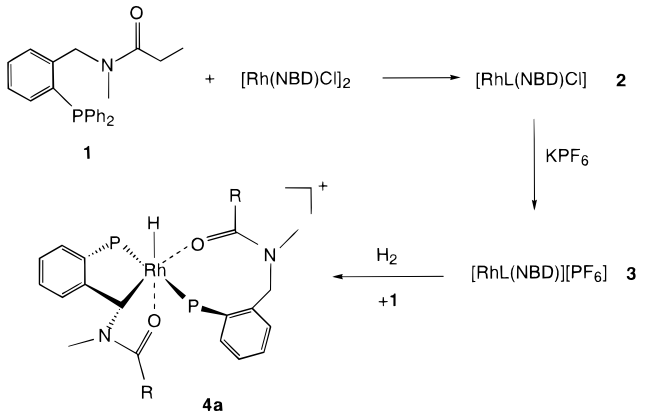
Scheme 1[a]



[a] Legend: NBD = 1,5-norbornadiene; R = Et; L = DPPBA. Phenyls on P are omitted for clarity in **4a**.

Results and Discussion

A dichloromethane solution of the dimeric rhodium−olefin complex $[Rh(NBD)Cl]_2$ (NBD = 2,5-norbornadiene) and 2 equiv of the ligand DPPBA (**1**; *N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine), stirred for 1 h at room temperature, yields after workup a yellow complex with the composition [Rh(NBD)(DPPBA)Cl] (**2**) (Scheme 1).

A $^{31}P\{^1H\}$ NMR spectroscopic analysis of this complex exhibits two doublets at 22.7 ($^1J_{RhP}$ = 164 Hz) and 22.1 ppm ($^1J_{RhP}$ = 165 Hz), respectively. The protons of the *N*-methyl group, N−C**H**$_3$, display two singlets in the ^1H NMR spectrum positioned at 3.15 and 3.05 ppm, respectively. The relative intensity of the two ^{31}P peaks, also seen for the two *N*-methyl ^1H peaks, is 1:0.7, clearly indicating an equilibrium between two isomers, probably caused by two different rotational conformations of the amide. The value of $^1J_{RhP}$ is typical for a rhodium(I)-complexed monodentate phosphine ligand trans to an alkene.[10] The infrared spectroscopic analysis shows two strong amide carbonyl absorptions at 1655 and 1645 cm^{-1}, which exactly match the frequencies of the free ligand **1**. Collective IR and NMR spectroscopic data for **2** are thus in agreement with a complex expected from a bridge cleavage of the precursor, the ligand **1** coordinating monodentately by its P donor and cis to the chloride ligand.

Carrying out an anion metathesis with complex **2** and potassium hexafluorophosphate yields the complex [Rh(NBD)(DPPBA)][PF_6] (**3**) (Scheme 1). Its amide carbonyl group stretching frequencies, at 1577 and 1569 cm^{-1}, are shifted to lower wavenumbers relative to the free ligand, thus indicating coordination of the carbonyl group to the formally three-coordinate metal center. P−O chelate coordination implies a fixed conformation of the phosphine ligand in complex **3,** and this is confirmed by the NMR spectroscopic data with the $^{31}P\{^1H\}$ NMR spectrum at −20 °C exhibiting a doublet at 24.5 ppm ($^1J_{RhP}$ = 167 Hz) and the ^1H NMR spectrum at −20 °C exhibiting a singlet at 2.58 ppm for N−C**H**$_3$.

Treatment of complex **3** with 1 equiv of ligand **1** under an atmosphere of hydrogen for 120 min at room temperature yields the complex [RhH(DPPBA)$_2$][PF_6] (**4**) (Scheme 1). The FAB mass spectrum, with the molecular ion peak at *m*/*z* 825, indicates a monomeric structure for **4**. An independent osmotic molecular weight determination supports this interpretation. In addition, an elemental analysis verifies the stoichiometric composition of **4**.

All attempts to grow single crystals of **4** have so far failed, and its structural features are therefore based on spectroscopic evidence. All NMR spectroscopic analyses of complex **4** were performed at −20 °C in order to slow down the dynamic processes, probably caused by the weak coordination of the amide oxygens to the transition-metal center. On the basis of ^{31}P and ^1H spectra alone it is evident that the complex contains two nonequivalent phosphine ligands and a hydride. The results obtained by $^{31}P\{^1H\}$ NMR spectroscopy reveal an ABX pattern with two doublets of doublets at 55.5 ($^1J_{RhP(1)}$ = 119 Hz, $^2J_{P(1)P(2)}$ = 401 Hz) and 33.7 ppm ($^1J_{RhP(2)}$ = 115 Hz, $^2J_{P(2)P(1)}$ = 401 Hz), respectively. The various coupling constants were verified by a $^{31}P\{^1H\}$ COSY NMR spectrum (Figure 1).

The ^1H NMR spectrum of **4** exhibits a hydride signal, a doublet of doublets of doublets, at −16.8 ppm with an intensity equal to one hydrogen. A $^1H\{^{31}P\}$ NMR experiment results in collapse of the hydride signal into a doublet at −16.8 ppm ($^1J_{RhH}$ = 24.7 Hz). Irradiation of the phosphorus signal at 55.5 ppm results in collapse into a doublet of doublets at −16.8 ppm ($^1J_{RhH}$ = 24.7 Hz, $^2J_{P(2)H}$ = 13.6 Hz). Analogously, irradiation of the other phosphorus signal at 33.7 ppm also gives a doublet of doublets at −16.8 ppm ($^1J_{RhH}$ = 24.7 Hz, $^2J_{P(1)H}$ = 8.84 Hz). Furthermore, the ^1H NMR spectrum exhibits three nontrivial resonances, with intensities equivalent to one hydrogen each, a doublet of doublets at 6.37 ppm and a doublet at 4.23 and 3.50 ppm, respectively. The assignment of these resonances follows from the ^1H COSY pattern, which reveals that the signals at 6.37 and 3.50 ppm are coupled and are interpreted to stem from the benzylic protons. Hence, the benzylic protons in one of the ligands are diastereotopic, which is in accord with different chemical environments above and below the plane of the aryl ring. On the other hand, the doublet at 4.23 ppm shows no ^1H coupling and this feature is indicative of rhodium insertion into the benzylic C−H bond of the second phosphine ligand, leaving a single proton at the benzylic carbon and unmasking the other proton as the observed hydride ligand. Combined with the $^1H\{^{31}P\}$ spectrum it is possible to determine the coupling constants: $^2J_{HH}$ = 14.8 and $^4J_{PH}$ = 3.90 Hz at 6.37 ppm, $^3J_{PH}$ = 15.3 Hz at 4.23 ppm, $^2J_{HH}$ = 14.8 Hz at 3.50 ppm. The different proton−phosphorus couplings observed, the proton resonance at 4.23 ppm being more strongly coupled, provide further evidence for the formation of a metallacycle by insertion into the benzylic C−H bond.

Final proof of the formation of a metallacyclic structure is obtained by further NMR experiments. The $^{13}C\{^1H\}$ NMR spectrum exhibits two different sets of signals, which is in accord with the two phosphine ligands being nonequivalent. Interestingly, there is a sharp doublet at 53.7 ppm and a broad doublet at 61.8 ppm. These stem from the benzylic carbons. In our interpretation, the splitting of the former is caused by a $^3J_{PC}$ (=5.13 Hz) coupling, and the splitting of the latter

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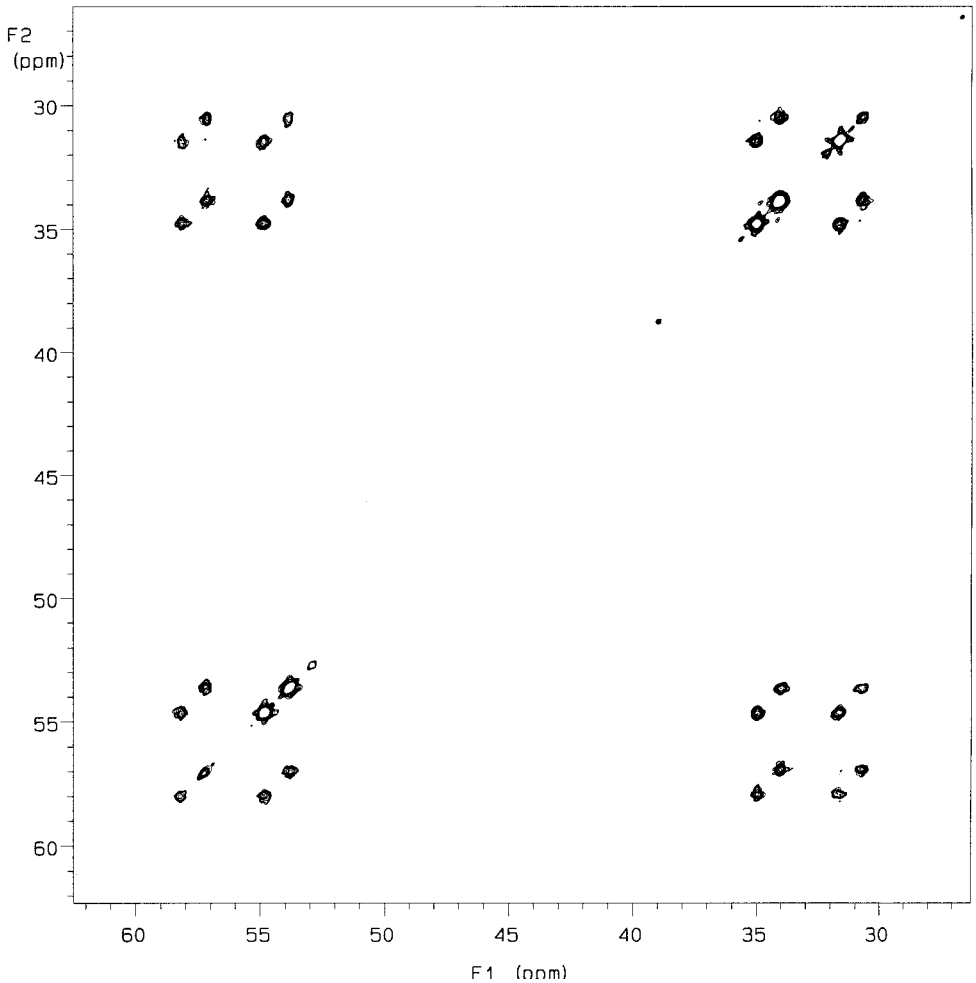

Figure 1. $^{31}P\{^{1}H\}$ COSY NMR spectrum of complex **4**.

Table 1. ^{1}H and ^{13}C Chemical Shifts and Coupling in the HMQC Spectrum of 4[a,b]

functional group	^{13}C	^{1}H
CH_3−	9.80	0.55
CH_3−	10.7	0.75
CH_3**CH_2**−	29.2	1.10; 1.48
CH_3**CH_2**−	30.4	1.48; 1.72
N−**CH_3**	36.1	1.89
N−**CH_3**	42.5	3.08
−**CH_2**−	53.7	3.50; 6.37
=**CH**−	61.8	4.23

[a] In CD_2Cl_2 at −20 °C. [b] Omitting chemical shifts of phenyls for clarity.

is caused by a $^{1}J_{RhC}$ (=31.1 Hz) coupling. $^{1}J_{RhC}$ coupling constants in the range of 31−40 ppm have been reported.[11ab] In order to verify this interpretation, an HMQC NMR experiment (2D inverse H,C correlation, where $^{1}J_{CH}$ spin couplings can be detected) was made (Table 1). The ^{13}C signal at 61.8 ppm couples to the ^{1}H signal at 4.23 ppm, and the ^{13}C signal at 53.7 ppm couples to the ^{1}H signals at 6.37 and 3.50 ppm. Unfortunately, the broad peaks in the 2D spectrum hamper the extraction of the individual $^{1}J_{CH}$ coupling constants.

Once the metallacyclic structure is verified, further features in the $^{31}P\{^{1}H\}$ spectrum are worth considering. The large coupling constant (J_{PP} = 401 Hz) is a consequence of the two phosphine ligands being mutually trans.[12] The magnitude of the coupling constant can also be explained in terms of trans influence, where both the hydride and the methine group impose greater trans influence than the phosphorus.[13] The signal at lower field is assigned to the phosphorus in the metallacycle, which falls within the well-known range 20−50 ppm downfield for a phosphorus involved in a five-membered chelate relative to its noncoordinated analogue.[14ab] Furthermore, the J_{RhP} value for the chelating ligand is larger than the J_{RhP} value for the unmetalated ligand, which opposes the trend seen in platinum complexes when the phosphorus atoms are trans.[15]

By running an HMBC NMR experiment (2D inverse H,C long-range correlation, where $^{2}J_{CH}$ and $^{3}J_{CH}$ spin couplings can be detected) and comparing the results with ^{1}H and ^{13}C NMR spectroscopic data, it is also possible to determine the chemical shifts versus the position of all the atoms in the side chains of the ligands (Table 2). Once again, the broad peaks in the 2D spectrum hamper the extraction of the individual $^{2}J_{CH}$ and $^{3}J_{CH}$ coupling constants.

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Table 2. ^{1}H and ^{13}C Chemical Shifts and Coupling in the HMBC Spectrum of 4[a]

functional group	^{13}C	^{1}H
−(**C**═O)−	182	6.37; 3.50; 3.08; 1.72; 1.48; 0.75
−(**C**═O)−[b]	179	4.23; 1.89; 1.48; 1.10; 0.55

[a] In CD_2Cl_2 at −20 °C. [b] The chelating ligand.

The two amide carbonyl stretching frequencies, at 1595 and 1575 cm^{-1}, are shifted to lower wavenumbers relative to the free ligand, verifying that the carbonyl groups in the ligands are nonequivalent and are coordinated to the rhodium atom.

This leaves us with the task of describing the actual geometry of the complex. The compound is a six-coordinate Rh(III) complex, regular or distorted, with the ligand donor set {**P**, **P**, **H**, −**C**H−, C═**O**, C═**O**}. On the basis of the large J_{PP} coupling a trans position of the two P-donors is highly likely, and this reduces the number of possible combinations. Furthermore, the P donor of the ligand forming the metallacycle is at the terminus, thus capping one of the triangular faces of the octahedron. Face capping is achieved by two five-membered metallacycles, Rh−P−C and Rh−O−C, which are interconnected by the methine carbon. This leaves two possibilities for the hydride ligand; either trans to the amide oxygen of the face-capping ligand or trans to the methine carbon atom. The rather low Rh−H stretching frequency (2070 cm^{-1}) indicates that the hydride is situated trans to a ligand high in the trans-influence series,[16] i.e. the methine carbon. However, taking the trans influence of both the hydride and the methine carbon and the results of a previous publication[17] into account, it is more likely that the hydride is located trans to the amide oxygen. The weak coordination of the second amide oxygen, trans to the methine carbon atom, then completes the octahedral coordination.

This complex shows remarkable stability under an atmosphere of air, as a solid for years and in a homogeneous solution for several weeks, which is an unusual feature for oxidative-addition products from the second row of the transition metals.[18]

Conclusion

The complex [RhH(DPPBA)$_2$][PF$_6$] (**4**) is rapidly formed by insertion into a benzylic C−H bond of one of the ligands. The major driving force for the C−H activation is the formation of a chelate, but steric and electronic factors are also of importance. Hydrogenation of the π-accepting norbornadiene ligand in the precursor **3** and simultaneous coordination of an additional σ-donating phosphine increase the steric crowding as well as the electron density at the Rh center. We believe that the steric bulk of the phosphine ligand, which brings the alkane bonds into the vicinity of the rhodium atom, plays a minor role compared to the electronic factor. In addition, the capability to form resonance structures in the side chains of the ligands enhances the acidity of the benzylic protons, thereby making oxidative addition by an electron-rich metal center more plausible. Furthermore, we believe that the hydride in complex **4** stems from the activated benzylic group, after passing through an intermediate dihydrido complex.[19ab] This is, of course, speculative, and an isotopic labeling experiment could clarify this.

Experimental Section

All experiments with metal complexes and the phosphine ligand were performed under an atmosphere of argon using standard Schlenk techniques. All non-deuterated solvents, reagent grade or better, were distilled over sodium/benzophenone ketyl under an atmosphere of nitrogen. Deuterated solvents were used as received. All solvents were thoroughly deoxygenated with argon prior to use. Commercially available reagents were used as received. The complex [Rh(NBD)Cl]$_2$ and the phosphine ligand DPPBA were prepared according to literature procedures.[20 21]

^{1}H and ^{31}P NMR spectra were recorded at 300 and 121 MHz, respectively, using a Varian Unity 300 MHz spectrometer. ^{13}C, ^{1}H COSY, HMBC, and HMQC NMR spectra were recorded at 125 and 500 MHz, respectively, using a Bruker ARX 500 MHz spectrometer. Unless otherwise stated, the NMR measurements were performed in CD_2Cl_2. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{1}H and ^{1}H COSY NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.25 ppm, chloroform; 5.31 ppm, dichloromethane; 2.50 ppm, DMSO). In the ^{13}C{^{1}H} NMR measurements the signal of CD_2Cl_2 (55.8 ppm) was used as reference. In the HMQC and HMBC experiments the same references were used separately as in the ^{1}H and ^{13}C{^{1}H} NMR measurements. ^{31}P NMR chemical shifts are reported in parts per million downfield from an external 85% solution of phosphoric acid. Abbreviations used in the description of NMR spectroscopic data are as follows: s, singlet; d, doublet; m, multiplet; b, broad; q, quartet; t, triplet. Fast atom bombardment (FAB) mass spectroscopic data were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Infrared spectra were recorded on a Bio-Rad FTS 6000 FT-IR spectrometer. Elemental analyses were performed by AB Mikro Kemi, Uppsala, Sweden.

Reaction of [Rh(NBD)Cl]$_2$ with Ligand 1. Formation of [Rh(NBD)(DPPBA)Cl] (2). To a dichloromethane solution (5 mL) of [Rh(NBD)Cl]$_2$ (235 mg, 0.501 mmol) was added a dichloromethane solution (10 mL) of DPPBA (**1**). After it was stirred for 1 h, the solution was reduced to 5 mL and *n*-hexane (40 mL) was added. The solution was reduced to 10 mL, yielding a yellow precipitate, which was filtered, washed with *n*-hexane (20 mL), and dried under vacuum. Yield: 490 mg (79%). ^{31}P{^{1}H} NMR in $CDCl_3$: 22.7 (d, $^1J_{RhP}$ = 164 Hz), 22.1 (d, $^1J_{RhP}$ = 165 Hz) (relative intensity of the doublets is 1:0.7). ^{1}H NMR in $CDCl_3$: 5.85 (bs, 1H, NBD), 5.50 (bs, 1H, NBD), 5.35 (bs, 2H, NBD), 3.80 (bs, 2H, Ar−C**H**$_2$−), 3.40 (bs, 2H, NBD), 3.15 (s, N−C**H**$_3$), 3.05 (s, N−C**H**$_3$), 2.55 (q, $^3J_{HH}$ = 7.50 Hz, −C**H**$_2$−), 2.31 (q, $^3J_{HH}$ = 7.50 Hz, −C**H**$_2$−), 1.47 (bd, 2H, NBD), 1.27 (t, $^3J_{HH}$ = 7.50 Hz, −C**H**$_3$), 1.14 (t, $^3J_{HH}$ = 7.50 Hz, −C**H**$_3$) (relative intensity of the alkane signals is 1:0.7). IR (CsI): 1655 and 1645 cm^{-1} (s, C═O). Anal. Calcd: C, 60.9; H, 5.5; P, 5.2. Found: C, 61.2; H, 5.9; P, 4.8.

Reaction of [Rh(NBD)(DPPBA)Cl] (2) with KPF$_6$. Formation of [Rh(NBD)(DPPBA)][PF$_6$] (3). To a dichloromethane solution (15 mL) of [Rh(NBD)(DPPBA)Cl] (**2**; 260

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mg, 0.439 mmol) was added an aqueous solution (7 mL) of potassium phosphate (298 mg, 1.62 mmol). After 1.5 h the organic layer was removed, washed with water (4 × 10 mL), and reduced to ca. 3 mL under vacuum. A 15 mL portion of diethyl ether was added slowly to complete the precipitation. The yellow precipitate was filtered, washed with diethyl ether (3 × 10 mL), and air-dried. Yield: 290 mg (94%). $^{31}P\{^1H\}$ NMR in DMSO: 24.5 (d, $^1J_{RhP} = 167$ Hz). ^1H NMR in DMSO: 7.80−6.90 (m, 14H, aromatic), 5.68 (bd, 2H, Ar−C**H**$_2$−), 4.31 (bs, 4H, NBD), 3.80 (bs, 2H, NBD), 2.58 (s, 3H, N-C**H**$_3$), 1.61 (q, $^3J_{HH} = 7.36$ Hz, 2H, −C**H**$_2$−), 1.22 (bs, 2H, NBD), 0.57 (t, $^3J_{HH} = 7.36$ Hz, 3H, −C**H**$_3$). IR (CsI): 1577 and 1569 cm^{-1} (s, C═O). Anal. Calcd: C, 51.7; H, 4.6; N, 2.0; P, 8.8. Found: C, 51.6; H, 4.8; N, 2.0; P, 8.8.

Reaction of [Rh(NBD)(DPPBA)][PF$_6$] (3) with Ligand 1. Formation of [Rh(DPPBA)$_2$H][PF$_6$] (4). A dichloromethane solution (5 mL) of DPPBA (**1**; 52.9 mg, 0.15 mmol) and [Rh(NBD)(DPPBA)][PF$_6$] (**3**; 102 mg, 0.15 mmol) was cooled to −10 °C. The argon atmosphere was replaced by molecular hydrogen, and the solution was warmed to room temperature at ambient pressure. After 2 h the reaction was terminated by adding 20 mL of diethyl ether, yielding a white precipitate. The cold suspension (−30 °C) was filtered, and the precipitate was washed with diethyl ether (2 × 10 mL). Yield: 108 mg (74%). $^{31}P\{^1H\}$ NMR: 55.5 (dd, $^1J_{RhP(1)} = 119$ Hz, $^2J_{P(1)P(2)} = 401$ Hz), 33.7 (dd, $^1J_{RhP(2)} = 115$ Hz, $^2J_{P(2)P(1)} = 401$ Hz). ^1H NMR: 7.65−7.15 (m, 28H, Ar), 6.37 (dd, $^2J_{HH} = 14.8$ Hz, $^4J_{PH} = 3.90$ Hz, 1H, Ar−C**H**$_2$−), 4.23 (d, $^3J_{PH} = 15.3$ Hz, 1H, Ar−C(R)**H**−Rh), 3.50 (d, $^2J_{HH} = 14.8$ Hz, 1H, Ar−C**H**$_2$−), 3.08 (s, 3H, N−C**H**$_3$), 1.89 (s, 3H, N−C**H**$_3$), 1.72 (m, 1H, −C**H**$_2$−), 1.48 (dm, 2H, −C**H**$_2$−), 1.10 (m, 1H, −C**H**$_2$−), 0.75 (t, $^3J_{HH} = 7.34$ Hz, 3H, −C**H**$_3$), 0.55 (t, $^3J_{HH} = 7.34$ Hz, 3H, −C**H**$_3$), −16.8 (ddd, $^1J_{RhH} = 24.7$ Hz, $^2J_{P(2)H} = 13.6$ Hz, $^2J_{P(1)H} = 8.84$ Hz) (assignment of ^1H NMR signals was confirmed by $^1H\{^{31}P\}$ and ^1H COSY NMR experiments). $^{13}C\{^1H\}$ NMR: 182 (s, −**C**(═O)−), 179 (s, −**C**(═O)−), 144−128 (md, **Ar**), 61.8 (bd, $^1J_{RhC} = 31.1$ Hz, Ar−**C**(R)H−Rh), 53.7 (d, $^3J_{PC} = 5.13$ Hz, Ar−**C**H$_2$−), 42.5 (s, N−**C**H$_3$), 36.1 (s, N−C**H**$_3$), 30.4 (s, −**C**H$_2$−), 29.2 (s, −**C**H$_2$−), 10.7 (s, −**C**H$_3$), 9.80 (s, −**C**H$_3$) (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by HMQC and HMBC NMR experiments). IR (Nujol): 2070 cm^{-1} (m, Rh−H), 1595 and 1575 cm^{-1} (s, C═O). FAB/MS: *m*/*z* 825, M$^+$. Anal. Calcd: C, 56.8; H, 5.1; N, 2.9; P, 9.6. Found: C, 56.4; H, 4.9; N, 2.8; P, 9.3.

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