

Preparation and Characterization of Ruthenium(II) Monophosphaferrocene Complexes. Reactivity, Dynamic Solution Behavior, and X-ray Structure of [RuH₂(η²-H₂)(PCy₃)₂(2-phenyl-3,4-dimethylphosphaferrocene)]

Andrew J. Toner,^{†,‡} Bruno Donnadieu,^{†,§} Sylviane Sabo-Etienne,^{*,†} Bruno Chaudret,[†] Xavier Sava,^{||} François Mathey,^{||} and Pascal Le Floch^{||}

Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 04, France, and Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653, Ecole Polytechnique, 91128 Palaiseau Cedex, France

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The bis(dihydrogen) complex RuH₂(H₂)₂(PCy₃)₂ (**1**) reacts with 2-phenyl-3,4-dimethylphosphaferrocene (**L**₁) to give RuH₂(H₂)(PCy₃)₂(**L**₁) (**2**). This dihydride–dihydrogen complex has been characterized by X-ray crystallography and variable-temperature ¹H and ³¹P NMR spectroscopy. The exchange between the dihydrogen ligand and the two hydrides is characterized by a ΔG[‡] of 46.2 kJ/mol at 263 K. H/D exchange is readily observed when heating a C₇D₈ solution of **2** (*J*_{H–D} = 30 Hz). The H₂ ligand in **2** can be displaced by ethylene or carbon monoxide leading to the corresponding ethylene or carbonyl complexes. The reaction of **1** with 2 equiv of 3,4-dimethylphosphaferrocene (**L**₂) yields the dihydride complex RuH₂(PCy₃)₂(**L**₂)₂ (**5**).

Introduction

Widespread research in the activation of C–H bonds is manifest in the wealth of publications found in the current literature.¹ More particularly, the activation of aryl C–H bonds has been recently exploited by Murai et al. to achieve the functionalization of a wide variety of aromatic compounds via the catalytic formation of carbon–carbon bonds.²

Our current interest has been stimulated by mechanistic studies on the catalytic alkylation of aryl-substituted ketones (benzophenone and acetophenone).³ We have found that catalytic ethylene insertion can be achieved by the bis(dihydrogen) complex RuH₂(H₂)₂(PCy₃)₂ (**1**),⁴ at room temperature. Similar catalytic activity was observed in the presence of the pre-isolated orthometalated complexes RuH(H₂)(PCy₃)₂(**L**) (**L** = acetophenato or benzophenato), confirming the presence of intermediary

orthometalated species in the catalytic cycle postulated by Murai.² We have also reported the orthometalation of 2-phenylpyridine by **1** leading to a hydrido, dihydrogen complex [RuH(H₂)(PCy₃)₂(*o*-C₆H₄py)] exhibiting quantum mechanical exchange couplings between the cis-disposed hydride and dihydrogen ligands.³ The protonation of the corresponding Pⁱ-Pr₃ complex with 1 equiv of HBARf·2Et₂O (BARf = [3,5-(CF₃)₂-(C₆H₃)₄B]) affords a novel hydrido, dihydrogen complex [RuH(H₂)(PⁱPr₃)₂(*o*-C₆H₅py)][BARf] containing a labile, agostic aryl C–H bond. This complex was shown to be in equilibrium with a metalated bis(dihydrogen) species.⁵

In light of these results we have extended the scope of possible substrates suitable for activation, but which retain the propensity to undergo orthometalation reactions, to include ligands with more diverse functionalities. Substituted monophosphaferrocenes offer us this possibility as, in addition to other reactive sites, they retain their lone pair donor capability.⁶ Recently these complexes, which incorporate an sp²-hybridized phosphorus atom, have been the subject of intense research work as a result of their inherent planar chirality.⁷ Some of us⁸ have recently prepared the first derivatives of Rh(I) and Ir(I) containing nonchiral monophosphaferrocenes with the aim of probing the catalytic activity in this new class of compound. Herein we report the reactivity of **1**, which is already known to exhibit a wide variety of chemical transformations,^{3–5,9} with 2-phenyl-3,4-dimethylphosphaferrocene (**L**₁), in which a phenyl substituent is readily available for orthoruthenation. We have also considered the chemistry of the non-α-substituted 3,4-dimethylphosphaferrocene (**L**₂) with the same ruthenium precursor to provide the first examples of ruthenium polyhydride complexes containing monophosphaferrocenes.

* To whom correspondence should be addressed. E-mail: sabo@lcc-toulouse.fr.

[†] Laboratoire de Chimie de Coordination du CNRS.

[‡] Current address: Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland.

[§] X-ray crystal structure analysis.

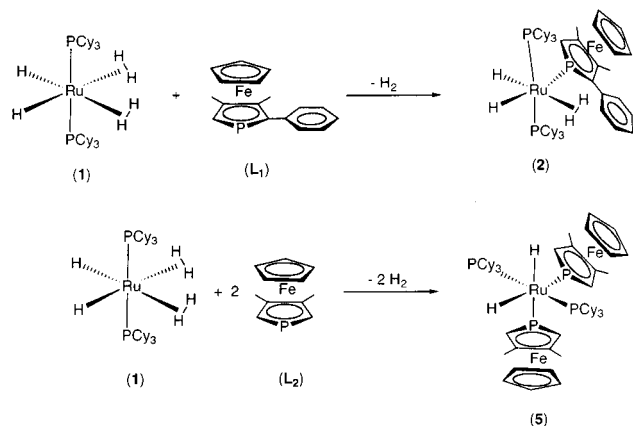
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Scheme 1



Results and Discussion

Synthesis and Spectroscopic Properties of [RuH₂(η^2 -H₂)(PCy₃)₂(2-phenyl-3,4-dimethylphosphaferrocene)] (2). The complex [RuH₂(η^2 -H₂)(PCy₃)₂(L₁)] (2) is readily prepared by stirring an equimolar, heterogeneous mixture of RuH₂(H₂)₂(PCy₃)₂ (1) and 2-phenyl-3,4-dimethylphosphaferrocene (L₁) in pentane at -20 °C (see Scheme 1). After the evolution of dihydrogen has ceased, filtration of the subsequent orange solution and cooling overnight affords 2·2C₅H₁₂ as small, orange cubes suitable for single-crystal X-ray diffraction. Microcrystalline samples of 2 can be isolated free of cocrystallized solvent by drying in a stream of argon. Complex 2 is very air sensitive and unusually unstable in the solid state, in the presence or in the absence of a dihydrogen atmosphere, yielding an intractable black solid.

The ¹H NMR spectrum (400 MHz) of 2 in toluene-*d*₈ at ambient temperature shows, as expected, a broad signal, with a half peak-height line width of 109 Hz, at -8.15 ppm consistent with the fast exchange of all the metal-bound hydrogen atoms. Other pertinent features include the nonequivalent methyl resonances (2.37 and 2.48 ppm), indicative of the planar chirality in the monophosphaferrocene precursor, a doublet (3.52 ppm) for the lone proton within the same π -ligand which has a reduced coupling constant (²J_{P-H} = 31 Hz), and a sharp singlet at 4.25 ppm for the unsubstituted iron-bound cyclopentadienyl ligand. However, most noteworthy is the retention of both *ortho* phenyl protons in 2 which shows the reluctance of the monophospha-

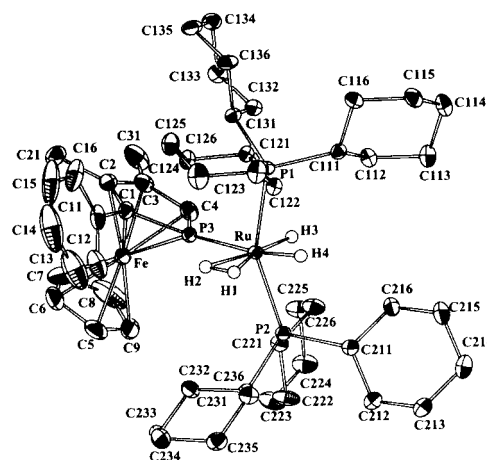


Figure 1. ZORTEP view (50% probability ellipsoids) of [RuH₂(η^2 -H₂)(PCy₃)₂(2-phenyl-3,4-dimethylphosphaferrocene)] (2). Selected bond lengths (Å): Ru–P(1), 2.3271(10); Ru–P(2), 2.3281(10); Ru–P(3), 2.2797(10); Ru–H(1), 1.70(3); Ru–H(2), 1.71(3); Ru–H(3), 1.60(4); Ru–H(4), 1.54(4); H(1)–H(2), 0.87(3). Selected bond angles (deg): P(1)–Ru–P(2), 154.39(3); P(1)–Ru–P(3), 96.08(4); P(2)–Ru–P(3), 103.16(4); P(3)–Ru–H(4), 172.0(15); H(3)–Ru–H(1), 163(2); H(2)–Ru–H(3), 167.7(19).

Table 1. Crystallographic Data for 2

formula	C ₅₃ H ₈₇ FeP ₃ Ru (0.75 pentane)
fw	1030.66
space group	P ₂ /c
a, Å	12.2591(14)
b, Å	13.7902(13)
c, Å	34.848(4)
β , deg	94.636(14)
Z; calcd density, mg/m ³	4; 1.1666
temp, K	140(2)
V, Å ³	5872.0(11)
λ , Å	0.710 73
μ , mm ⁻¹	0.618
R1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0439
wR2	0.1136

ferrocene to undergo an orthometalation reaction at room temperature (*vide infra*). Integration, with a repetition time delay of 30 s, of all the observed resonances, is consistent with the proposed structure for 2. The ³¹P{¹H} NMR spectrum of 2 at room temperature shows a triplet at 33.61 ppm (²J_{P-P} = 25 Hz) and a broad signal at 75.53 ppm.

The molecular structure of 2, depicted in Figure 1, confirms the displacement of one dihydrogen ligand from 1 by the phosphosphaferrocene ligand acting as a two electron donor ligand. Crystal data are reported in Table 1. The structure is approximately octahedral with two *trans* tricyclohexylphosphines (the P1–Ru–P2 angle is 154.39(3)°) bent away from the phosphosphaferrocene ligand to reduce steric repulsion (the P3–Ru–P1 and P3–Ru–P2 angles are 96.08(4) and 103.16(4)°, respectively). The Ru–H bond lengths vary from 1.54(4) to 1.71(3) Å, and the dihydrogen ligand is characterized by a H1–H2 distance of 0.87(3) Å. The phosphosphaferrocene coordination to the ruthenium is characterized by a Ru–P(3) distance of 2.2797(10) Å, slightly shorter than the Ru–P1 and Ru–P2 values (2.3271(10) and 2.3281(10) Å, respectively) and an angle Ru–P3–Ct of 160.2° (Ct for P–C1–C2–C3–C4 centroid) reflecting the strong s character of the phosphorus lone pair.

Dynamic Behavior of 2. Complex 2 is fluxional on the NMR time scale. The process can be followed by ¹H and ³¹P NMR spectroscopies. The variable-temperature, high-field ¹H NMR spectra (400 MHz) obtained on cooling a sample of 2 in toluene-*d*₈ are shown in Figure 2. At 293 K, a single broad resonance

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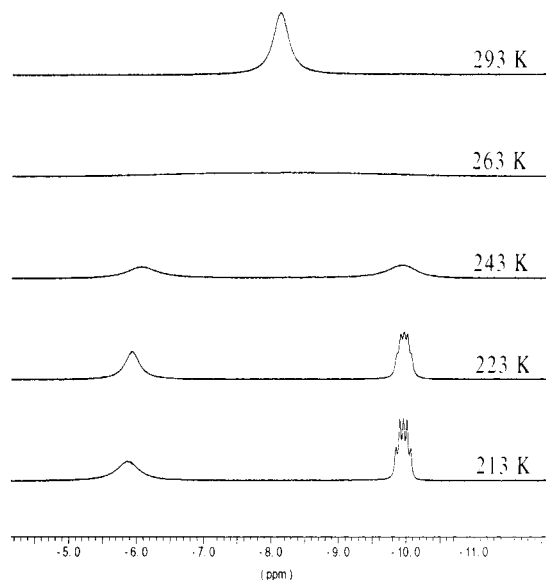


Figure 2. ^1H NMR spectra (400.13 MHz) of **2** in C_7D_8 at various temperatures.

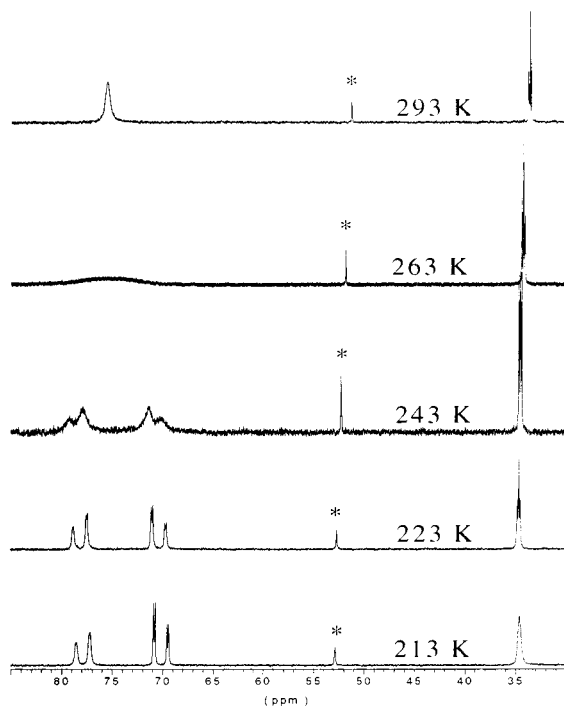
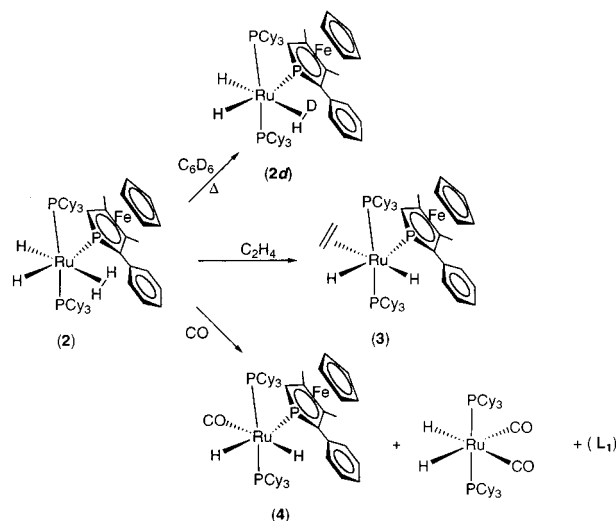


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (161.98 MHz) of **2** in C_7D_8 at various temperatures (asterisk = impurity).

is observed at -8.15 ppm assigned to the four hydrogen atoms in fast exchange. Coalescence is observed at 263 K leading to two broad signals at -6 and -10 ppm of equal intensity. The latter signal appears as a pseudoquintet at 213 K. The exchange between the dihydrogen ligand and the two hydrides is characterized by a ΔG^\ddagger of 46.2 kJ/mol at 263 K. T_1 measurements were performed using the inverse-recovery method. The minimum is observed at 263 K (37 ms), and as the temperature is decreased further, the T_1 values for the two signals increase but much faster for the signal at -10 ppm. The variable-temperature, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained on cooling a sample of **2** in toluene- d_8 are shown in Figure 3. The spectrum shows at 293 K a triplet at 33.61 ppm ($^2J_{\text{P-P}} = 24$ Hz) assigned to the phosphorus (P_C) of the phosphaferrrocene ligand coupled to the two PCy_3 (P_A and P_B) which resonate as a broad signal at 75.53

Scheme 2



ppm. A coalescence occurs at 263 K, and at 243 K, the triplet remains unchanged whereas the broad signal is resolved into a broad AB spectrum. The activation energy for this process is $\Delta G^\ddagger = 46.7$ kJ/mol at 263 K, thus identical to the value found by ^1H NMR for the exchange between the hydrides and the dihydrogen ligand. Finally at 213 K, the signal at 34.4 becomes broad and the AB spectrum is now well defined by two doublets of doublets ($\delta(\text{P}_\text{A}) = 77.7$ ppm, $\delta(\text{P}_\text{B}) = 70.0$, $^2J_{\text{A-B}} = 215$ Hz and $^2J_{\text{A-C}} = ^2J_{\text{B-C}} = 24$ Hz). The values of the coupling constants are in agreement with a trans position for the two PCy_3 groups and a cis position for the phosphaferrrocene ligand. It can be noted that the line width decreases for the two PCy_3 whereas it increases for the phosphaferrrocene ligand when the temperature is lowered. This behavior can be explained either by different τ_c 's resulting in different T_2 's or to two slightly different exchange processes occurring between P_C and P_A and P_C and P_B .

Exchange between hydrides and dihydrogen ligands is commonly observed in dihydrogen complexes, but there are only a few precedents in the literature in which decoalescence has been observed by ^1H NMR at low temperature. This is the case for the carbonyl complex $\text{RuH}_2(\text{H}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ¹⁰ and for $\text{RuH}_2(\text{H}_2)(\text{PhP}[\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{Cy}_2)]_2)$ ¹¹ with a chelating triphosphine whereas decoalescence has never been reached in the cases of $\text{RuH}_2(\text{H}_2)(\text{PR}_3)_3$ with $\text{R} = \text{Ph}$ or Cy .¹²

Reactivity Studies on 2. **2** is indefinitely stable in solution at 10^{-2} Torr (flame-sealed NMR tube) and shows no propensity to decompose at higher temperatures in solution (vide infra). However, solid **2** decomposes readily at -20 °C (ca. 1 d) even under an atmosphere of dihydrogen (3 bar). **2** was found to be remarkably stable when a C_7D_8 solution, in a sealed NMR tube, was heated from 40 to 80 °C for 6 h. No decomposition was noted, but H–D exchange occurred leading to the observation of the HD isotopomer $\text{RuH}_2(\text{HD})(\text{PCy}_3)_2(\text{L}_1)$ as evidenced by ^1H and ^{31}P NMR studies at 293 and 213 K (see Scheme 2). At 213 K the pseudoquintet at -9.95 ppm remains unchanged whereas the broad signal observed at -5.95 ppm (with no isotopic shift) is now resolved into a broad triplet which transforms into a singlet upon ^2H decoupling. The two signals

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integrate in a ratio 2:1, and the coupling constant J_{H-D} value is 30 Hz, in agreement with the formation of an HD isotopomer. Estimation of the d_{HH} distance from this value using the equation developed by Morris leads to 0.92 Å, in good agreement with the X-ray data.¹³

Substitution of the dihydrogen ligand in **2** was readily achieved with ethylene or CO (see Scheme 2). Thus, bubbling ethylene into a C_6D_6 solution of **2** leads to a total conversion into a new complex $RuH_2(C_2H_4)(PCy_3)_2(L_1)$ (**3**) resulting from the substitution of the dihydrogen ligand by ethylene. However, further attempts should be performed (in particular at low temperature) in order to isolate the complex, as decomposition was rapidly observed, leading to a mixture of unidentified complexes in addition to free phosphines. The spectroscopic data are given in the Experimental Section. The analogous carbonyl complex $RuH_2(CO)(PCy_3)_2(L_1)$ (**4**) was similarly characterized. In this case, bubbling CO into a C_6D_6 solution of **2** leads to partial conversion into **4** with concomitant formation of the known dicarbonyl complex $RuH_2(CO)_2(PCy_3)_2$ ¹⁴ and free 2-phenyl-3,4-dimethylphosphaferrocene (**L**₁). **3** and **4** have very similar spectroscopic data.

Synthesis of $[RuH_2(PCy_3)_2(3,4\text{-dimethylphosphaferrocene})_2]$ (5**).** The preparation of **5** was achieved by reaction of **1** with a 2-fold equivalent of 3,4-dimethylphosphaferrocene (**L**₂), in cold pentane (−20 °C). Stirring was continued for ca. 45 min to yield a deep orange solution. Following filtration and removal of the solvent in vacuo, **5** was obtained in 64% yield as an orange microcrystalline solid (see Scheme 1). An equimolar ratio of **1** and **L**₂ under identical conditions affords **5** and the recovery of **1** (ca. 40%). The ³¹P{¹H} NMR spectrum of **5** shows two triplets at 9.64 and 67.53 ppm with a small J_{P-P} coupling constant ($^2J_{P-P} = 25$ Hz) consistent with two types of phosphines in a cis disposition. The ¹H NMR spectrum shows a doublet of triplets for the hydrides centered at −9.69 ppm ($^2J_{P_{cis}-H} = 26$ Hz, $^2J_{P_{trans}-H} = 89$ Hz) which simplifies to a triplet upon selective decoupling of the ³¹P signal at 9.64 ppm and to a doublet upon selective decoupling of the ³¹P signal at 67.53 ppm. The resonance of the CH protons α-bound to the phosphorus of the phosphaferrocene ligands appears as a doublet at 3.19 ppm ($^2J_{P-H} = 30.7$ Hz) which transforms into a singlet upon selective decoupling of the ³¹P signal at 9.64 ppm. This allows the attribution of the signal at 9.64 ppm to the resonance of the phosphaferrocene ligands.

In summary, it is amazing to note that, despite the bulkiness of the tricyclohexylphosphine, the ruthenium can still accommodate in its coordination sphere one or two presumed bulky phosphaferrocene ligands leading to the formation of **2** and **5**. Complex **2** is a rare example of a dihydride dihydrogen complex in which decoalescence between the classical hydrides and the dihydrogen ligand can be observed by NMR. X-ray data and a deuteration experiment are in favor of an unstretched dihydrogen ligand. Thus, this dihydrogen ligand is labile as illustrated by the preliminary reactivity studies we have performed on **2**. Our primary goal to induce orthometalation by using a ligand such as **L**₁ was not achieved; however, we have opened access to a wide variety of ruthenium complexes accommodating phosphaferrocene ligands and other phosphines. Investigations of

the catalytic properties of this new family of ruthenium complexes will be developed.

Experimental Section

General Considerations. Inert-atmosphere glovebox and Schlenk-line techniques were used throughout the preparative procedures unless otherwise indicated. The following solvents were refluxed over the appropriate drying agent and subsequently distilled under an atmosphere of dinitrogen or argon. Toluene was distilled from sodium; diethyl ether and tetrahydrofuran were distilled from purple sodium/benzophenone. Dichloromethane and pentane were refluxed over, and distilled from, calcium hydride. All deuterated solvents (toluene-*d*₈, benzene-*d*₆, tetrahydrofuran-*d*₈, and dichloromethane-*d*₂) were pre-stored over oven-dried molecular sieves and then thoroughly degassed during four freeze, degass, and thaw cycles. All NMR samples were prepared in either flame-sealed (ca. 10^{−2} Torr) or Teflon-stoppered NMR tubes unless otherwise stated. ¹H (200.13, 250.13, 300.13, or 400.13 MHz), ¹³C (62.90, 75.47, or 100.61 MHz), and ³¹P NMR (81.01, 121.49, or 161.98 MHz) spectra were recorded on Bruker instruments. Chemical shifts (δ) for ¹H NMR spectra are reported relative to the residual protons in the deuterated solvents and for ¹³C NMR spectra relative to the carbons in the deuterated solvent. ³¹P NMR spectra are reported relative to phosphoric acid (δ = 0.0 ppm) as the external standard. Δ*G*[‡] values were obtained from ¹H and ³¹P NMR data. They were calculated using the coalescence temperatures and frequency differences between the coalescing signals in the limit of slow exchange.¹⁵

Preparation of $[RuH_2(\eta^2-H_2)(PCy_3)_2(2\text{-phenyl-3,4-dimethylphosphaferrocene})]$ (2**).** Pentane (ca. 20 mL) was added, with stirring, to a Schlenk containing $RuH_2(H_2)_2(PCy_3)_2$ (**1**) (430 mg, 0.65 mmol) and 2-phenyl-3,4-dimethylphosphaferrocene (**L**₁) (200 mg, 0.65 mmol) cooled to −20 °C. The mixture was subsequently stirred until the starting materials had been consumed and dihydrogen evolution had ceased to afford a deep orange solution. After filtration and refrigeration, orange crystals of $[RuH_2(\eta^2-H_2)(PCy_3)_2(L_1)] \cdot 2C_5H_{12}$ suitable for single-crystal X-ray diffraction analysis were collected by decantation of the mother liquor. A further crop of unsolvated, analytically pure, microcrystalline material was collected by cooling the filtrate. Yield: 568 mg, 90%. Anal. Calcd for **2**, $RuFeP_3C_53H_{87}$: C, 65.36; H, 8.94. Found: C, 64.90; H, 8.79. ¹H NMR at 400.13 MHz in toluene-*d*₈: at 293 K, −8.15 (br, RuH_4 , 4H), 1.1–2.5 (m, 66H, $P(C_6H_{11})_3$), 2.37 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 3.52 (d, 1H, C_4HPMe_2 , $^2J_{P-H}$ 31 Hz), 4.25 (s, 5H, C_5H_5), 7.31 (t, H_p , 1H, $^3J_{H-H}$ 7.4 Hz), 7.48 (t, H_m , 2H, $^3J_{H-H}$ 7.6 Hz), 7.80 (d, H_o , 2H, $^3J_{H-H}$ 7.6 Hz); at 213 K (selected data), −5.90 (br, $Ru(\eta^2-H_2)$, 2H), −9.95 (pq, RuH_2 , 2H, $^2J_{P(AB)-H}$ 21 Hz, $^2J_{P(C)-H}$ 42 Hz). ³¹P{¹H} NMR at 161.98 MHz in toluene-*d*₈: at 293 K, 33.61 (t, $^2J_{P-P}$ 24 Hz, P_C), 75.53 (br, P_A , P_B); at 213 K, 34.64 (br), 77.7 and 70.0 (AB type, $^2J_{P(A)-P(C)} = ^2J_{P(B)-P(C)}$ 24 Hz, $^2J_{P(A)-P(B)}$ 215 Hz). ¹³C{¹H} NMR at 100.61 MHz in toluene-*d*₈ at 293 K: 16.47 (s, C_4HPMe_2), 17.33 (d, C_4HPMe_2 , $^3J_{C-P}$ 3.2 Hz), 27.83 (s, $P(C_6H_{11})_3$), 28.80 (vt, $P(C_6H_{11})_3$, J_{C-P} 4.5 Hz), 28.89 (vt, $P(C_6H_{11})_3$, J_{C-P} 4.5 Hz), 30.57 (s, $P(C_6H_{11})_3$), 31.07 (s, $P(C_6H_{11})_3$), 39.52 (br, C_α , $P(C_6H_{11})_3$), 72.47 (d, C_α , C_4HPMe_2 , $^1J_{C-P}$ 9.8 Hz), 74.57 (s, C_5H_5), 86.64 (d, C_β , C_4HPMe_2 , $^2J_{C-P}$ 2.5 Hz), 90.03 (d, arylated C_α , C_4HPMe_2 , $^1J_{C-P}$ 15.3 Hz), 91.59 (d, C_β , C_4HPMe_2 , $^2J_{C-P}$ 2.5 Hz), 127.75 (s, C_m , C_5H_5), 129.48 (s, C_p , C_5H_5), 131.75 (d, C_{ortho} , C_6H_5 , $^3J_{C-P}$ 5.1 Hz), 141.57 (d, C_{ipso} , C_6H_5 , $^2J_{C-P}$ 14.9 Hz).

X-ray Analysis of **2.** Data collection were collected at low temperature ($T = 140$ K) on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device and using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 well-measured reflections, and crystal decay was monitored by measuring 200 reflections by image. No significant fluctuation of the intensity was observed over the course

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of the data collection. Numerical absorption corrections¹⁶ were applied on the data. The structure was solved by direct methods using SIR92¹⁷ and refined by least-squares procedures on a F^2 with the aid of SHELXL97 by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are respectively the observed and calculated structure factors.¹⁸ The atomic scattering factors were taken from ref 19. All hydrogen atoms were located on a difference Fourier maps and refined in a riding model, except for the hydrides H(1), H(2) and hydrogen atoms H(3), H(4) of the dihydrogen ligand; their positions have been refined using restraints and isotropic thermal parameters of hydrides and the hydrogens atoms of H_2 ligand have been set to be equivalent, respectively. All remaining non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was applied, where weights have been calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecule was performed with the program ZORTEP with 50% probability displacement ellipsoids for non-hydrogen atoms.²⁰

Reaction of 2 with Ethylene. An NMR tube containing an orange, benzene- d_6 (ca. 0.7 mL) solution of **2** (20 mg, 0.02 mmol) was treated with a slow stream of ethylene for ca. 10 min at room temperature during which time there were no observable color changes. Only one complex was observed and characterized as $[RuH_2(C_2H_4)(PCy_3)_2(L_1)]$ (**3**). 1H NMR at 200.13 MHz in benzene- d_6 at 293 K: -9.88 (pqd, RuH, 1H, $J_{H-H} = 7.3$ Hz, $J_{H-P} = 26$ Hz), -11.65 (dtd, RuH, 1H, $J_{H-H} = 7.3$ Hz, $J_{H-PA} = J_{H-PB} = 27$ Hz, $J_{H-PX} = 126$ Hz), 1.07–2.30 (broad multiplets, $P(C_6H_{11})_3$ and C_2H_4), 2.07 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.53 (br, 2H, C_2H_4), 3.25 (d, 1H, $C_4H_2PMe_2$, $^2J_{P-H} = 30.52$ Hz), 4.10 (s, 5H, C_5H_5), 7.16 (t, H_{para} , partially hidden by solvent peak), 7.26 (t, H_{meta} , 2H, $^3J_{H-H} = 7.85$ Hz), 7.54 (d, H_{ortho} , 2H, $^3J_{H-H} = 7.32$ Hz). $^{31}P\{^1H\}$ NMR at 81.01 MHz in benzene- d_6 at 293 K: ABX type, 65.1 and 62.7 (ddd, 2 PCy_3 , P_A and P_B , $J_{PA-PB} = 189$ Hz, $J_{PA,B-PX} = 21$ Hz), 11.6 (br, P_X).

Reaction of 2 with CO. An NMR tube containing a benzene- d_6 solution (ca. 0.7 mL) of $[RuH_2(\eta^2-H_2)(PCy_3)_2(L_1)]$ (20 mg, 0.02 mmol) was treated with a slow stream of carbon monoxide for ca. 5 min during which time the orange solution gradually darkened in color. The reaction was subsequently conducted on a 100 mg scale, but all attempts to separate $[RuH_2(CO)(PCy_3)_2(L_1)]$ (**4**) from 2-phenyl-3,4-dimethylphosphapherrocene (L_1) and $[RuH_2(CO)_2(PCy_3)_2]$ by column chromatography (aluminum oxide 90, Merck) failed.

Data for 4. 1H NMR at 200.13 MHz in benzene- d_6 at 293 K: -8.53 (pqd, RuH, 1H, $J_{H-H} = 6$ Hz, $J_{H-P} = 25$ Hz), -9.35 (dtd, RuH, 1H, $J_{H-H} = 6$ Hz, $J_{H-PA} = J_{H-PB} = 27$ Hz, $J_{H-PX} = 114$ Hz), 1.0–2.3 (broad multiplets, $P(C_6H_{11})_3$), 2.06 (s, CH_3), 2.18 (s, CH_3), 3.40 (d, 1H, $C_4H_2PMe_2$, $^2J_{P-H} = 30$ Hz), 4.08 (s, 5H, C_5H_5), 7.10 (t, H_{para} , partially hidden by solvent peak), 7.30 (t, H_{meta} , 2H, $^3J_{H-H} = 7.8$ Hz), 7.64 (d, H_{ortho} , 2H, $^3J_{H-H} = 7.3$ Hz). $^{31}P\{^1H\}$ NMR at 81.01 MHz in benzene- d_6 at 293 K: ABX type, 67.7 and 62.8 (mbr, 2 PCy_3 , P_A and P_B , $J_{PA-PB} = 206$ Hz), 14.5 (br, P_X).

Preparation of $[RuH_2(PCy_3)_2(3,4\text{-dimethylphosphapherrocene})_2]$ (5**).** Pentane (ca. 20 mL) was added, with stirring, to a Schlenk tube charged with $[RuH_2(\eta^2-H_2)_2(PCy_3)_2]$ (860 mg, 1.29 mmol) and 3,4-dimethylphosphapherrocene (L_2) (598 mg, 2.58 mmol) at -20 °C. Stirring was continued for ca. 45 min to yield a deep orange solution. After filtration, to remove a little insoluble material, the solvent was removed in vacuo to yield crude $[RuH_2(PCy_3)_2(L_2)_2]$ (930 mg, 64%) as a bright orange, microcrystalline solid. Recrystallization from pentane at ca. -20 °C gave an analytically pure sample containing cocrystallized solvent. Anal. Calcd for $5 \cdot C_5H_{12}$, $RuFe_2P_4C_{63}H_{106}$: C, 63.05; H, 8.84. Found: C, 63.26; H, 8.92. 1H NMR at 300.13 MHz in toluene- d_8 at 293 K: -9.69 (dt, RuH_2 , 2H, $^2J_{P_{cis}-H} = 26$ Hz, $^2J_{P_{trans}-H} = 89$ Hz), 1.31–2.22 (broad multiplets, $P(C_6H_{11})_3$), 2.07 (s, 12H, CH_3), 3.19 (d, 4H, $C_4H_2PMe_2$, $^2J_{P-H} = 30.7$ Hz), 4.09 (s, 10H, C_5H_5). $^{31}P\{^1H\}$ NMR at 121.94 MHz in toluene- d_8 at 293 K: 9.64 (t), 67.53 (t), ($^2J_{P-P} = 25$ Hz). $^{13}C\{^1H\}$ NMR at 75.47 MHz in toluene- d_8 at 293 K: 16.50 (s, $C_4H_2PMe_2$), 27.57 (s, $P(C_6H_{11})_3$), 28.60 (vt, $P(C_6H_{11})_3$, $J_{C-P} = 4.60$ Hz), 31.38 (s, $P(C_6H_{11})_3$), 38.01 (br, vt, $P(C_6H_{11})_3$, $J_{C-P} = 9.7$ Hz), 72.59 (s, C_5H_5), 73.27 (d, C_{α} of $C_4H_2PMe_2$, $^1J_{P-C} = 7.8$ Hz), 89.96 (s, C_{β} of $C_4H_2PMe_2$).

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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