A Facile Synthesis of a Wide Variety of Cationic Ruthenium Hydrido-Arene Complexes of binap (= 1,1′-Binaphthalene-2,2′-diylbis(diphenylphosphane)) and MeO–biphep (= 6,6′-Dimethoxybiphenyl-2,2′-diylbis(diphenylphosphane))

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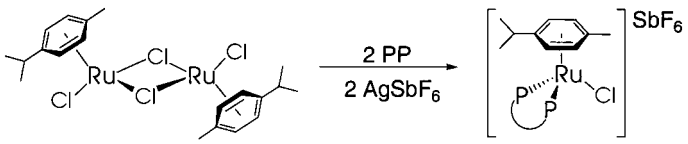
It is our pleasure to dedicate this contribution to Professor *Dieter Seebach*

A straightforward high-yield synthetic route to the cationic hydrido-arene complexes [RuH(η^6-arene)(binap or MeO–biphep)](CF_3SO_3), with a variety of arenes containing both donor and acceptor substituents, is described. ^{13}C-NMR Data for these complexes are reported. Several of these Ru-complexes have been used as transfer-hydrogenation catalysts in the reduction of acetophenone.

1. Introduction. – There is increasing interest in the organometallic chemistry of ruthenium, as a number of these compounds find application in organic synthesis [1–4]. Specifically, complexes of Ru^{II} have been shown to be excellent hydrogenation [5][6] and transfer-hydrogenation [7–13] catalysts.

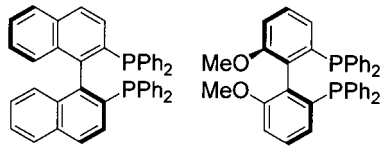
In many cases the Ru-catalyst precursor contains an η^6-arene ligand [4][7][11][14–16], together with nitrogen or phosphorus ligands. These complexes can be prepared by allowing commercially available Cl-bridged η^6-arene (*e.g.*, *p*-cymene) Ruthenium complexes to react with monodentate or bidentate N- or P-donors to afford catalyst precursors in good yield [17a] (see *Scheme 1*). Such complexes are often stable enough to be characterized by X-ray diffraction methods [16][18–27]. The vast majority of these η^6-arene ligands stem from either alkyl benzenes (*e.g.*, toluene, mesitylene or *p*-cymene) or benzene itself. Interestingly, there is a dearth of literature concerned with Ru(η^6-arene) complexes with a variety of substituents on the complexed aromatic moiety. As it is not certain that the η^6-arene ligand remains complexed at the end of all of the various catalytic reactions, it would be useful to have ready access to η^6-arene Ruthenium compounds with both strongly and weakly bound arenes.

Scheme 1



Ruthenium hydride complexes are stable [21][22][25][28][29] and often thought to be involved in hydrogenation chemistry [30]. Several structures of Ru-complexes containing both hydrides and η^6-arene ligands are known [23][25][30–33]. We report

here a general synthetic route to cationic phosphanyl-hydride complexes of the type [RuH(η^6-arene)(binap (**1a**) or MeO–biphep (**1b**))](CF_3SO_3) that allows the use of a wide variety of arene ligands.

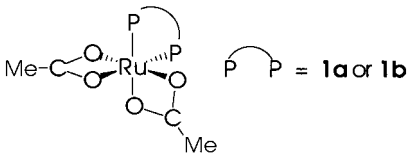


1a: binap **1b**: MeO-biphep

2. Syntheses. – Many ruthenium(II) hydride complexes are prepared *via* addition of H_2 [34–40] to a suitable Ru^{II} compound or, occasionally, *via* oxidative addition with Ruthenium(0) carbonyl complexes [20][41]. We have found it convenient to use i-PrOH as the hydride source (although the synthesis can also be carried out with MeOH), and there is precedence for the use of alcohols in this way [9][32][42].

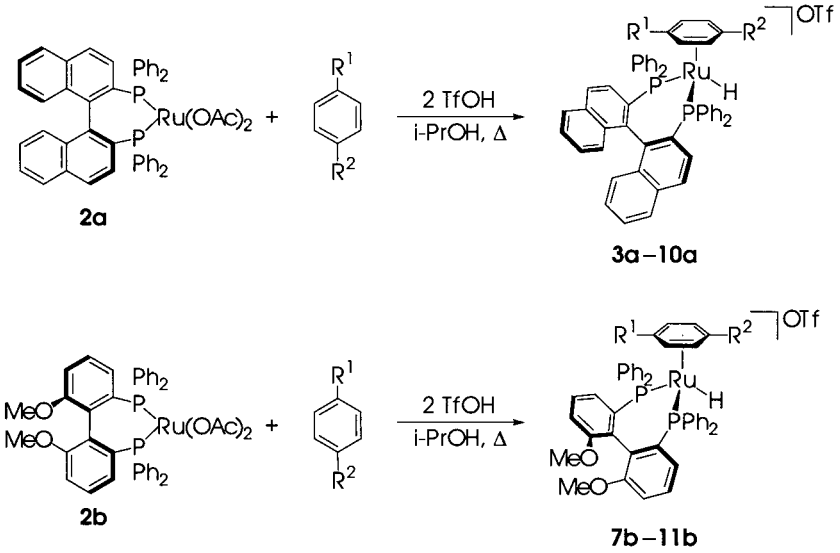
Our synthetic approach involves alcohol complexation followed by β-H elimination; a summary of the new complexes prepared is given in *Scheme 2*. The starting six-coordinate [Ru(OAc)$_2$(binap or MeO–biphep)] complexes **2a** and **2b** are known [5][43][44] and can be prepared in good yield. Protonation of the complexed acetate by trifluoromethanesulfonic acid (TfOH) frees two equivalents of AcOH, thereby allowing the solvent alcohol to coordinate. We presume that a labile cation of the type [Ru(solvent)$_x$(phosphanediyl)]$^{2+}$, $x = 3$ or 4, exists after AcOH loss, and that this complex can readily provide an open coordination position for the β-H elimination. The hydride species that forms, [RuH(solvent)$_x$(binap or MeO–biphep)](CF_3SO_3), $x = 2$ or 3, is relatively stable. A solid-state structure for a five-coordinate compound, [RuH(i-PrOH)$_2$(MeO–biphep-type)](BF_4), [45] is known and [RuH((+)binap)-$(MeCN)_3]^+$ and related derivatives [30] have been reported. The strong hydride ligand labilizes the Ru-coordination sphere, thereby facilitating solvent dissociation and, thus, allowing the arene to complex. The products, [RuH(η^6-arene)(binap)](CF_3SO_3), and [RuH(η^6-arene)(MeO–biphep)] (CF_3SO_3), shown in *Scheme 2*, have been isolated with yields on the order of 68–94%; however, all reactions proceed quantitatively with the material losses arising during the workup.

Clearly, both electron-donating and electron-withdrawing groups on the arene can be accommodated by this preparative route. It is worth noting that these complexes need not have a classical 'piano-stool' structure, and that the plane defined by the two P-atoms and the metal can be *ca.* perpendicular to the arene plane [33].



2a, 2b

Scheme 2



3: $R^1 = R^2 = H$
4: $R^1 = H$; R^2 = Me
5: $R^1 = H$; R^2 = Cl
6: $R^1 = H$; R^2 = C(O)-NH_2
7: $R^1 = H$; R^2 = CH(OH)–Me
8: $R^1 = H$; R^2 = C(O)–Me
9: $R^1 = CH_3$; R^2 = NH-C(O)–Me
10: $R^1 = R^2$ = NH-C(O)–Me
11: $R^1 = H$; R^2 = NH-C(O)-Ph

NMR Spectroscopy. – The complexes were characterized by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. The hydride signals represent the *X* part of an *ABX* spin system and fall in the range of *ca.* -8 to -11 ppm. The ^{31}P-NMR spectra show *AB* spins systems and, occasionally, only a broad singlet, due to the very similar (often separated by < 2 ppm) ^{31}P chemical shifts. The complexed arene was identified *via* its expected [46] low frequency ^{13}C chemical shift (see *Table 1*). These data are best obtained *via* a ^{13}C,^{1}H long-range correlation (see *Fig. 1*), in that all six nonequivalent C-atoms are readily detected *via* their various $^3J(^{13}C,^1H)$ values. There are two cross-peaks per C-atom resonance, thus the assignment is unequivocal. The observed chemical shifts of *ca.* 85–123 ppm correspond to coordination chemical shifts ($\Delta\delta = \delta$(arene complex) $- \delta$(free arene) of *ca.* -15 to -35 ppm. Details of the $\Delta\delta$ values for **4a** and **6a** are shown in *Table 2* and support an η^6-structure, *i.e.*, all six C-atoms are complexed. We do not find a correlation of the C(14) resonance with literature *Hammett* constants.

Aspects of the 3-D solution structure were determined by standard NOE methods. Interestingly, for many of the complexes, the sterically more demanding substituent of the arene is pointing towards the phosphane backbone. *Fig. 2* shows a slice through the hydride region of the NOESY spectrum of **9b**. The strongest contacts stem from two P-phenyls (one being dynamic on the NMR time scale) with additional substantial contacts to H–C(13) of the complexed arene and the tolyl Me group. Notably, there is no contact to either the NH resonance or amide Me group. On the other hand, NOESY

Table 1. *Chemical Shifts of the Hydride and the Complexed Arenes in CD_2Cl_2*

Complex	Hydride	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)
3a	– 8.99	95.5					
4a	– 9.16	111.4	95.1	98.1	91.8	99.1	94.1
5a	– 8.74	113.3	96.5	97.2	91.8	98.2	94.3
6a	– 8.80	97.2	99.0	93.9	95.0	92.3	95.7
7a (major)	– 9.12	121.3	87.8	101.3	94.2	95.4	90.1
7a (minor)	– 8.85	119.5	91.3	98.1	94.1	95.4	92.5
7b (major)	– 9.47	118.6	93.6	97.6	94.0	95.3	91.7
7b (minor)	– 9.24	119.8	89.0	101.3	94.5	95.2	90.7
8a	– 8.73	97.0	101.2	96.5	98.3	93.9	94.1
8b	– 9.03	96.5	101.8	96.2	98.0	94.0	93.1
9a	– 10.36	122.5	87.2	99.6	102.0	93.2	86.6
9b	– 10.71	122.3	86.7	99.6	101.8	92.9	87.2
10a	– 10.24	116.3	85.1	85.6	116.3	85.6	85.1
10b	– 10.64	116.4	85.2	85.8	116.4	85.8	85.2
11b	– 10.16	123.4	86.4	94.4	86.2	99.6	86.4

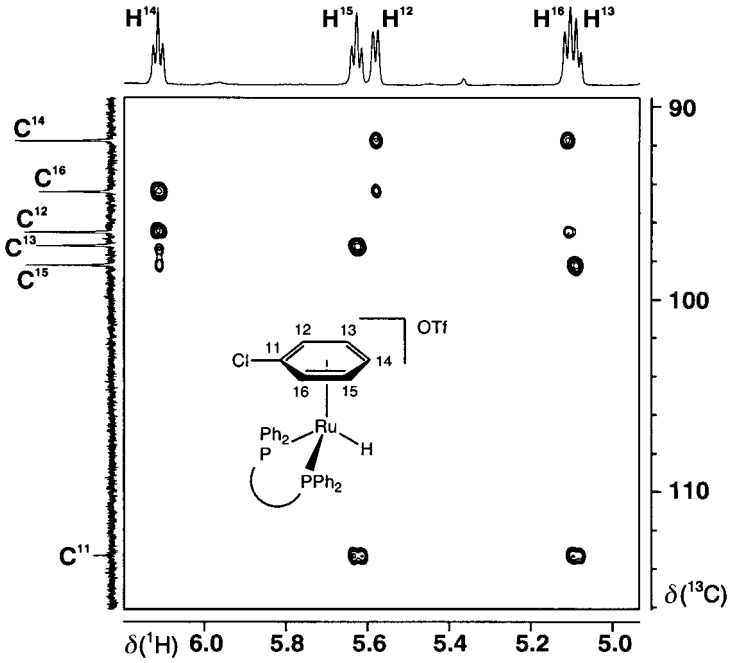
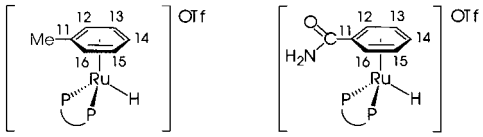


Fig. 1. *Section of the C,H-long range spectrum of* **5a** *in CD_2Cl_2 showing the cross-peaks from the complexed arene due to $^3J(C,H)$*

Table 2. *Coordination Chemical Shifts* ($\Delta\delta = \delta$ (arene complex) – δ (free arene)) *for the binap Complexes* **4a** *and* **6a** *in* CD_2Cl_2



4a **6a**

Arene C-atom	$\Delta\delta$ **4a**	$\Delta\delta$ **6a**
C(11)	– 26.3	– 37.1
C(12)	– 34.1	– 26.6
C(13)	– 30.3	– 33.9
C(14)	– 33.7	– 36.2
C(15)	– 29.3	– 35.7
C(16)	– 35.1	– 30.9

data for the two diastereomeric complexes **7**, reveal contacts from the hydride to the methine and OH-signals of the arene side-chain. As H-bonding of TfO^- to the alcohol can be excluded from pulsed-gradient spin echo (PGSE) diffusion measurements[1]), this difference in arene orientation might arise due to the greater steric bulk of a sp^3-hybridized substituent.

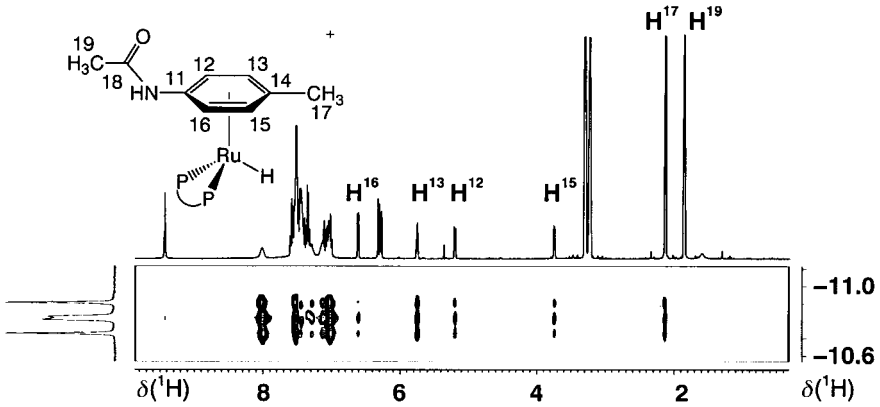


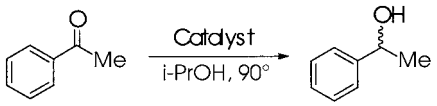
Fig. 2. *Cross-section of the hydride region of the NOESY spectrum of* **9b** *in* CD_2Cl_2. The strongest cross-peaks arise from interactions with P-phenyl protons H–C(13) and H–C(17).

Catalysis. – Several of the hydrido complexes were tested as catalysts in the transfer-hydrogenation reduction of acetophenone (see *Scheme 3*).

The simple arene complexes with, *e.g.*, benzene or toluene, were not active. Neither was the acetophenone analogue **5**, which might conceivably develop during the

[1]) The TfO^- ion moves much faster than the cation, whereas, in the presence of H-bonding, similar rates of diffusion are expected. Moreover, the diffusion constant for the cation is, as expected, only slightly faster than that for [RuCl(η^6-*p*-cymene)(binap)]OTf.

Scheme 3



catalysis due to an arene-exchange reaction. Those arene compounds containing a readily deprotonated group are relatively active (*e.g.*, **7**–**11**), and, for these complexes, the reaction rates are basically independent of the nature of the arene. The MeO–biphep derivatives showed faster rates than the analogous binap complexes. *Fig. 3* shows the formation of the alcohol product as a function of time for both **9b** and the known catalyst $RuCl_2(PPh_3)_3$ **13** [9]. Compound **13** should be a relatively good catalyst, as it contains a monodentate phosphine that can dissociate, thereby facilitating substrate complexation. Nevertheless, complex **9b** is only *ca.* a factor of two slower than **13**. This, together with a lack of arene influence, suggests that the active catalyst has a structure that differs notably from the above compounds.

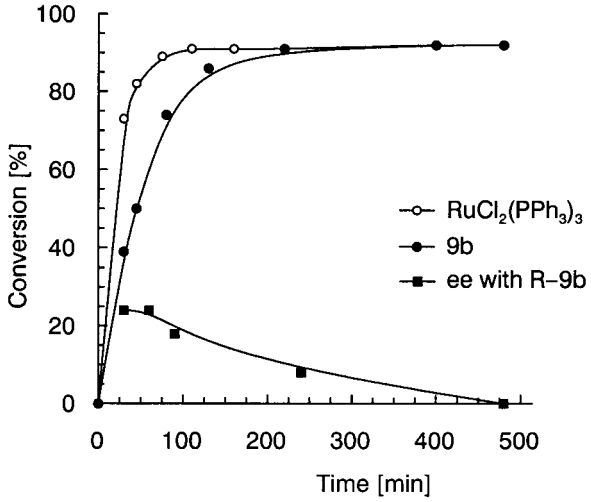


Fig. 3. *Kinetic data for the transfer hydrogenation of acetophenone/i-PrOH at 90° and change in ee over time*

A solution containing complex **9a** together with 2.5 equiv. of KOH in (D_8)i-PrOH was studied *via* NMR spectroscopy. *Ca.* 20 minutes after mixing, a new species is formed quantitatively (see *Table 3* for its ^{13}C characteristics), which we believe arises from deprotonation at the N-atom. After *ca.* 30 min, signals due to uncomplexed *p*-methylacetanilide are observed, *i.e.*, in a basic medium *the arene ligand is lost*. Presumably, this arene loss results in exposure of three additional coordination

Table 3. *Effect of Base on Chemical Shifts of* **9a** (in (D_8)i-PrOH)

	Hydride	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(18)
9a	– 10.26	121.1	88.1	97.9	103.7	93.7	86.8	170.8
9a + base	– 11.23	136.8	91.9	97.4	99.6	93.6	91.3	178.7

positions, which, then, are occupied by i-PrOH and/or substrate. It is likely that this complex is the catalytically active species.

Fig. 3 also shows the observed enantiomeric excess as a function of time. Clearly, the substantial observed decrease in enantiomeric excess with time makes this class of complex unsuitable for enantioselective work. We believe that the loss of the arene ligand gives rise to a labile (and, thus, relatively fast) catalyst capable of racemizing the product $PhCH(OH)CH_3$ *via* oxygen complexation and the usual β-H elimination mechanism [9].

Summarizing, although our preparative route allows access to a wider variety of arene complexes, these are not necessarily the most suitable precursors for transfer hydrogenation.

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Experimental Part

Catalysis: General procedure for the transfer hydrogenation of acetophenone: in an ampoule, a soln. of the catalyst (0.01 mmol) in 10 ml degassed i-PrOH was treated with acetophenone (1.20 g, 10 mmol) and 0.1M i-PrOK/i-PrOH (0.5 ml, 0.05 mmol) and stirred at 90°. The conversion was monitored by NMR, and ee by HPLC (*Chiralcel OB-H*).

Preparation of a Representative Complex: [1,1′-Binaphthalene-2,2′-diylbis(diphenylphosphane)-κ^2-P,P′]hydrido[N-(η^6-tol-4-yl)acetamide]ruthenium(II) Trifluoromethanesulfonate (**9a**). A suspension of $[Ru(OAc)_2$(binap)] (150 mg, 0.178 mmol) and *p*-methylacetanilide (28 mg, 0.188 mmol) in i-PrOH (15 ml) was heated to 75° and subsequently treated with TfOH (35 µl, 0.399 mmol). Upon addition of the acid, the remaining solids dissolved and the soln. color changed to pale yellow. The soln. was allowed to cool to r.t. and concentrated *in vacuo* to *ca.* 1 ml. Addition of pentane led to precipitation of the product, which was collected by filtration. After washing with Et_2O and drying, 108 mg (89%) of complex **9a** was obtained as a pale yellow solid (see below for data).

(η^6-Benzene)[1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane)-κ^2P,P′]-hydridoruthenium(II) Trifluoromethanesulfonate (**3a**): Yield: 94%. ^{1}H-NMR (CD_2Cl_2, 300 MHz): 8.10 (*m*, H–C(5′)); 8.02 (br., 1 H); 7.81–7.43 (*m*, 15 H); 7.40–7.29 (*m*, 4 H); 7.26 (*t*, ^3J(H,H) = 7.3, H–C(9)); 7.00–6.76 (*m*, 7 H); 6.72 (*m*, 1 H); 6.51 (br., 1 H); 6.31 (*d*, ^3J(H,H) = 8.4, H–C(7)); 6.22 (*d*, ^3J(H,H) = 8.4, H–C(7′)); 5.49 (*s*, 6 H, H–C(11)); –8.99 (*dd*, ^2J(P,H) = 39.6, ^2J(P,H) = 29.5). ^{13}C-NMR (CD_2Cl_2, 75 MHz): 138.9 (*m*, C(1′)); 138.2 (*m*, C(1)); 134.6 (*d*, *J*(C,P) = 9); 134.1 (*d*, *J*(C,P) = 12); 133.7, 133.5 (C(3′)); 133.4 (*m*, C(2′), C(3)); 132.9 (*d*, ^3J(C,P) = 8, C(2)); 131.0 (*d*, ^4J(C,P) = 2); 130.7 (*d*, ^4J(C,P) = 2); 130.1 (*d*, ^4J(C,P) = 2); 129.8 (*d*, ^4J(C,P) = 2); 129.2 (C(4)); 129.1 (C(4′)); 128.8 (*d*, *J*(C,P) = 9); 128.6 (*d*, *J*(C,P) = 9); 128.3, 128.2 (C(10′)); 128.0 (C(7), C(10)); 127.7 (C(7′)); 127.6 (C(9′)); 127.5 (C(9)); 126.5 (C(8′)); 126.4 (C(8)); 126.1 (*d*, ^2J(C,P) = 7, C(5′)); 124.8 (*d*, ^2J(C,P) = 8, C(5)); 95.5 (*t*, ^2J(C,P) = 2, C(11)). ^{31}P-NMR (CD_2Cl_2, 202 MHz): 52.5 (*d*, ^2J(P,P) = 45); 51.9 (*d*, ^2J(P,P) = 45). ESI-MS: 803.2 (M^+), 722.9 (100, [M – arene – H_2]$^+$). Anal. calc. for $C_{51}H_{39}F_3O_3P_2RuS$: C 64.35, H 4.13; found: C 64.39, H 4.25.

[1,1′-Binaphthalene-2,2-diylbis(diphenylphosphane)-κ^2P,P′]hydrido(η^6-toluene)ruthenium(II) Trifluoromethanesulfonate (**4a**): Yield: 95%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 8.11 (*m*, C(5′)); 7.99 (br.); 7.79 (*m*, 2 H); 7.74–7.47 (*m*, 14 H); 7.38–7.23 (*m*, 4 H); 6.96–6.76 (*m*, 7 H); 6.73 (*t*, ^3J(H,H) = 7.3, 1 H); 6.49 (br.); 6.33 (*d*, ^3J(H,H) = 8.7, H–C(7)); 6.21 (*d*, ^3J(H,H) = 8.8, H–C(7′)); 6.04 (*t*, ^3J(H,H) = 6.0, H–C(14)); 5.69 (*t*, ^3J(H,H) = 6.0, H–C(15)); 5.27 (*d*, ^3J(H,H) = 6.0, H–C(12)); 4.89 (*t*, ^3J(H,H) = 6.0, H–C(13)); 4.70 (*d*, ^3J(H,H) = 6.4, H–C(16)); 2.14 (*s*, Me); –9.16 (*dd*, ^2J(P,H) = 39.3, ^2J(P,H) = 30.2). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 138.8 (*m*, C(1′)); 138.2 (*m*, C(1)); 134.7 (*d*, *J*(C,P) = 9); 134.0 (*d*, *J*(C,P) = 11); 133.7, 133.5 (C(3′)); 133.4 (*m*, C(2′), C(3)); 132.9 (*d*, ^3J(C,P) = 9, C(2)); 131.0 (*d*, ^4J(C,P) = 2); 130.7 (*d*, ^4J(C,P) = 2); 130.1 (*d*, ^4J(C,P) = 2); 129.8 (*d*, ^4J(C,P) = 2); 129.2 (C(4), C(4′)); 128.8 (*d*, *J*(C,P) = 9); 128.6 (*d*, *J*(C,P) = 9); 128.3, 128.2 (C(10′)); 128.0 (C(7)); 127.7 (C(10)); 127.6 (C(9′)); 127.5 (C(9)); 126.5 (C(8), C(8′)); 126.1 (*d*, ^2J(C,P) = 8, C(5′)); 124.8 (*d*, ^2J(C,P) = 8,

C(5)); 111.4 (C(11)); 99.1 (C(15)); 98.1 (br., C(13)); 95.1 (*d*, ^2J(C,P) = 4, C(12)); 94.1 (*m*, C(16)); 91.8 (C(14)); 21.0. ^{19}F-NMR (CD_2Cl_2, 202 MHz): −79.21 (s). ^{31}P-NMR (CD_2Cl_2, 162 MHz): 53.1 (*d*, ^2J(P,P) = 45); 52.6 (*d*, ^2J(P,P) = 45). ESI-MS: 816.9 (100, M^+), 723.1 ([M^+ − arene − H_2]$^+$). Anal. calc. for $C_{52}H_{41}F_3O_3P_2RuS$: C 64.66, H 4.28; found: C 64.40, H 4.57.

[1,1′-Binaphthalene-2,2′-diylbis(diphenylphosphane)-κ^{2}P,P′](η^6-chlorobenzene)hydridoruthenium(II) Trifluoromethanesulfonate (**5a**): Yield: 91%. ^{1}H-NMR (CD_2Cl_2, 500 MHz): 8.13 (*dd*, ^3J(P,H) = 8.8, ^3J(H,H) = 8.8, H−C(5)); 8.01 (br., 1 H); 7.82 (*m*, H−C(4), H−C(5′)); 7.75 (*d*, ^3J(H,H) = 8.7, H−C(4′)); 7.69 (*m*, 2 H); 7.66 (*d*, ^3J(H,H) = 7.8, H−C(10)); 7.63–7.51 (*m*, 8 H); 7.35 (*m*, 3 H); 7.30 (*t*, ^3J(H,H) = 7.3, H−C(9)); 6.97 (br., 1 H); 6.93 (*m*, H−C(8), H−C(8′)); 6.84 (*m*, 3 H); 6.77 (*m*, 1 H); 6.52 (br., 1 H); 6.36 (*d*, ^3J(H,H) = 8.7, H−C(7)); 6.25 (*d*, ^3J(H,H) = 8.7, H−C(7′)); 6.11 (*t*, ^3J(H,H) = 6.0, H−C(14)); 5.63 (*t*, ^3J(H,H) = 6.0, H−C(15)); 5.58 (*d*, ^3J(H,H) = 6.4, H−C(12)); 5.11 (*d*, ^3J(H,H) = 6.8, H−C(16)); 5.09 (*t*, ^3J(H,H) = 6.0, H−C(13)); −8.74 (*dd*, ^2J(P,H) = 41.2, 29.7). ^{13}C-NMR (CD_2Cl_2, 125 MHz): 139.0 (C(1′)); 138.2 (C(1)); 134.8 (*d*, *J*(C,P) = 9); 134.3 (C(6′)); 134.1 (*d*, *J*(C,P) = 12); 133.8 (C(3), C(3′)); 133.5 (*d*, *J*(C,P) = 10); 133.3 (C(2′)); 133.0 (C(2)); 132.5 (C(61)); 131.3 (*d*, *J*(C,P) = 3); 131.0 (*d*, *J*(C,P) = 3); 130.3 (*d*, *J*(C,P) = 3); 130.1 (*d*, *J*(C,P) = 3); 129.5 (*d*, *J*(C,P) = 9, C(4)); 129.3 (*d*, *J*(C,P) = 9, C(4′)); 128.9 (*d*, *J*(C,P) = 10); 128.7 (*d*, *J*(C,P) = 10); 128.3 (C(10′)); 128.0 (C(10)); 127.7 (C(9′)); 127.6 (C(9)); 126.6 (C(8), C(8′)); 126.2 (*d*, ^2J(C,P) = 8, C(5′)); 124.7 (*d*, ^2J(C,P) = 8, C(5)); 113.3 (br., C(11)); 98.2 (br., C(15)); 97.2 (br., C(13)); 96.5 (*d*, ^2J(C,P) = 3, C(12)); 94.4 (br., C(16)); 91.8 (*d*, ^2J(C,P) = 2, C(14)). ^{31}P-NMR (CD_2Cl_2, 202 MHz): 51.4 (*d*, ^2J(P,P) = 43); 50.6 (*d*, ^2J(P,P) = 43). ESI-MS: 837.0 (M^+), 722.9 (100, [M^+ − arene − H_2]$^+$). Anal. calc. for $C_{51}H_{38}ClF_3O_3P_2RuS$: C 62.10, H 3.88; found: C 61.47, H 4.27.

(η^6-Benzamide)[1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane)-κ^{2}P,P′]hydridoruthenium(II) Trifluoromethanesulfonate (**6a**): Yield: 72%. ^{1}H-NMR (CD_2Cl_2, 500 MHz): 8.13 (*dd*, ^3J(P,H) = 8.7, ^3J(H,H) = 8.7, H−C(5′)); 7.83–7.49 (*m*); 7.37–7.30 (*m*); 7.28 (*t*, ^3J(H,H) = 7.3, H−C(9)); 6.94–6.77 (*m*); 6.74 (*m*, 1 H); 6.68 (*d*, ^3J(H,H) = 6.0, H−C(16)); 6.32 (*m*, H−C(7), H−C(14)); 6.26 (*d*, ^3J(H,H) = 8.2, H−C(7′)); 5.76 (*t*, ^3J(H,H) = 6.0, H−C(13)); 5.36 (*d*, ^3J(H,H) = 6.4, H−C(12)); 4.45 (*t*, ^3J(H,H) = 6.4, H−C(15)); −8.80 (*dd*, ^2J(P,H) = 41.2, ^2J(P,H) = 28.9). ^{13}C-NMR (CD_2Cl_2, 75 MHz): 164.5 (C(17)); 138.2 (br., C(1)); 137.5 (br., C(1′)); 134.1 (*d*, *J*(C,P) = 9); 133.7 (C(3), C(3′)); 133.4 (*d*, *J*(C,P) = 12); 133.0 (C(2), C(2′)); 132.9 (*d*, *J*(C,P) = 2); 132.7 (C(6), C(6′)); 130.3 (*d*, *J*(C,P) = 14); 129.5 (C(4)); 129.2 (C(4′)); 128.8 (C(10), C(10′)); 128.7 (*d*, *J*(C,P) = 9); 128.4 (*d*, *J*(C,P) = 9); 128.1 (C(7)); 128.0 (C(7′)); 127.7 (C(9′)); 127.5 (C(9)); 126.9 (C(8′)); 126.7 (C(8)); 125.6 (C(5′)); 124.2 (C(5)); 99.0 (br., C(12)); 97.2 (*d*, ^2J(C,P) = 3, C(11)); 95.7 (C(16)); 95.0 (C(14)); 93.9 (C(13)); 92.3 (br., C(15)). ^{31}P-NMR (CD_2Cl_2, 202 MHz): 51.3 (*d*, ^2J(P,P) = 44); 50.5 (*d*, ^2J(P,P) = 44). ESI-MS: 846.0 (M^+), 722.9 ([M^+ − arene − H_2]$^+$). Anal. calc. for $C_{52}H_{40}F_3NO_4P_2RuS$: C 62.77, H 4.05; found: C 59.41, H 4.20.

[1,1′-Binaphthalene-2,2′-diylbis(diphenylphosphane)-κ^{2}P,P′]hydrido[1-(η^6-phenyl)ethanol]ruthenium(II) Trifluoromethanesulfonate (**7a**): Yield: 90%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 8.15 (*m*); 8.05 (br.); 7.88–7.46 (*m*); 7.42–7.22 (*m*); 6.97–6.62 (*m*); 6.40 (*m*); 6.23 (*m*); 5.77 (H−C(12), H−C(13), minor); 5.46 (*t*, br., ^3J(H,H) = 5.5, H−C(13), major); 5.18 (*d*, ^3J(H,H) = 5.9, H−C(12), major); 5.00 (br., H−C(15), major); 4.78 (*d*, ^3J(H,H) = 5.9, H−C(16), major); 4.70 (br. *m*, H−C(17), major); 4.44 (br. *m*, H−C(17), minor); 4.40–4.33 (*m*, H−C(15), H−C(16), minor); 3.80 (*d*, ^3J(H,H) = 4.2, OH, minor); 3.61 (*d*, ^3J(H,H) = 4.2, OH, major); 1.42 (*d*, ^3J(H,H) = 6.4, H−C(18), major); 1.37 (*d*, ^3J(H,H) = 6.4, H−C(18), minor); −8.85 (*dd*, ^2J(P,H) = 38.2, ^2J(P,H) = 30.4, major); −9.11 (*dd*, ^2J(P,H) = 39.2, ^2J(P,H) = 30.6, major). ^{31}P-NMR (CD_2Cl_2, 162 MHz): 52.7 (*d*, ^2J(P,P) = 31, major); 52.6 (*d*, ^2J(P,P) = 31, major); 52.2 (*d*, ^2J(P,P) = 31, minor); 52.1 (*d*, ^2J(P,P) = 31, minor). ESI-MS: 846.9 (M^+), 722.8 (100, [M − arene − H_2]$^+$). Anal. calc. for $C_{53}H_{43}F_3O_4P_2RuS$: C 63.91, H 4.35; found: C 63.44, H 4.49.

[6,6′-Dimethoxybiphenyl-2,2′-diylbis(diphenylphosphane)-κ^{2}P,P′]hydrido[1-(η^6-phenyl)ethanol]ruthenium-(II) Trifluoromethanesulfonate (**7b**): Yield: 91%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 8.21 (br.); 7.59–7.31 (*m*); 7.15–7.04 (*m*); 6.99 (br.); 6.46 (*t*, ^3J(H,H) = 6.0, H−C(14), minor); 6.36–6.29 (*m*, 4 H); 5.92 (*d*, ^3J(H,H) = 6.0, H−C(16), major); 5.83 (*d*, ^3J(H,H) = 6.0, H−C(13), major); 5.47 (*m*, H−C(13), minor); 4.96 (*d*, ^3J(H,H) = 6.0, H−C(12), minor); 4.92 (*d*, ^3J(H,H) = 6.0, H−C(16), minor); 4.77 (*m*, H−C(15), minor); 4.73 (*q*, ^3J(H,H) = 6.4, H−C(17), minor); 4.37 (*q*, ^3J(H,H) = 6.4, H−C(17), major); 4.20 (*t*, ^3J(H,H) = 6.0, H−C(15), major); 4.16 (*d*, ^3J(H,H) = 6.0, H−C(12), major); 3.31 (*s*, Me, major); 3.29 (*s*, Me, minor); 3.25 (*s*, Me, minor); 3.24 (*s*, Me, major); 1.41 (*d*, ^3J(H,H) = 6.4, H−C(18), minor); 1.36 (*d*, ^3J(H,H) = 6.4, H−C(18), major); −9.24 (*dd*, ^2J(P,H) = 40.3, ^2J(P,H) = 30.2, minor); −9.47 (*dd*, ^2J(P,H) = 40.8, ^2J(P,H) = 29.8, major). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 119.8 (C(11), minor); 118.6 (C(11), major); 101.3 (C(13), minor); 97.6 (C(13), major); 95.3 (br., C(15), major); 95.2 (br., C(15), minor); 94.5 (C(14), minor); 94.0 (C(14), major); 93.6 (br., C(12), major); 91.7 (*d*, ^2J(C,P) = 4, C(16), major); 90.7 (br., C(16), minor); 89.0 (*d*, ^2J(C,P) = 6, C(12), minor); 67.5 (C(17), major); 67.3 (C(17), minor); 55.0 (C(7), C(7′)); 54.9 (C(7), C(7′)); 25.9 (C(18), major); 25.7 (C(18), minor). ^{31}P-NMR (CD_2Cl_2,

162 MHz): 50.8 (*d*, ^2J(P,P) = 46, major); 50.5 (*d*, ^2J(P,P) = 45, minor); 50.1 (*d*, ^2J(P,P) = 45, minor); 49.8 (*d*, ^2J(P,P) = 46, major). ESI-MS: 806.9 (M^+), 682.8 (100, $[M - \text{arene} - H_2]^+$). Anal. calc. for $C_{47}H_{43}F_3O_6P_2RuS$: C 59.05, H 4.53; found: C 58.62, H 4.91.

[1,1′-Binaphthalene-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydrido[(η⁶-phenyl)acetone]ruthenium(II) Trifluoromethanesulfonate (**8a**): Synthesis performed in MeOH. Yield: 68%. ^{1}H-NMR (CD_2Cl_2, 500 MHz): 8.06 (*dd*, ^3J(P,H) = 9.2, ^3J(H,H) = 9.2, H–C(5′)); 7.81–7.26 (*m*, 19 H); 6.99–6.76 (*m*, 10 H); 6.66 (*m*, H–C(14)); 6.51 (*d*, ^3J(H,H) = 6.4, H–C(16)); 6.35 (br., H–C(13)); 6.29 (*d*, ^3J(H,H) = 8.7, H–C(7)); 6.25 (*d*, ^3J(H,H) = 8.7, H–C(7′)); 5.03 (*d*, ^3J(H,H) = 6.4, H–C(12)); 4.28 (br., H–C(15)); 2.08 (*s*, H–C(18)); –8.73 (*dd*, ^2J(P,H) = 41.2, ^2J(P,H) = 28.0). ^{13}C-NMR (CD_2Cl_2, 125 MHz): 195.6 (C(17)); 139.0 (C(1′)); 138.0 (C(1)); 137.7 (*d*, *J*(C,P) = 46); 134.6 (*d*, *J*(C,P) = 9); 134.1 (*d*, *J*(C,P) = 13); 134.0 (*d*, *J*(C,P) = 10); 133.8 (C(3), C(3′)); 133.4 (*d*, ^3J(C,P) = 8, C(2′)); 132.8 (*d*, ^3J(C,P) = 9, C(2)); 132.5 (C(6), C(6′)); 131.1 (*m*); 130.3 (*d*, *J*(C,P) = 2); 129.5 (*d*, ^3J(C,P) = 9, C(4′)); 129.3 (*d*, ^3J(C,P) = 9, C(4)); 129.0 (*d*, *J*(C,P) = 10); 128.8 (*d*, *J*(C,P) = 10); 128.3 (*d*, *J*(C,P) = 11); 128.0 (C(7), C(9′)); 127,8 (C(7′)); 127.7 (C(9)); 126.6 (C(8), C(8′)); 126.1 (*d*, ^2J(C,P) = 8, C(5′)); 124.6 (*d*, ^2J(C,P) = 9, C(5)); 101.2 (*d*, ^2J(C,P) = 4, C(12)); 98.3 (C(14)); 97.0 (*d*, ^2J(C,P) = 6, C(11)); 96.5 (C(13)); 94.1 (*d*, ^2J(C,P) = 3, C(16)); 93.9 (*d*, ^2J(C,P) = 5, C(15)); 26.1 (C(18)). ^{31}P-NMR (CD_2Cl_2, 202 MHz): 50.9 (*d*, ^2J(P,P) = 44); 49.6 (*d*, ^2J(P,P) = 44). ESI-MS: 845.0 (M^+), 722.9 ($[M - \text{arene} - H_2]^+$). Anal. calc. for $C_{53}H_{41}F_3O_4P_2RuS$: C 64.04, H 4.16; found: C 62.29, H 4.50.

[6,6′-Dimethoxybiphenyl-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydrido[η⁶-phenyl)acetone]ruthenium-(II) Trifluoromethanesulfonate (**8b**): Yield: 81%. ^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.92 (br., 1 H); 7.67–6.85 (*m*, 23 H); 6.63 (*t*, ^3J(H,H) = 6.0, H–C(14)); 6.52 (*d*, ^3J(H,H) = 6.6, H–C(16)); 6.40 (*t*, ^3J(H,H) = 6.0, H–C(13)); 6.31 (*d*, ^3J(H,H) = 8.2, H–C(3), H–C(3′)); 4.88 (*d*, ^3J(H,H) = 6.0, H–C(12)); 4.03 (*t*, ^3J(H,H) = 6.6, H–C(15)); 3.29 (*s*, MeO, H–C(7)); 3.24 (*s*, MeO, H–C(7′)); 2.04 (*s*, Me, H–C(18)); –9.03 (*dd*, ^2J(P,H) = 42.3, ^2J(P,H) = 29.1, 1 H). ^{13}C-NMR (CD_2Cl_2, 75 MHz): 195.7 (C(17)); 157.9 (*d*, ^3J(C,P) = 12, C(2′)); 157.7 (*d*, ^3J(C,P) = 12, C(2)); 137.6 (*d*, *J*(C,P) = 46); 136.3 (*d*, *J*(C,P) = 60); 134.5 (*m*); 134.2 (*d*, *J*(C,P) = 9); 133.8 (*d*, *J*(C,P) = 10); 131.2 (*m*); 129.5 (*d*, ^3J(C,P) = 11, C(4), C(4′)); 128.7 (*m*); 128.4 (*d*, ^4J(C,P) = 4, C(5), C(5′)); 122.3 (*d*, *J*(C,P) = 7); 120.4 (*d*, *J*(C,P) = 7); 112.0 (*d*, ^2J(C,P) = 24, C(3), C(3′)); 101.8 (*d*, ^2J(C,P) = 5, C(12)); 98.0 (C(14)); 96.2 (*d*, ^2J(C,P) = 1, C(13)); 94.0 (*d*, ^2J(C,P) = 6, C(15)); 93.7 (*d*, ^2J(C,P) = 4, C(16)); 55.1 (C(7)); 55.0 (C(7′)); 26.1 (C(18)). ^{31}P-NMR (CD_2Cl_2, 121 MHz): 49.0 (d, ^2J(P,H) = 46); 47.4 (*d*, ^2J(P,H) = 46). ESI-MS: 805.0 (M^+), 682.7 ($[M - \text{arene} - H_2]^+$), 604.8 (100, $[M - \text{arene} - \text{Ph}]^+$). Anal. calc. for $C_{47}H_{41}F_3O_6P_2RuS \cdot$ MeOH: C 58.53, H 4.50; found: C 58.66, H 4.99.

*[1,1′-Binaphthalene-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydrido[*N*-(η⁶-tol-4-yl)acetamide]ruthenium-(II) Trifluoromethanesulfonate* (**9a**): Yield: 89%. ^{1}H-NMR (CD_2Cl_2, 500 MHz): 9.45 (*s*, NH); 8.22 (*m*, H–C(5)); 7.89 (br., 1 H); 7.79 (*m*, H–C(4), H–C(5′)); 7.71–7.52 (*m*, 12 H); 7.32 (3 H); 7.24 (*t*, ^3J(H,H) = 7.3, H–C(9′)); 6.92–6.84 (*m*, 7 H); 6.75 (*t*, ^3J(H,H) = 7.3, 1 H); 6.59 (*m*, 2 H); 6.23 (*d*, ^3J(H,H) = 8.3, H–C(7′)); 6.21 (*d*, ^3J(H,H) = 8.3, H–C(7)); 5.76 (*d*, ^3J(H,H) = 6.9, H–C(15)); 5.36 (*d*, ^3J(H,H) = 6.9, H–C(16)); 3.85 (*d*, ^3J(H,H) = 6.9, H–C(13)); 2.09 (*s*, Me, H–C(19)); 1.81 (*s*, Me, H–C(18)); –10.36 (1 H). ^{13}C-NMR (CD_2Cl_2, 125 MHz): 170.5 (C(18)); 139.1 (*m*, C(1)); 137.7 (*m*, C(1′)); 136.4 (*d*, ^1J(C,P) = 39, C(6′)); 136.0 (C(6)); 134.8 (*d*, ^4J(C,P) = 3, C(3)); 134.7 (*d*, ^4J(C,P) = 3, C(3′)); 134.4 (*d*, *J*(C,P) = 3); 134.3 (*d*, *J*(C,P) = 3); 133.8 (*d*, ^3J(C,P) = 3, C(2)); 133.7 (*d*, ^3J(C,P) = 3, C(2′)); 130.6 (*d*, *J*(C,P) = 6); 129.8, 128.9 (*m*, C(5′)); 128.8 (*d*, ^3J(C,P) = 3, C(4)); 128.7 (*d*, ^3J(C,P) = 3, C(4′)); 128.5 (*d*, *J*(C,P) = 3); 128.4 (*d*, *J*(C,P) = 3); 128.2 (C(10)); 128.1 (C(10′)); 127.8 (C(7′)); 127.7 (C(7)); 127.3 (C(9)); 127.1 (C(9′)); 126.4 (*m*, C(5)); 126.2 (C(8)); 126.1 (C(8′)); 122.5 (C(11)); 102.0 (*m*, C(14)); 99.6 (*m*, C(13)); 93.2 (*m*, C(15)); 87.2 (C(12)); 86.6 (*m*, C(16)); 24.3 (C(19)); 20.5 (C(17)). ^{31}P-NMR (CD_2Cl_2, 162 MHz): 52.5 (*s*). ESI-MS: 873.4 (M^+), 722.6 (100, $[M - \text{arene} - H_2]^+$). Anal. calc. for $C_{54}H_{43}F_3NO_4P_2RuS$: C 63.46, H 4.24, N 1.37; found: C 62.79, H 4.31, N 1.33.

*[6,6′-Dimethoxybiphenyl-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydrido[*N*-(η⁶-tol-4-yl)acetamide]ruthenium(II) Trifluoromethanesulfonate* (**9b**): Yield: 93%. ^{1}H-NMR (CD_2Cl_2, 500 MHz): 9.42 (*s*, NH); 8.02 (br., 1 H); 7.60 (*t*, ^3J(H,H) = 7.3, 2 H); 7.56–7.32 (*m*, 16 H); 7.30 (br., 1 H); 7.15 (br., 1 H); 7.14–7.00 (*m*, 3 H); 6.62 (*m*, H–C(16)); 6.32 (*d*, ^3J(H,H) = 8.4, H–C(3′)); 6.28 (*d*, ^3J(H,H) = 8.0, H–C(3)); 5.76 (*d*, ^3J(H,H) = 7.3, H–C(15)); 5.20 (*m*, H–C(12)); 3.75 (*d*, ^3J(H,H) = 6.5, H–C(13)); 3.30 (*s*, MeO, H–C(7′)); 3.23 (*s*, MeO, H–C(7)); 2.14 (*s*, Me, H–C(17)); 1.87 (*s*, Me, H–C(19)); –10.71 (*dd*, ^2J(P,H) = 39.0, ^2J(P,H) = 31.7, 1 H). ^{13}C-NMR (CD_2Cl_2, 125 MHz): 170.5 (C(18)); 157.8 (*d*, ^3J(C,P) = 1, C(2′)); 157.6 (*d*, ^3J(C,P) = 1, C(2)); 139.0 (*d*, ^1J(C,P) = 45, C(6)); 134.9 (*m*); 134.4 (*m*); 133.6 (*m*); 130.7 (*d*, *J*(C,P) = 1); 130.5, 130.4, 129.1 (*m*); 128.9 (*m*); 128.5 (*m*); 128.3 (*m*); 127.7 (*m*); 126.6 (*m*); 122.4 (*d*, ^2J(C,P) = 6, C(5′)); 122.3 (C(11)); 120.3 (*d*, ^2J(C,P) = 7, C(5)); 111.7 (*d*, ^4J(C,P) = 1, C(3′)); 111.1 (*d*, ^4J(C,P) = 1, C(3)); 101.8 (*m*, C(14)); 99.6 (*m*, C(13)); 92.9 (*m*, C(15)); 87.3 (C(16)); 86.7 (*m*, C(12)); 54.9 (C(7), C(7′)); 24.4 (C(19)); 20.7 (C(17)). ^{31}P-NMR (CD_2Cl_2,

202 MHz): 50.5 (*s*). ESI-MS: 833.9 (100, M^+), 776.9 ([$M - C_2H_3NO$]$^+$), 683.0 ([M – arene – H_2]$^+$). Anal. calc. for $C_{48}H_{44}F_3NO_6P_2RuS$: C 58.65, H 4.51, N 1.42; found: C 58.50, H 4.61, N 1.45.

{N-[4-(Acetylamino)-η⁶-phenyl]acetamide}[1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydridoruthenium(II) Trifluoromethanesulfonate (**10a**): Yield: 74%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 9.20 (*s*, 2 NH); 8.08 (*t*, ^3J(H,H) = 7.3, H–C(5)); 7.78 (br., 1 H); 7.73–7.64 (*m*, 3 H); 7.62–7.46 (*m*, 8 H); 7.39–7.31 (*m*, 3 H); 7.27 (*m*, H–C(9)); 7.22–7.14 (*m*, 4 H); 6.94–6.80 (*m*, 4 H); 6.76–6.67 (*m*, 4 H); 6.50 (br., 1 H); 6.22 (*m*, 3 H); 6.16 (*d*, ^3J(H,H) = 8.6, H–C(7)); 4.95 (*d*, ^3J(H,H) = 7.0, H–C(12), H–C(16)); 1.96 (*s*, 2 Me, H–C(18)); –10.24 (*dd*, ^2J(P,H) = 41.2, ^2J(P,H) = 29.1, 1 H). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 170.3 (C(17)); 139.1 (*m*, C(1)); 137.7 (*m*, C(1′), C(6)); 136.1 (C(6′)); 134.0, 133.6, (C(3), C(3′)); 133.4 (*d*, ^3J(C,P) = 8, C(2)); 132.9 (*d*, ^3J(C,P) = 10, C(2′)); 130.5 (*d*, J(C,P) = 11); 129.7 (*d*, J(C,P) = 10); 129.0 (*d*, J(C,P) = 10); 128.6 (C(4)); 128.3, 128.1, 128.0 (C(10)); 129.7 (C(4′), C(7′)); 127.7 (C(7), C(10)); 127.2 (C(9)); 127.0 (C(9′)); 126.5 (C(5)); 126.1 (C(8′)); 126.0 (C(8)); 124.9 (C(5′)); 116.3 (br., C(11), C(14)); 85.8 (br., C(13), C(15)); 85.4 (br., C(12), C(16)); 24.2 (C(15)). ^{31}P-NMR (CD_2Cl_2, 162 MHz): 53.4 (*d*, ^2J(P,P) = 44); 52.5 (*dd*, ^2J(P,P) = 44). ESI-MS: 917.0 (100, M^+), 814.9. Anal. calc. for $C_{55}H_{45}F_3N_2O_5P_2RuS$: C 61.97, H 4.25, N 2.63; found: C 61.23, H 4.86, N 2.51.

{N-[4-(N-Acetylamino)-η⁶-phenyl]acetamide}[6,6′-dimethoxybiphenyl-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydridoruthenium(II) Trifluoromethanesulfonate (**10b**): Yield: 74%. ^{1}H-NMR (CD_2Cl_2, 500 MHz): 9.32 (*s*, NH); 7.88 (br., 1 H); 7.47–7.21 (*m*); 7.11–6.95 (*m*); 6.28 (*m*, H–C(3), H–C(3′)); 6.22 (*d*, ^3J(H,H) = 6.4, H–C(15), H–C(13)); 4.83 (*d*, ^3J(H,H) = 6.4, H–C(12), H–C(16)); 3.28 (*s*, H–C(7), MeO); 3.23 (*s*, H–C(7′), MeO); 2.03 (*s*, H–C(18)); –10.64 (*dd*, ^2J(P,H) = 42.2, ^2J(P,H) = 29.8, 1 H). ^{13}C-NMR (CD_2Cl_2, 125 MHz): 170.3 (C(17)); 157.8 (*d*, ^3J(C,P) = 11, C(2)); 157.6 (*d*, ^3J(C,P) = 12, C(2′)); 138.5 (*d*, ^1J(C,P) = 58); 137.8 (*d*, ^1J(C,P) = 45); 136.1 (*d*, ^1J(C,P) = 50); 134.8 (*d*, J(C,P) = 13); 134.3 (C(6), C(6′)); 134.1 (*d*, J(C,P) = 9); 133.9 (*d*, J(C,P) = 10); 132.7 (*d*, ^1J(C,P) = 58); 130.5 (*d*, J(C,P) = 20); 130.4 (*d*, J(C,P) = 9); 129.1 (*d*, ^3J(C,P) = 10, C(4′)); 128.9 (*d*, ^3J(C,P) = 10, C(4)); 128.1 (*d*, J(C,P) = 10); 128.0 (*d*, J(C,P) = 10); 122.5 (*d*, ^2J(C,P) = 6, C(5′)); 120.4 (*d*, ^2J(C,P) = 7, C(5)); 116.4 (br., C(11), C(14)); 111.6 (C(3)); 111.1 (C(3′)); 85.8 (C(13), C(15)); 85.2 (C(12), C(16)); 54.9 (C(7), C(7′)); 24.3 (C(18)). ^{31}P-NMR (CD_2Cl_2, 162 MHz): 53.4 (*d*, ^2J(P,H) = 44); 52.5 (*d*, ^2J(P,H) = 44). ESI-MS: 877.0 (100, M^+), 684.7 ([M – arene – H_2]$^+$). Anal. calc. for $C_{49}H_{45}N_2O_7P_2RuS$: C 57.36, H 4.42, N 2.73; found: C 56.90, H 4.68, N 2.62.

[6,6′-Dimethoxybiphenyl-2,2′-diylbis(diphenylphosphane)-κ²P,P′]hydrido[N-(η⁶-phenyl)benzamide]ruthenium(II) Trifluoromethanesulfonate (**11b**): Synthesis performed in MeOH. Yield: 78%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 9.33 (*s*, NH); 8.18 (br., 1 H); 7.79 (*m*, 2 H); 7.57–7.22 (*m*, 21 H); 7.14–6.98 (*m*, 5 H); 6.83 (*m*, H–C(16)); 6.30 (*d*, ^3J(H,H) = 6.4, H–C(3), H–C(3′)); 5.84 (*m*, H–C(13)); 5.77 (*d*, ^3J(H,H) = 6.4, H–C(12)); 5.46 (*t*, ^3J(H,H) = 5.7, H–C(14)); 4.60 (*t*, ^3J(H,H) = 6.4, H–C(15)); 3.29 (*s*, MeO); 3.26 (*s*, MeO); –10.16 (*dd*, ^2J(P,H) = 40.6, ^2J(P,H) = 29.6, 1 H). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 166.8 (C(17)); 157.8 (*d*, ^3J(C,P) = 11, C(2′)); 157.7 (*d*, ^3J(C,P) = 11, C(2)); 138.2 (*dd*, ^1J(C,P) = 42, ^3J(C,P) = 3, C(6)); 136.6 (*dd*, ^1J(C,P) = 47, ^3J(C,P) = 5); 134.8 (*d*, J(C,P) = 12); 134.4 (*d*, J(C,P) = 9); 133.4 (*d*, J(C,P) = 10); 133.2, 132.6, 130.6 (*dd*, J(C,P) = 10, J(C,P) = 2); 130.4 (*dd*, J(C,P) = 8, J(C,P) = 2); 129.3 (*d*, ^3J(C,P) = 9, C(4)); 129.1 (*m*); 128.7, 128.5, 128.4, 128.3 (C(4′)); 123.4 (C(11)); 122.8 (*d*, ^2J(C,P) = 7, C(5′)); 120.6 (*d*, ^2J(C,P) = 7, C(5)); 111.6 (*d*, ^4J(C,P) = 2, C(3)); 111.3 (*d*, ^4J(C,P) = 2, C(3′)); 99.6 (br., C(15)); 94.4 (br., C(13)); 86.5 (C(16)); 86.4 (*d*, ^2J(C,P) = 4, C(12)); 86.2 (*d*, ^2J(C,P) = 4, C(14)); 54.9 (C(7), C(7′)). ^{31}P-NMR (CD_2Cl_2, 162 MHz): 51.5 (d, ^2J(P,H) = 45); 51.0 (*d*, ^2J(P,H) = 45). ESI-MS: 882.0 (100, M^+), 682.8 ([M – arene – H_2]$^+$). Anal. calc. for $C_{52}H_{44}F_3NO_6P_2RuS \cdot MeOH$: C 59.88, H 4.55, N 1.32; found: C 59.89, H 4.86, N 1.12.

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