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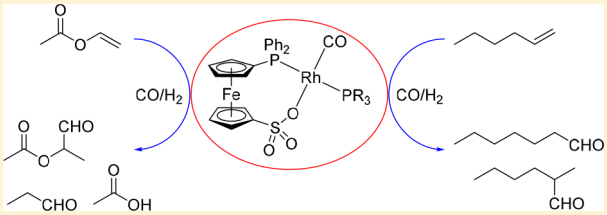
Synthesis, Structural Characterization, and Hydroformylation Activity of Rhodium(I) Complexes with a Polar Phosphinoferrocene Sulfonate Ligand

Martin Zábranský,[†] Ivana Císařová,[†] Anna M. Trzeciak,[‡] Waleed Alsalahi,[‡] and Petr Štěpnička*[,†]

[†]Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague, Czech Republic
[‡]Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland

Supporting Information

ABSTRACT: 1′-(Diphenylphosphino)ferrocene-1-sulfonic acid (HL), isolated from the salt (Et_3NH)**L** on an ion exchanger, reacts with Rh(I) complexes $[Rh(acac)(CO)(PR_3)]$ (acac = acetylacetonato-κ^2O,O') to give complexes of the type $[Rh(CO)(PR_3)(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ (**1a**−**d**; R = Ph (**a**), Cy (**b**), 2-furyl (**c**), and OMe (**d**); fc = ferrocene-1,1′-diyl). In an analogous reaction with $[Rh(acac)(nbd)]$ (nbd = η^2:η^2-norbornadiene), HL produces $[Rh(nbd)(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ (**2**). Adding (Et_3NH)**L** (2 equiv per Rh) to $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and $[Rh(acac)(CO)_2]$ gives rise to the cationic complexes *trans*-$(Et_3NH)_2[RhCl(CO)(Ph_2PfcSO_3\text{-}\kappa P)_2]$ (**3**) and $(Et_3NH)[Rh(CO)(Ph_2PfcSO_3\text{-}\kappa^2O,P)(Ph_2PfcSO_3\text{-}\kappa P)]$ (**4**), respectively. In complex **4**, resulting from the simultaneous substitution of a CO ligand and acid−base replacement of the acac ligand, the P-monodentate and O,P-chelating phosphinoferrocene sulfonate ligands rapidly interconvert (in a solution). All compounds were characterized by spectroscopic methods and by elemental analysis, and the crystal structures of **1a**·Me_2CO, solvated **1b**, **2**, and **4**·H_2O were determined. Furthermore, the catalytic activity of all Rh(I) complexes was assessed in hydroformylation of vinyl acetate under solvent-free conditions at 80 °C and at 20 bar of synthesis gas (H_2/CO = 1:1). High conversion with good selectivity to *iso*-aldehyde was observed for **1a**·$^1/_2H_2O$ and **4**·$^1/_2H_2O$. When applied to "on-water" hydroformylation of 1-hexene (80 °C/10 bar), the complexes mainly promoted 1-hexene isomerization to 2-hexene. However, two of them, **1a**·$^1/_2H_2O$ and **1c**, exhibited reasonable selectivity to aldehydes and preferentially produced the linear product (*n*/*iso* ratios up to 3).

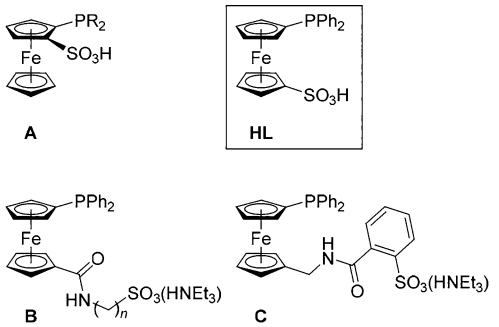


INTRODUCTION

As highly hydrophilic supporting ligands, sulfonated phosphines allow transferring metal-catalyzed reactions from organic solvents to environmentally less demanding aqueous reaction media, including water itself.[1] The prominent example of their practical use is the Ruhrchemie/Rhône-Poulenc process for propene hydroformylation, performed in an aqueous mixture with a water-soluble Rh-TPPTS catalyst (TPPTS = triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt).[2] Consequently, numerous sulfonated phosphines have been reported to date, thus demonstrating the viability of the sulfonation approach toward preparing efficient hydrophilic ligands.[1] However, this has not been adequately reflected in the chemistry of phosphinoferrocene ligands.[3]

In 2011, Erker et al. synthesized a series of 2-phosphinoferrocene-1-sulfonic acids **A**,[4,5] which were applied as supporting ligands in a range of transition-metal-catalyzed (co)polymerization reactions.[4,6] Focusing on functional analogues[7] of the ubiquitous 1,1′-bis(diphenylphosphino)-ferrocene (dppf),[8] we have independently prepared several phosphinoferrocene amidosulfonate ligands (**B**[9,10] and **C**[11] in Scheme 1) and, more recently, also the ring-sulfonated ferrocene derivative HL, which was isolated in the form of the stable ammonium salt (Et_3NH)**L**.[12]

Scheme 1. Examples of Phosphinoferrocene Sulfonate Ligands



Thus far, we have synthesized a series of Pd(II) complexes containing this new ligand and tested them as defined precatalysts in Suzuki−Miyaura-type cross-coupling reactions performed in biphasic reaction media. This contribution extends these investigations toward the preparation of Rh(I) complexes and their use in hydroformylation reactions[2d,13] of

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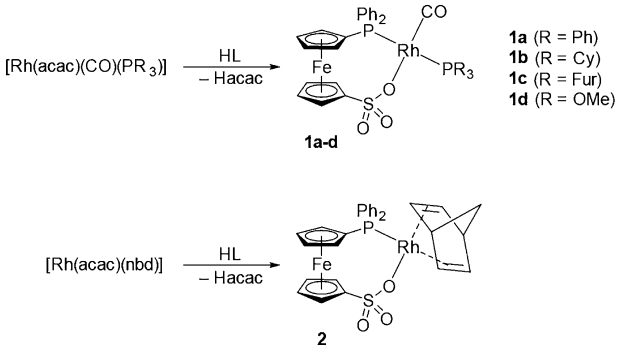
practically relevant substrates under solventless conditions and in aqueous reaction systems.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Rh(I) Complexes with 1′-(Diphenylphosphino)ferrocene-1-sulfonate Ligand. The proposed syntheses of Rh(I)−**L** complexes were based on the replacement of labile ligands with (Et_3NH)**L** as a phosphine and on the reactions between acid H**L** and Rh(I)−acetylacetonate (acac) complexes analogous to the reactions of 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) that directly produce O,P-chelate phosphinocarboxylate complexes.[14] Free 1′-(diphenylphosphino)ferrocene-1-sulfonic acid (H**L**), required for these experiments, was prepared by passing an ethanolic solution of (Et_3NH)**L** through a cation exchanger and was isolated as a relatively stable yellow solid by precipitation, albeit in a heavily solvated form (typically with approximately half molar equivalents of hexane and chloroform per mole of H**L**). Solvent-free H**L** was obtained after carefully evaporating dichloromethane solutions of the acid. In contrast to (Et_3NH)**L**, which is virtually indefinitely stable when stored under ambient conditions, the free acid (particularly solvent-free) gradually decomposes (the decomposition is first indicated by the darkening of the samples and by the broadening of the NMR signals). Hence, fresh samples of H**L** were used for all reactions.

Gratifyingly, H**L** reacted with Rh(I)−acetylacetonate complexes $[Rh(acac)(CO)(PR_3)]$[15] as anticipated, producing the O,P-chelate phosphinosulfonate complexes $[Rh(CO)(PR_3)(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ (**1a**−**d**; Scheme 2). In view of the planned catalytic experiments, complexes **1** were prepared with supporting ligands that differed by steric and electronic properties,[16] namely, with triphenylphosphine (**1a**), tricyclohexylphosphine (PCy_3; **1b**), tri(2-furyl)phospine ($PFur_3$; **1c**), and trimethyl phosphite (**1d**).

Scheme 2. Preparation of Rh(I)−L Complexes by Protonation of the Rh-Bound acac Ligand[a]



[a]Hacac = acetylacetone, Cy = cyclohexyl, Fur = 2-furyl, and nbd = norbornadiene.

In all cases, complexes **1** were isolated as relatively poorly soluble, air-stable solids and as pure *trans*-P,P isomers. This was confirmed by $^{31}P\{^1H\}$ NMR spectra showing two double doublets due to coupling with ^{103}Rh ($I = {}^1/_2$, $^1J_{RhP} \approx 120-135$ Hz) and with the other phosphorus atom in the *trans* position ($^2J_{PP} \approx 320-370$ Hz for **1a**−**c** and 511 Hz for **1d**). The ^{13}C NMR resonances of the carbonyl ligand of **1a** and **1b** were observed as a doublet of triplets ($^1J_{RhC} \approx 77$ Hz, $^2J_{PC} \approx 17-18$ Hz) at $\delta_C \approx 190$. In the IR spectra, the CO ligands gave rise to distinct intense $\nu_{C\equiv O}$ bands near 2000 cm^{-1}, specifically at 1987 (**1a**), 1979 (**1b**), 2016 (**1c**), and 2001 (**1d**) cm^{-1}.

In addition to spectroscopic characterization, the structures of **1a**·Me_2CO and **1b**·$^1/_2H_2O$ were determined by X-ray diffraction analysis (Figure 1, Table 1). Compound **1b**

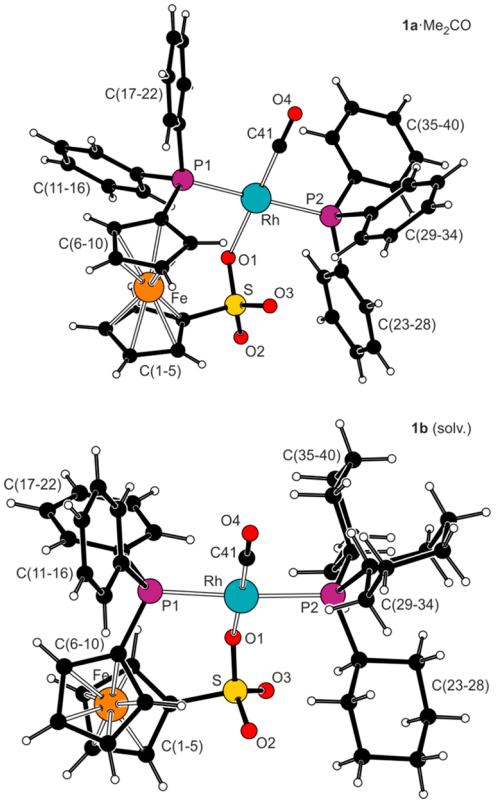


Figure 1. View of the complex molecules in the structures of **1a**·Me_2CO and hydrated **1b** (complete structural diagrams are available in the Supporting Information).

Table 1. Selected Distances and Angles for 1a·Me_2CO and Solvated 1b (in Å and deg)[a]

parameter	**1a**·Me_2CO	**1b**
Rh−P1	2.3308(6)	2.3349(5)
Rh−O1	2.097(2)	2.106(1)
Rh−P2	2.3401(6)	2.3556(5)
Rh−C41	1.809(3)	1.792(2)
P1−Rh−O1	88.51(5)	88.62(3)
P2−Rh−O1	92.78(5)	90.19(3)
P1−Rh−C41	91.12(9)	89.98(5)
P2−Rh−C41	87.63(9)	90.97(5)
C41−O4	1.143(4)	1.150(2)
Rh−C41−O4	178.3(3)	179.8(2)
S−O1	1.489(2)	1.486(1)
S−O2/O3	1.439(2)/1.451(2)	1.440(2)/1.442(2)
Fe−C	2.011(2)−2.069(3)	2.009(2)−2.067(2)
tilt	1.3(2)	3.0(1)
τ	43.1(2)	55.5(1)

[a]Definitions: Fe−C is the range of Fe−C(1−10) distances. Tilt is the dihedral angle of the least-squares cyclopentadienyl planes, and τ is the torsion angle C1−Cg1−Cg2−C6, where Cg1 and Cg2 are the centroids of the cyclopentadienyl rings C(1−5) and C(6−10), respectively.

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crystallized partly hydrated, accommodating extensively disordered water molecules in the structure, which had to be excluded from the refinement (see the Experimental Section).

The molecular structures of **1a** and **1b** are similar to the structure of the carboxylate complex [Rh(dpf-κ^2O,P)(CO)-(PCy_3)].[14] In both cases, the sum of the interligand angles (360.04 and 359.76°) and the τ_4 indexes[17] (0.02 and 0.06; ideal value: $\tau_4 = 0$) consistently indicate that the coordination spheres around Rh(I) are essentially planar. The individual interligand angles also differ from 90° only marginally, the widest being the P1−Rh−O1 (ligand bite) angle in the structure of **1a**·Me_2CO (≈93°; N.B. in **1b**, the same angle practically does not differ from the ideal 90°). Compared with the structure of the mentioned carboxylate complex in which an approximately 6°-widening of the P−Rh−O angle was observed, this suggests that the O,P-chelating ligand $\mathbf{L}^-$, which bears a larger and rotationally adaptable sulfonate moiety, causes a lower steric distortion. The Rh−O1 distances in **1a** and **1b**, approximately 2.1 Å, are ∼0.03 Å longer than the Rh−O distance in the aforementioned phosphinocarboxylate complex. This corresponds with a relatively lower polarization of the sulfonate oxygens (N.B. the negative charge of the sulfonate moiety is distributed over three oxygen atoms, whereas, in the carboxylate moiety, it can spread over two oxygen atoms only).[18] In both complexes, the S−O bond involved in coordination is appreciably longer than the uncoordinated bonds.

The molecules of **1a** and **1b** differ in the conformation of their ferrocene units (more open in **1b**) and, mainly, in the mutual orientation of their phosphine moieties: whereas the PC_3 fragments in **1a** are staggered, those in **1b** appear eclipsed when looking along the P1···P2 diagonal. The six-membered rings of the PCy_3 ligand in **1b** adopt a chair conformation and bind to the phosphorus in the equatorial position.[19]

The reaction of H**L** with [Rh(acac)(nbd)] (nbd = η^2:η^2-norbornadiene) proceeded similarly, producing bis-chelate complex [Rh(nbd)(Ph_2PfcSO_3-κ^2O,P)] (**2**) as the sole product (Scheme 2). This compound, isolated in the form of hemihydrate **2**·$^1/_2H_2O$, is also poorly soluble and, therefore, could not be characterized by ^{13}C NMR spectroscopy or by ESI MS spectrometry. Nonetheless, the ^1H NMR spectra and elemental analysis supported the formulation, and the $^{31}P\{^1H\}$ NMR spectra suggested the coordination of only one phosphine moiety to the Rh(I) center [δ_P 27.4 (d, $^1J_{RhP}$ = 176 Hz)]. Eventually, the assigned structure was corroborated by X-ray diffraction analysis on unsolvated **2** (Figure 2).

The ferrocene cyclopentadienyls in **2** are tilted by 3.9(2)° (Fe—C 2.024(3)−2.057(3) Å) and adopt an intermediate conformation (τ = −53.5(2)°),[8a] which allows the coordination of both functional substituents without significant twisting of the coordination sphere around Rh(I) (P—Rh—O1 = 94.81(5)°). Notably, the Rh—C distances of the double bond *trans* to the phosphine donor are significantly longer that those *trans* to the sulfonate oxygen, reflecting a different *trans*-influence of these donor moieties,[20] which also affects the η^2-coordinated double bonds (C31—C32 1.370(3) Å, C34—C35 1.408(3) Å). A similar dissymmetry was noted in the structure of [Rh(nbd)($Ph_2PCH_2S(=O)Ph$-κ^2O,P)]-(CF_3SO_3).[21] The nbd ligand in **2** is somewhat asymmetrically coordinated with the C32/C34 atoms inclined closer to Rh than their bonding partners C31/C35, as shown by the angles at which the π-coordinated double bonds intersect the {Rh,P,O1} plane (approximately 83°). The coordinated S—O1 bond (1.488(2) Å) is elongated with respect to the remaining S—O bonds (S—O2 1.445(2) Å, S—O3 1.443(2) Å), suggesting a localized nature of the sulfonate S—O bonds (S—O vs S═O).

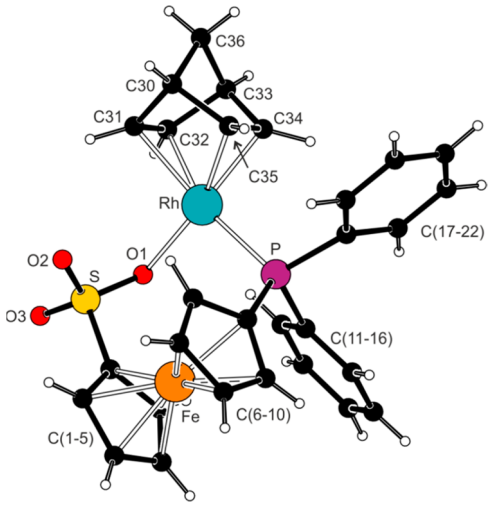
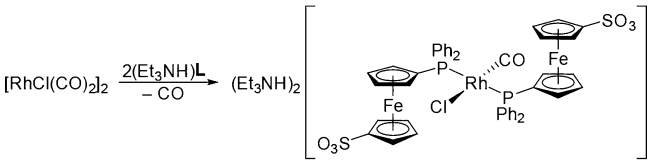


Figure 2. View of the molecular structure of **2** (complete structural diagram is available in the Supporting Information). Selected distances and angles (in Å and deg): Rh−P 2.3049(8), Rh−O1 2.126(2), Rh−C31 2.232(2), Rh−C32 2.216(2), Rh−C34 2.088(3), Rh−C35 2.091(3), P−Rh−O1 94.81(5).

In subsequent experiments, aimed at obtaining Rh(I) complexes featuring P-monodetate anion $\mathbf{L}^-$, we reacted (Et_3NH)**L** with [Rh(μ-Cl)$(CO)_2$]$_2$. The reaction proceeded as expected, affording the bis(phosphine) complex *trans*-(Et_3NH)$_2$[RhCl(CO)(**L**-κP)$_2$] (**3** in Scheme 3) in a good yield. The NMR spectra of this compound confirmed the presence of Et_3NH^+ cations and a pair of equivalent phosphinosuflonate ligands. In particular, the signals due to ^{31}P-coupled carbons in cyclopentadienyl and phenyl moieties were observed as nonbinomial triplets typical for symmetrical bis(phosphine complexes).[22] The ^{13}C NMR signal of the carbonyl ligand was observed as a doublet of triplets at δ_C 187.31 ($^1J_{RhC}$ = 74 Hz, $^2J_{PC}$ = 16 Hz), and the $\nu_{C\equiv O}$ band in the IR spectrum of **3** was identified at 1960 cm^{-1} (in Nujol mull).

Scheme 3. Synthesis of Complex 3



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Lastly, we focused on the reactivity of (Et_3NH)**L** with the dicarbonyl complex [Rh(acac)$(CO)_2$]. Because both the acac and the carbonyl ligands can be replaced, the initial reaction tests were performed at 1:1 and 1:2 Rh:(Et_3NH)**L** ratios. The reaction of [Rh(acac)$(CO)_2$] with 2 equiv of (Et_3NH)**L** proceeded cleanly, producing complex **4** (Scheme 4). Conversely, when only one molar equivalent of (Et_3NH)**L** was employed, the reaction gave rise to a mixture of two compounds, different from complex **4**, according to NMR analysis. The more abundant product was tentatively

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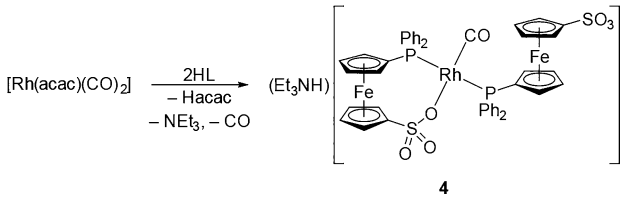
Scheme 4. Preparation of Rh(I)−L Complex 4[a]



[a]Hacac = acetylacetone.

formulated as the CO-substitution product $(Et_3NH)[Rh(acac)(CO)(\mathbf{L}\text{-}\kappa P)]$ ($\delta_P \approx 47$ (d); signals due to coordinated acac ligand were identified in the ^1H NMR spectrum). The other, minor component [$\delta_P \approx 27$ (d)] was presumably formed via replacement of the acac ligand (with the Et_3NH^+ cation acting as a proton source; free acetylacetone[23] was detected in the reaction mixture). Unfortunately, these compounds could not be isolated and, hence, were disregarded.

The formation of complex **4** formally involves the replacement of one CO ligand by a "phosphine" and the protonation of the acac ligand by $HNEt_3$ (under elimination of triethylamine and Hacac), concomitantly forming the O,P-chelate ring. Remarkably, the compound shows only one set of NMR signals due to the phosphinosulfonate ligands (in solution!). This indicates a rapid (on an NMR time scale) interconversion of the P-monodentate and of the O,P-chelating form of anion $\mathbf{L}^-$ and, hence, its hemilabile coordination.[24] Accordingly, complex **4** gives rise to a single ^{103}Rh-coupled doublet ($^1J_{RhP}$ = 128 Hz) at δ_P 21.3 in its ^{31}P NMR spectra. Similarly to **3**, the ^{13}C NMR signals due to carbons in the $C_5H_4PPh_2$ fragment of **4** are observed as apparent triplets due to virtual coupling in the AA′X spin system of the $^{13}C-^{31}P-Rh-^{31}P-^{12}C$ type.[22] The presence of the CO ligand is confirmed by a doublet of triplets ($^1J_{RhC}$ = 76 Hz, $^2J_{PC}$ = 19 Hz) at δ_C 189.34 in the $^{13}C\{^1H\}$ NMR spectrum and through a strong $\nu_{C\equiv O}$ band at 1973 cm^{-1} in the IR spectrum. In addition, the compound displays ions attributable to $\{(Et_3NH)[RhCl(CO)(\mathbf{L})_2]\}^-$ anions (m/z 1029) in its ESI−mass spectrum.

Complex **4** is hygroscopic and was isolated in the form of hemihydrate in the bulk synthesis. It is extremely difficult to crystallize, forming oils that slowly crystallize to give aggregates consisting of tiny plate-like crystals. Adventitious water apparently assists the crystallization; it is incorporated into the crystals and enters into H-bonding interactions, as indicated by the structure determination on dihydrate **4**·$2H_2O$ (Figure 3; for a complete structural diagram and discussion of the H-bond interactions, see the Supporting Information). This, however, is quite typical of hydrophilic phosphinosulfonate ligands and of their complexes.[25]

The Rh(I) center in the complex cation of **4**·$2H_2O$ (Figure 3) has an essentially planar coordination environment with all interligand angles near the ideal 90°. In fact, asymmetry is only observed in Pd-donor distances, which render the P1···P2 diagonal approximately 20% longer than the O1···C23 diagonal. The ferrocene units show the expected geometries, with Fe1−C and Fe2−C distances in the ranges 2.009(4)−2.057(4) and 2.021(4)−2.064(4) Å, respectively, but with different conformations. In the chelating ligand $\mathbf{L}^-$, the functional groups are expectedly closer to each other (τ = −47.2(3)°) than in the P-coordinated one (τ = 146.8(3)°).

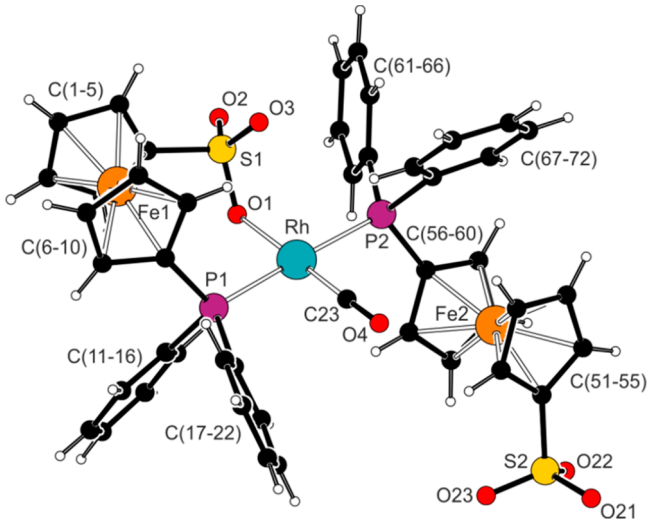
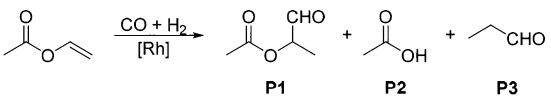


Figure 3. View of the complex anion in the structure of **4**·$2H_2O$. Selected distances and angles (in Å and deg): Rh−P1 2.332(1), Rh−P2 2.351(1), Rh−O1 2.096(2), Rh−C23 1.786(4), C23−O4 1.152(5), P1−Rh−O1 89.50(7), P1−Rh−C23 90.0(1), P2−Rh−O1 91.65(7), P2−Rh−C23 88.8(1), Rh−C23−O4 178.1(4).

The variation in the S−O distances indicates that the sulfonate moieties are partly localized: similarly to the structures discussed above, the S2−O21 bond (1.463(4) Å) in the free sulfonate (ligand 2) is longer that the other two S−O bonds (S2−O22 1.441(4) Å, S2−O23 1.426(4) Å). This difference in bond lengths is even larger in the Rh-bound sulfonate moiety, thus reflecting the weakening of the S1−O1 bond upon coordination (S1−O1 1.494(3) Å vs S1−O2 1.437(3) Å/S1−O3 1.442(3) Å).

Catalytic Tests. All synthesized Rh(I) complexes were tested as (pre)catalysts in hydroformylation reactions under solventless and "on-water" conditions *without* any additional coligands. Vinyl acetate, reacting at considerably slower rates than terminal alkenes,[26] was chosen as the model substrate for the solventless hydroformylation catalyzed by the Rh(I)−**L** complexes (0.125 mol %) at 80 °C and at 20 bar of synthesis gas (H_2/CO = 1:1). As expected, *iso*-aldehyde (2-acetoxypropanal (**P1**)) was the main product,[27] and acetic acid (**P2**) and propanal (**P3**), resulting from the decomposition of 3-acetoxypropanal (linear aldehyde), were also detected (Scheme 5). Notably, 3-acetoxypropanal itself was not observed in the reaction mixture.[28]

Scheme 5. Hydroformylation of Vinyl Acetate



The results outlined in Table 2 illustrate the different activities of the studied rhodium catalysts. Conversions up to 80 and 88% were obtained when using **1a**·$^1/_2H_2O$ and **4**·$^1/_2H_2O$, respectively, with the same 70% yield of the isoaldehyde (entries 1 and 7). With other complexes, the conversion and selectivity to **P1** decreased (from 52 to 17% and from 42 to 7%, respectively; entries 2−5), whereas catalyst **3** showed no catalytic activity under the conditions used (Table 2, entry 6).

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Table 2. Catalytic Results Achieved with Rh(I)−L Complexes in Solvent-Free Hydroformylation of Vinyl Acetate[a]

entry	catalyst	conv. (%)	P1 (%)	P2 (%)	P3 (%)
1	**1a**·$^1/_2H_2O$	80	70	5.0	5.0
2	**1b**	52	42	6.2	3.6
3	**1c**	41	28	10	2.4
4	**1d**	31	15	15	1.7
5	**2**·$^1/_2H_2O$	17	7.0	9.0	1.0
6	**3**	0			
7	**4**·$^1/_2H_2O$	88	70	15	2.8

[a]Reaction conditions: vinyl acetate (1 mL), [substrate]/[Rh] = 800, T = 80 °C, $p(H_2{:}CO$ = 1:1) = 20 bar, t = 6 h.

On-Water 1-Hexene Hydroformylation. 1-Hexene hydroformylation was initially performed in different reaction media using **1a**·$^1/_2H_2O$ as the catalyst (Table 3). The reaction produced aldehydes, namely, 1-heptanal (linear aldehyde) and 2-methylhexanal (*iso*-aldehyde), along with some 2-hexene as the isomerization product (N.B. hexane and 3-hexene were not detected). In the reaction performed under solventless conditions, low conversion (19%) was achieved, with dominant isomerization (2-hexene: 16%; entry 1). When using toluene as a solvent, the conversion increased to 71% but the fraction of the isomerized product in the reaction mixture remained nearly the same (2-hexene: 58%, entry 2). A similar conversion (70%), albeit with a higher selectivity to aldehydes, 65% (n/iso = 1.2), was achieved when adding water to the system (entry 3). Even better results, with a higher conversion of 1-hexene (85%) and a significantly increased selectivity to the aldehydes, 81% (i.e., only ca. 4% of 2-hexene were formed; n/iso = 2.0), were obtained when using water as the sole reaction medium (entry 4). Conversely, lower conversion and selectivity to aldehydes (75 and 56%) were noted when replacing **1a**·$^1/_2H_2O$ with **1c** in water (entry 6), whereas catalysts **1b** and **1d** mainly promoted the isomerization reaction (particularly **1d**; entries 5 and 7).

In 1-hexene hydroformylations, **1**-type complexes with weaker σ-donor auxiliary phosphine ligands were more active and selective toward linear aldehyde than **1b** containing the more basic PCy_3 ligand. This finding is in line with the general observations[13] and also with the trend noted for dppf analogues with varied phosphine substituents whose catalytic activity, selectivity to linear aldehydes, but also isomerization efficiency increased after introducing electron-withdrawing substituents to phosphorus.[29] Among **1**-type complexes, compound **1a**·$^1/_2H_2O$ exerted the best selectivity toward aldehydes but the lowest n/iso ratio. Finally, complexes **3** and **4** showed lower catalytic activity and mainly promoted substrate isomerization to 2-hexene (entries 9 and 10).

Overall, the catalytic activity and selectivity of the Rh−**L**/Rh−**HL** complexes (in the absence of added free phosphine ligands) are similar to those reported for analogous complexes with coordinated 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) and the corresponding carboxylate (dpf^-)[30] but rather low in comparison with the state-of-the-art hydroformylation catalysts.[13,31] The catalytic activity of the Rh−**L**/Rh−**HL** complexes appears to be mainly affected by low solubility of these compounds in both pure educts and even in biphase reaction systems.[32] Without added free ligands, the tested compounds are likely to convert under the reaction conditions (at least partly) into dissociation products such as $[RhH(CO)_2(PR_3)]$[13,33] (or even phosphine-free Rh(I) carbonyl complexes $[RhH(CO)_n]$ and carbonyl clusters[34]) that become the real (but less selective, especially in terms of the n/iso ratio) catalysts in the studied system.[35]

CONCLUSIONS

Depending on its source (H**L** or (Et_3NH)**L**) and on the nature of the substituted ligand (neutral or protonizable), 1′-(diphenylphosphino)ferrocene-1-sulfonate anion ($\mathbf{L}^-$) can coordinate in square-planar Rh(I) complexes as a P-monodentate or as an O,P-chelating donor. Proton exchange between these two forms in solutions of the neutral complex $[Rh(CO)(Ph_2PfcSO_3\text{-}\kappa^2O,P)(Ph_2PfcSO_3\text{-}\kappa P)]$ (**4**) is rapid on the NMR time scale, implying hemilabile coordination of the hard−soft donor $\mathbf{L}^-$ to the soft Rh(I) center. The Rh−**L** (and Rh−**HL**) complexes give rise to moderately active and selective hydroformylation catalysts (at 80 °C under 10 or 20 bar of synthesis gas). However, their catalytic performance is mainly limited by their relatively low solubility in both neat starting materials (alkenes) and the solvents used (water and biphase aqueous mixtures) and may thus be further enhanced by further structural modifications (e.g., via introducing auxiliary hydrophilic ligands).

EXPERIMENTAL SECTION

General Considerations. All syntheses were performed under an argon atmosphere using standard Schlenk techniques. Compounds (Et_3NH)**L**,[12] $[Rh(acac)(CO)_2]$,[36] $[Rh(acac)(CO)(PR_3)]$ (R = Ph, Cy, OMe),[15,37] and $[Rh(CO)_2Cl]_2$[38] were prepared according to

Table 3. Catalytic Results Achieved with Rh(I)−L Complexes in Hydroformylation of 1-Hexene[a]

entry	catalyst	solvent[b]	t (h)	conv. (%)	2-hexene (%)	aldehydes (%)	n/iso[c]
1	**1a**·$^1/_2H_2O$	none	1	19	16	2.5	2.1
2	**1a**·$^1/_2H_2O$	T	1	71	58	13	2.7
3	**1a**·$^1/_2H_2O$	T−W	5	70	5.7	65	1.2
4	**1a**·$^1/_2H_2O$	W	4	85	3.7	81	2.0
5	**1b**	W	4	40	35	5.0	2.6
6	**1c**	W	5	75	19	56	3.0
7	**1d**	W	4	82	74	8.7	2.5
8	**2**·$^1/_2H_2O$	W	19	100	67	33	2.0
9	**3**	W	4	22	19	2.5	2.6
10	**4**·$^1/_2H_2O$	W	4	33	27	6.4	2.8

[a]Conditions: 1-hexene (1.5 mL), [substrate]/[Rh] = 800, solvent (1.5 mL), T = 80 °C, $p(H_2{:}CO$ = 1:1) = 10 bar. [b]Solvent: T = toluene, W = water, T−W = toluene−water mixture (1:1). [c]The ratio of linear and branched aldehyde.

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procedures reported in the literature. All other chemicals were obtained from commercial suppliers (Sigma-Aldrich, Alfa-Aesar) and were used without any additional purification. Dichloromethane was dried with a PureSolv MD5 solvent purification system (Innovative Technology, Inc., Amesbury, MA, USA). Acetone was dried over potassium carbonate and distilled under argon. The solvents were used in workup, chromatography, and crystallizations without further purification (reagent grade; Lach-Ner, Neratovice, Czech Republic). Ion exchange resin DOWEX 50WX4 (Sigma-Aldrich) was used in all experiments. Prior to use, an aqueous suspension of this resin was washed with an equal volume of 3 M HCl and then with an excess of absolute ethanol.

NMR spectra were recorded at 25 °C on Varian UNITY Inova 400 or Bruker Avance III 600 spectrometers. Chemical shifts (δ in ppm) are given in relation to internal tetramethylsilane (^{1}H and ^{13}C) and to external 85% aqueous H_3PO_4[31], all set to 0 ppm. Apart from the standard notation of signal multiplicity (s = singlet, d = doublet, t = triplet, etc.),[39] vt and vq are used to denote virtual multiplets arising from the AA′BB′ and AA′BB′X spin systems (A, B = ^{1}H, X = ^{31}P) consisting of the protons in the sulfonate- and Ph_2P-substituted cyclopentadienyl rings, respectively. FTIR spectra were measured on a Thermo Fisher Nicolet 6700 spectrometer in the range 400−4000 cm^{-1}. Electrospray ionization (ESI) mass spectra were recorded with a Compact QTOF-MS spectrometer (Bruker Daltonics). Elemental analyses were performed using a PerkinElmer PE 2400 CHN analyzer. The amount of residual solvent (if applicable) was always verified by NMR analysis.

Syntheses. *Synthesis of HL.* Salt (Et_3NH)**L** (551.8 mg, 1.0 mmol) was dissolved in absolute ethanol (5 mL) under sonication and gentle warming. The solution was transferred to the top of a column filled with DOWEX 50WX4 in H^+-form (≈20 mL) and slowly soaked into the ion exchanger. After standing for 30 min, the column was eluted with absolute ethanol, and the collected orange eluate (≈100 mL) was evaporated under reduced pressure, affording an oily orange residue. This residue was dried under a vacuum and then taken up with chloroform (5 mL). The solution was slowly added to cold pentane (4 °C, 100 mL), depositing free acid as a yellow precipitate, and was left standing at 4 °C overnight. Subsequently, the deposited solid was filtered off, washed with pentane, and carefully dried under a vacuum. The resulting acid H**L** is a yellow hygroscopic solid, which contains significant amounts of solvents that cannot be removed by prolonged storage under a vacuum. Yield: 481.8 mg (H**L** content, 83%; yield, 89%).

^{1}H NMR ($CDCl_3$): δ 4.22 (br s, 2 H, fc), 4.57 (br s, 2 H, fc), 4.83 (br s, 2 H, fc), 4.86 (br s, 2 H, fc), 7.56−7.62 (br m, 4 H, PPh_2), 7.66−7.70 (br m, 2 H, PPh_2), 7.74−7.80 (br m, 4 H, PPh_2), very broad singlet centered at $\delta_H \approx 8.5$ (1 H, SO_3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.6 (s). HRMS (ESI+) calcd for $C_{22}H_{20}FeO_3PS$ ([M + H]$^+$) 451.0215, found: 451.0213. Anal. Calcd for $C_{22}H_{19}FeO_3PS\cdot 0.6C_5H_{12}\cdot 0.4CHCl_3$: C 56.36, H 4.95%. Found: C 56.67, H 4.92%.

Before the complexation reactions, the sample of H**L** was dissolved in a minimum amount of anhydrous dichloromethane, and the solution was evaporated under a vacuum. The oily residue was lyophilized at 0.02 Torr overnight, providing H**L** with only traces of the solvents. However, this procedure is associated with partial (minute) decomposition, as shown by the broadening of the NMR resonances.

Preparation of [Rh(acac)(CO)(PFur$_3$)]. The procedure was adapted from ref 15. Tri(2-furyl)phosphine (255.6 mg, 1.10 mmol) dissolved in warm diethyl ether (10 mL) was added to a solution of [Rh(acac)$(CO)_2$] (258.0 mg, 1.0 mmol) in the same solvent (10 mL). The resulting yellow mixture was filtered, and the filtrate was left standing at room temperature for 3 h. Then, it was diluted with methanol (20 mL), concentrated to approximately 10 mL under a vacuum, and stored at −18 °C overnight. The resulting yellow microcrystalline solid was filtered off, washed with methanol, and dried under a vacuum. Yield: 353 mg (76%), yellow microcrystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (s, 3 H, Me), 2.18 (s, 3 H, Me), 5.48 (s, 1 H, CH of acac), 6.49 (ddd, J = 3.4, 1.7, 1.7 Hz, 3 H, Fur), 7.13 (ddd, J = 3.4, 2.4, 0.8 Hz, 3 H, Fur), 7.72 (ddd, J = 1.7, 1.7, 0.8 Hz, 3 H, Fur). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −4.0 (d, $^1J_{RhP}$ = 181 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 26.36 (s, Me), 27.43 (d, J = 7.3 Hz, Me), 100.89 (d, J = 2.4 Hz, CH of acac), 111.01 (d, J_{PC} = 9 Hz, CH of Fur), 123.75 (d, J_{PC} = 22 Hz, CH of Fur), 144.29 (dd, J_{PC} = 79.6 Hz, J_{RhC} = 1.5 Hz, C_{ipso} of Fur), 148.22 (d, J_{PC} = 5.5 Hz, CH of Fur), 185.64 (s, CO of acac), 187.37 (s, CO of acac), 187.74 (dd, $^1J_{RhC}$ = 74 Hz, $^2J_{PC}$ = 26 Hz, RhCO). IR (Nujol): ν_{max}/cm^{-1} 1985 (vs), 1571 (s), 1525 (s), 1273 (m), 1214 (m), 1207 (m), 1162 (w), 1129 (m), 1120 (m), 1062 (vw), 1017 (m), 1008 (s), 933 (vw), 906 (m), 882 (w), 836 (vw), 809 (w), 769 (m), 756 (s), 656 (vw), 646 (m), 630 (vw), 592 (m), 547 (m), 529 (m), 506 (m), 444 (m). HR MS (ESI+) calcd for $C_{18}H_{16}NaO_6PRh$ ([M + Na]$^+$): 484.9632, found 484.9630. Anal. Calcd for $C_{18}H_{16}O_6PRh$ (462.20): C 46.78, H 3.49%. Found: C 46.53, H 3.43%.

Synthesis of 1a·$^1/_2H_2O$. A mixture of solid [Rh(acac)(CO)(PPh_3)] (98.4 mg, 0.2 mmol) and H**L** (90.0 mg, 0.2 mmol) was dissolved in dry acetone (4 mL) under argon. The mixture was briefly sonicated and then stirred at room temperature for 30 min. During this time, the starting materials dissolved, and the product partly precipitated as a yellow solid. The mixture was added to cold pentane (4 °C, 20 mL) using 2 × 0.5 mL of acetone to rinse the reaction flask. The mixture was allowed to stand at 4 °C for 3 h before the separated product solid was filtered off, washed with pentane, and vacuum-dried. Yield of **1a**·$^1/_2H_2O$: 129.9 mg (76%), yellow solid. Single crystals were obtained by layering an acetone solution of the complex with hexane and by slow crystallization by liquid-phase diffusion. This procedure afforded the stoichiometric solvate **1a**·Me_2CO.

^{1}H NMR (400 MHz, acetone-d_6): δ 4.08 (vt, J' = 2.0 Hz, 2 H, fc), 4.27 (vt, J' = 2.0 Hz, 2 H, fc), 4.74 (br dvt, J' = 2.0, 0.7 Hz, 2 H, fc), 4.94 (br vq, J' = 2.0 Hz, 2 H, fc), 7.46−7.54 (m, 15 H, PPh_3), 7.68−7.74 (m, 4 H, PPh_2), 7.81−7.87 (m, 6 H, PPh_2). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): δ 21.6 (dd, $^2J_{PP}$ = 345, $^1J_{RhP}$ = 129 Hz, fcPPh_2), 28.1 (dd, $^2J_{PP}$ = 345, $^1J_{RhP}$ = 128 Hz, PPh_3). ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 70.45 (s, CH of fc), 70.74 (s, CH of fc), 73.43 (dd, $^1J_{PC}$ = 46 Hz, $^3J_{PC}$ = 4 Hz, C−P of fc), 74.27 (d, J_{PC} = 7 Hz, CH of fc), 77.97 (d, J_{PC} = 13 Hz, CH of fc), 94.89 (s, C−SO_3), 129.32 (d, $^3J_{PC}$ = 10 Hz, CH_{meta} of PPh_2), 129.38 (d, $^3J_{PC}$ = 10 Hz, CH_{meta} of PPh_3), 131.37 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_3), 131.49 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 133.23 (dd, $^1J_{PC}$ = 42 Hz, $^3J_{PC}$ = 4 Hz, C_{ipso} of PPh_3), 134.43 (d, $^2J_{PC}$ = 12 Hz, CH_{ortho} of PPh_2), 135.50 (d, $^2J_{PC}$ = 12 Hz, CH_{ortho} of PPh_3), 135.77 (br d, $^1J_{PC}$ = 47 Hz, C_{ipso} of PPh_2), 189.07 (d vt, $^1J_{RhC}$ = 77 Hz, $^2J_{PC}$ = 18 Hz, CO). IR (Nujol): ν_{max}/cm^{-1} 1987 (vs), 1307 (w), 1278 (s), 1198 (m), 1170 (m), 1147 (s), 1097 (m), 1067 (w), 1037 (m), 1028 (m), 998 (m), 896 (vw), 846 (vw), 827 (w), 747 (m), 705 (m), 694 (s), 641 (s), 584 (m), 544 (m), 526 (m), 516 (s), 492 (m), 482 (m), 453 (w). ESI+ MS: m/z 843.01 ([M + H]$^+$). Anal. Calcd for $C_{41}H_{33}FeO_4P_2RhS\cdot{}^1/_2H_2O$ (851.47): C 57.83, H 4.02%. Found: C 57.56, H 3.86%.

Synthesis of 1b. [Rh(acac)(CO)(PCy_3)] (102.0 mg, 0.2 mmol) and H**L** (90.0 mg, 0.2 mmol) were reacted in acetone (4 mL) as described for compound **1a**. Isolation, as described above, gave compound **1b** as a yellow solid. Yield: 80.4 mg (47%). Crystallization from acetone−hexane (liquid-phase diffusion) afforded single crystals of partly solvated **1b**.

^{1}H NMR (400 MHz, acetone-d_6): δ 1.29−1.48 (m, 9 H, PCy_3), 1.72−1.88 (m, 15 H, PCy_3), 2.16−2.24 (m, 6 H, PCy_3), 2.45−2.55 (m, 3 H, PCy_3), 4.09 (vt, J' = 1.9 Hz, 2 H, fc), 4.33 (vt, J' = 1.9 Hz, 2 H, fc), 4.69 (br vq, J' = 1.9 Hz, 2 H, fc), 4.72 (br vt, J' = 1.9 Hz, 2 H, fc), 7.46−7.54 (m, 6 H, PPh_2), 7.68−7.74 (m, 4 H, PPh_2). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): δ 19.2 (dd, $^2J_{PP}$ = 123, $^1J_{RhP}$ = 320 Hz, fcPPh_2), 42.9 (dd, $^2J_{PP}$ = 123, $^1J_{RhP}$ = 319 Hz, PCy_3). ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 27.33 (s, CH_2 of PCy_3), 28.21 (d, J^2 = 11 Hz, CH_2 of PCy_3), 31.25 (s, CH_2 of PCy_3), 35.26 (d, $^1J_{PC}$ = 19 Hz, CH of PCy_3), 70.39 (s, CH of fc), 71.04 (s, CH of fc), 74.03 (d, J_{PC} = 7 Hz, CH of fc), 74.27 (dd, $^1J_{PC}$ = 43 Hz, $^3J_{PC}$ = 3 Hz, C−P of fc), 77.76 (d, J_{PC} = 12 Hz, CH of fc), 95.09 (s, C−SO_3), 129.15 (d, $^3J_{PC}$ = 10 Hz, CH_{meta} of PPh_2), 131.27 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 134.52 (d, $^2J_{PC}$ = 13 Hz, CH_{ortho} of PPh_2), 136.32 (d, $^1J_{PC}$ = 45 Hz, C_{ipso} of PPh_2), 190.29 (d vt, $^1J_{RhC}$ = 77 Hz, $^2J_{PC}$ = 17 Hz, CO). IR

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(Nujol): ν_{max}/cm^{-1} 3931 (vw), 3652 (w), 3483 (w), 1979 (vs), 1307 (w), 1300 (w), 1271 (s), 1230 (vw), 1192 (s), 1164 (s), 1156 (vs), 1131 (w), 1112 (w), 1099 (m), 1058 (m), 1040 (s), 1022 (m), 1007 (m), 918 (vw), 898 (w), 887 (w), 860 (vw), 847 (m), 828 (w), 816 (w), 751 (m), 742 (m), 698 (m), 694 (m), 660 (m), 637 (s), 583 (m), 542 (m), 508 (m), 489 (m), 470 (m), 444 (w). ESI+ MS: m/z 861.15 ($[M + H]^+$). Anal. Calcd for $C_{41}H_{51}FeO_4P_2RhS$ (860.60): C 57.22, H 5.97%. Found: C 57.35, H 6.04%.

Synthesis of ***1c***. Starting with [Rh(acac)(CO)($PFur_3$)] (92.3 mg, 0.2 mmol) and H**L** (90.0 mg, 0.2 mmol), the procedure described above for **1a** afforded complex **1c** as a yellow solid. Yield: 128.4 mg (79%).

^{1}H NMR (400 MHz, acetone-d_6): δ 4.13 (vt, J' = 2.0 Hz, 2 H, fc), 4.34 (vt, J' = 2.0 Hz, 2 H, fc), 4.79 (d vt, J' = 1.9, J = 0.8 Hz, 2 H, fc), 4.85 (br vq, J' = 1.9 Hz, 2 H, fc), 6.62 (vp, J' = 1.7 Hz, 3 H, $PFur_3$), 7.36 (br ddd, J = 3.2, 2.1, 0.7 Hz, 3 H, $PFur_3$), 7.49−7.58 (m, 6 H, PPh_2), 7.71−7.76 (m, 4 H, PPh_2), 7.92 (br dvt, J = 0.7 Hz, J' = 1.6 Hz, 3 H, $PFur_3$). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ −27.1 (dd, $^2J_{PP}$ = 368, $^1J_{RhP}$ = 132 Hz, $PFur_3$), 22.4 (dd, $^2J_{PP}$ = 368, $^1J_{RhP}$ = 135 Hz, fcPPh$_2$). IR (Nujol): ν_{max}/cm^{-1} 3136 (w), 2016 (vs), 1711 (vw), 1552 (vw), 1306 (vw), 1274 (s), 1214 (w), 1196 (m), 1166 (m), 1147 (s), 1130 (w), 1101 (w), 1059 (vw), 1034 (m), 1027 (m), 1015 (w), 1008 (m), 999 (m), 908 (w), 883 (vw), 844 (vw), 830 (w), 754 (m), 744 (m), 696 (m), 643 (s), 591 (w), 581 (m), 542 (m), 531 (m), 510 (m), 500 (m), 480 (m), 471 (m), 446 (w). ESI+ MS: m/z 812.94 ($[M + H]^+$). Anal. Calcd for $C_{35}H_{27}FeO_7P_2RhS$ (812.35): C 51.75, H 3.35%. Found: C 51.49, H 3.47%.

Synthesis of ***1d***. A solution of trimethyl phosphite (24.8 mg, 0.2 mmol) in acetone (0.5 mL + 1 mL for washing the vial) was added to a suspension of [Rh(acac)$(CO)_2$] (51.6 mg, 0.2 mmol) in the same solvent (0.5 mL), whereupon the solid educt dissolved to give an orange solution. This was added to an acetone suspension of H**L** (90.0 mg, 0.2 mmol), and the resulting mixture was briefly sonicated and then stirred at ambient temperature for 30 min. Then, the cloudy reaction mixture was added to vigorously stirred, cold pentane (4 °C, 20 mL) using 1 mL of acetone to wash the reaction flask. The suspension was aged at 4 °C for 3 h and then filtered. The precipitate was washed pentane and dried under a vacuum to give **1d** as a yellow solid. Yield: 109.4 mg (78%).

^{1}H NMR (400 MHz, acetone-d_6): δ 3.94 (d, $^2J_{PH}$ = 12.3 Hz, 9 H, OMe), 4.12 (vt, J' = 1.9 Hz, 2 H, fc), 4.34 (vt, J' = 1.9 Hz, 2 H, fc), 4.75−4.78 (m, 4 H, fc), 7.48−7.57 (m, 6 H, PPh_2), 7.62−7.68 (m, 4 H, PPh_2). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 18.9 (dd, $^2J_{PP}$ = 511, $^1J_{RhP}$ = 119 Hz, fcPPh$_2$), 127.3 (dd, $^2J_{PP}$ = 511, $^1J_{RhP}$ = 210 Hz, P(OMe)$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6): δ 53.14 (d, $^1J_{PC}$ = 1 Hz, OMe), 70.61 (s, CH of fc), 70.75 (s, CH of fc), 73.40 (dd, $^1J_{PC}$ = 46 Hz, $^3J_{PC}$ = 4 Hz, C−P of fc), 74.29 (d, J_{PC} = 8 Hz, CH of fc), 78.07 (dd, J_{PC} = 13, 2 Hz, CH of fc), 94.33 (s, C−SO_3), 129.44 (d, $^3J_{PC}$ = 10 Hz, CH_{meta} of PPh_2), 131.60 (d, $^4J_{PC}$ = 2 Hz, CH_{para} of PPh_2), 134.28 (dd, $^2J_{PC}$ = 12, 2 Hz, CH_{ortho} of PPh_2), 135.05 (ddd, $^1J_{PC}$ = 46 Hz, J = 3, 2 Hz, C_{ipso} of PPh_2). The compound is poorly soluble, which makes the weak signal due to coordinated CO unobservable. IR (Nujol): ν_{max}/cm^{-1} 2001 (vs), 1712 (m), 1307 (w), 1275 (s), 1195 (s), 1170 (m), 1150 (s), 1101 (m), 1057 (m), 1018 (s), 894 (vw), 832 (w), 809 (m), 757 (m), 702 (m), 697 (m), 657 (w), 641 (m), 580 (m), 541 (m), 518 (m), 505 (m), 494 (m), 484 (m), 472 (m), 442 (w). Anal. Calcd for $C_{26}H_{27}FeO_7P_2RhS$ (704.25): C 44.34, H 3.86%. Found: C 44.52, H 3.89%.

Synthesis of ***2***. [Rh(acac)(nbd)] (58.8 mg, 0.2 mmol) and H**L** (90.1 mg, 0.2 mmol) were mixed in dry acetone (4 mL) under brief sonication. The reaction mixture was stirred for 30 min, during which time the starting materials dissolved and the product partly separated as a yellow solid. The reaction mixture was poured into cold pentane (4 °C, 20 mL) using 1 mL of acetone to wash the reaction flask. The mixture was aged at 4 °C for 3 h and then filtered. The solid product was washed with pentane and dried under a vacuum to give **2**·$^1/_2H_2O$ as a yellow solid. Yield: 110.6 mg, 86%. The mother liquor was evaporated, and the residue crystallized from acetone−hexane (liquid-phase diffusion), giving crystals of nonsolvated **2** suitable for structure determination.

^{1}H NMR (400 MHz, acetone-d_6): δ 1.29 (s, 2 H, nbd), 1.31 (br s, 2 H, nbd), 3.87 (br s, 2 H, nbd), 4.08 (vt, J' = 1.9 Hz, 2 H, fc), 4.31 (vt, J' = 1.9 Hz, 2 H, fc), 4.75 (d vt, J' = 1.9, J = 0.7 Hz, 2 H, fc), 4.85 (br vq, J' = 1.9 Hz, 2 H, fc), 7.43−7.54 (m, 10 H, PPh_2). An additional resonance due to the nbd ligand (2 H) is obscured by the water signal. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 27.4 (d, $^1J_{RhP}$ = 176 Hz). Poor solubility prevented recording ^{13}C NMR and MS spectra. IR (Nujol): ν_{max}/cm^{-1} 1713 (s), 1310 (m), 1261 (s), 1195 (m), 1147 (vs), 1098 (m), 1058 (w), 1028 (m), 1002 (s), 948 (vw), 889 (vw), 847 (w), 831 (w), 800 (vw), 753 (m), 743 (m), 723 (m), 695 (m), 652 (m), 641 (s), 584 (vw), 539 (m), 522 (m), 492 (s), 473 (m), 455 (w), 445 (w). Anal. Calcd for $C_{29}H_{26}FeN_2O_3PRhS{\cdot}0.5H_2O$ (653.31): C 53.31, H 4.17%. Found: C 53.49, H 4.28%.

Synthesis of ***3***. [Rh(μ-Cl)$(CO)_2]_2$ (38.8 mg, 0.1 mmol) and (Et_3NH)**L** (220.2 mg, 0.4 mmol) were dissolved in dry acetone (5 mL), and the resulting red solution was stirred for 3 h, depositing the product as an orange precipitate. The precipitation was completed by storing the reaction mixture at −20 °C overnight. The separated solid was filtered off, washed with acetone, and dried under a vacuum to give an amorphous solid (240 mg). This solid was redissolved in methanol (3 mL), and the solution was layered with methanol−methyl *t*-butyl ether (2 mL of 1:1 mixture) and then with pure methyl *t*-butyl ether (20 mL). The orange crystals which formed within 2 weeks were filtered off, washed with methyl *t*-butyl ether, and dried under a vacuum to give pure **3**. Yield: 220.2 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, NEt_3), 3.10 (q, $^3J_{HH}$ = 7.3 Hz, 6 H, NEt_3), 4.58 (vt, J' = 1.9 Hz, 2 H, fc), 4.60 (br s, 2 H, fc), 4.67 (vt, J' = 1.9 Hz, 2 H, fc), 4.74 (br vt, J' = 1.9 Hz, 2 H, fc), 7.32−7.43 (m, 6 H, PPh_2), 7.63−7.69 (m, 4 H, PPh_2), 10.48 (br s, 1 H, $HNEt_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 21.7 (d, $^1J_{RhP}$ = 127 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 8.66 (s, CH_3 of NEt_3), 46.06 (s, CH_2 of NEt_3), 68.84 (s, CH of fc), 72.24 (s, CH of fc), 75.15 (vt, J_{PC} = 3 Hz, CH of fc), 75.25 (vt, J_{PC} = 26 Hz, C−P of fc), 75.87 (vt, J_{PC} = 5 Hz, CH of fc), 94.52 (s, C−SO_3), 127.82 (vt, $^3J_{PC}$ = 5 Hz, CH_{meta} of PPh_2), 129.83 (s, CH_{para} of PPh_2), 133.93 (vt, $^2J_{PC}$ = 6 Hz, CH_{ortho} of PPh_2), 134.77 (vt, $^1J_{PC}$ = 23 Hz, C_{ipso} of PPh_2), 187.31 (dt, $^1J_{RhC}$ = 74 Hz, $^2J_{PC}$ = 16 Hz, CO). IR (Nujol): ν_{max}/cm^{-1} 2687 (br m), 2525 (m), 1960 (vs), 1307 (w), 1242 (vs), 1181 (m), 1162 (s), 1151 (s), 1095 (m), 1064 (w), 1036 (vs), 1007 (m), 893 (vw), 836 (m), 810 (vw), 756 (w), 748 (m), 698 (m), 656 (s), 651 (s), 629 (w), 576 (w), 564 (w), 540 (w), 533 (w), 504 (vs), 471 (m), 460 (w), 440 (w). ESI+ MS: m/z 1030.92 ($[M - 2NEt_3 - Cl]^+$), 1052.91 ($[M - 2NEt_3 - HCl + Na]^+$), 1074.89 ($[M - 2HNEt_3 - Cl + 2Na]^+$); ESI− MS: m/z 448.99 ($[Ph_2PfcSO_3]^-$). Anal. Calcd for $C_{57}H_{68}ClFe_2N_2O_7P_2RhS_2$ (1269.29): C 53.94, H 5.40, N 2.21%. Found: C 53.82, H 5.36, N 1.87%.

Synthesis of ***4***·$^1/_2H_2O$. Acetone (5 mL) was added to a solid mixture of [Rh(acac)$(CO)_2$] (51.6 mg, 0.2 mmol) and (Et_3NH)**L** (220.6 mg, 0.4 mmol), and the resulting mixture was stirred at room temperature for 3 h. The solid educts rapidly dissolved with effervescence (CO evolution) and formed a clear orange solution. This solution was added dropwise to rapidly stirred hexane (30 mL), and the mixture was left standing at 4 °C for 30 min. Then, the precipitated product was filtered off, washed with hexane and pentane, and dried under a vacuum to give **4**·0.5H_2O as a yellow hygroscopic solid. Yield: 211.0 mg (92%). Crystals of dihydrate **4**·2H_2O were obtained when the reaction mixture was crystallized by successive layering with acetone−hexane (1:1) and hexane and by slow crystallization, whereupon the initially formed oily product slowly converted into aggregates of fine yellow needles.

^{1}H NMR (400 MHz, acetone-d_6): δ 1.33 (t, $^3J_{HH}$ = 7.2 Hz, 9 H, NEt_3), 3.21 (q, $^3J_{HH}$ = 7.2 Hz, 6 H, NEt_3), 4.44 (vt, J' = 1.9 Hz, 2 H, fc), 4.51 (vt, J' = 1.9 Hz, 2 H, fc), 4.63 (br s, 2 H, fc), 4.75 (vt, J' = 1.9 Hz, 2 H, fc), 7.45−7.52 (m, 6 H, PPh_2), 7.73−7.79 (m, 4 H, PPh_2). The signal due to Et_3NH coincides with the water resonance. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 21.3 (d, $^1J_{RhP}$ = 128 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6): δ 9.06 (s, CH_3 of NEt_3), 46.88 (s, CH_2 of NEt_3), 70.27 (s, CH of fc), 71.24 (s, CH of fc), 74.18 (vt, J_{PC} = 25 Hz, C−P of fc), 75.35 (vt, J_{PC} = 4 Hz, CH of fc), 76.77 (vt, J_{PC} = 6 Hz, CH of fc), 96.40 (s, C−SO_3), 129.13 (vt, $^3J_{PC}$ = 5 Hz, CH_{meta} of

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PPh_2), 131.30 (s, CH_{para} of PPh_2), 134.69 (vt, $^2J_{PC}$ = 7 Hz, CH_{ortho} of PPh_2), 135.09 (d vt, $^1J_{PC}$ = 24 Hz, $^2J_{RhC}$ = 1 Hz, C_{ipso} of PPh_2), 189.34 (dt, $^1J_{RhC}$ = 76 Hz, $^2J_{PC}$ = 19 Hz, CO). IR (Nujol): ν_{max}/cm^{-1} 3448 (br m), 1973 (vs), 1648 (vw), 1301 (w), 1280 (s), 1243 (m), 1194 (m), 1166 (m), 1147 (s), 1097 (m), 1060 (m), 1043 (s), 1029 (m), 1011 (w), 993 (m), 896 (vw), 838 (w), 823 (w), 746 (m), 707 (w), 695 (m), 665 (m), 656 (m), 640 (m), 582 (m), 566 (w), 546 (w), 541 (w), 516 (m), 504 (m), 495 (m), 490 (m), 480 (m), 444 (w). ESI+ MS: *m/z* 102.13 ($[HNEt_3]^+$); ESI− MS: *m/z* 1028.93 ($[M - HNEt_3]^-$). Anal. Calcd for $C_{51}H_{52}Fe_2NO_7P_2RhS_2 \cdot 0.5H_2O$ (1140.64): C 53.70, H 4.68, N 1.23%. Found: C 53.66, H 4.68, N 1.31%.

X-ray Crystallography. Full-sphere diffraction data were collected on a Bruker D8 VENTURE Kappa diffractometer equipped with a Duo PHOTON100 detector, a IμS microfocus sealed tube source, and a Cryostream cooler at 120 or 150 K. Mo Kα radiation was used in all cases. The structures were solved by direct methods using SHEXLT-2014[40] and refined by least-squares against F^2 with SHELXL-2014 or SHELXL-2017.[41]

Non-hydrogen atoms were refined with anisotropic displacement parameters. The NH and OH hydrogens in the structure of **4**·$2H_2O$ and the CH═ hydrogens of the π-coordinated nbd ligand in **2** were identified on difference electron density maps and refined as riding atoms with U_{iso}(H) set to 1.2U_{eq} of their bonding partner. Other hydrogen atoms (CH_n) were included in their theoretical positions and refined similarly (i.e., as riding atoms). The disordered water molecule in the structure of partly hydrated **1b** could not be successively modeled and was therefore removed from the refinement using PLATON SQUEEZE.[42] Relevant crystallographic data and structure refinement parameters are given in the Supporting Information (Table S2).

PLATON[43] was used to create all structural drawings and to perform geometric calculations. The numerical values are rounded with respect to their estimated standard deviations (ESDs), given with one decimal place. The parameters pertaining to atoms in constrained positions are given without ESDs.

Catalytic Experiments. *Vinyl Acetate Hydroformylation under Solventless Conditions.* Hydroformylation reactions were performed in a 50 mL stainless steel autoclave equipped with a manometer, a thermostat, a magnetic stirrer, and a gas inlet/outlet system. The weighed catalyst was placed in the autoclave, and vinyl acetate (1 mL) was introduced under a nitrogen atmosphere. The autoclave was closed, flushed three times with hydrogen (5 bar) and thereafter pressurized with syngas (H_2/CO = 1:1) to 20 bar and heated to 80 °C. The pressure drop was monitored during the reaction, and after the reaction was completed, the autoclave was cooled to ambient temperature and depressurized. The organic phase was separated from the residual catalyst by a vacuum transfer procedure and analyzed by GC (Hewlett-Packard 5890 II) and GC-MS (Hewlett-Packard 5971A).

On-Water 1-Hexene Hydroformylation. These experiments were performed in the same autoclave. The catalyst was placed in the autoclave. Subsequently, 1-hexene (1.5 mL) and water (1.5 mL) were introduced under a nitrogen atmosphere. The autoclave was closed, flushed three times with hydrogen (5 bar), and, finally, pressurized with syngas (H_2/CO = 1:1) to 10 bar and heated to 80 °C. When the reaction was finished, the autoclave was cooled to ambient temperature and depressurized. The organic phase was separated from the residual catalyst by vacuum transfer and analyzed by GC and GC-MS as described above.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00800.

Additional structural diagrams, summary of relevant crystallographic data, and copies of the NMR spectra (PDF)

Accession Codes

CCDC 1876459−1876462 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: petr.stepnicka@natur.cuni.cz.

ORCID

Petr Štěpnička: 0000-0002-5966-0578

Notes

The authors declare no competing financial interest.

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