Bimetallic Catalysts

Combinatorial Catalysis with Bimetallic Complexes: Robust and Efficient Catalysts for Atom-Transfer Radical Additions

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Methods of combinatorial chemistry such as high-throughput screenings are increasingly being employed for the discovery and optimization of homogeneous transition-metal catalysts.[1] So far, most efforts have focused on mononuclear catalysts with ligands that are preferably built in a modular fashion. The screening of bi- or oligometallic catalysts represents a special challenge since the synthesis of a catalyst library is generally more difficult. Nevertheless, it would be interesting to include such compounds in screening assays because of the potentially superior performance of polynuclear catalysts as compared to their mononuclear counterparts.[2] In this context, complexes of the late transition metals in which two different metal fragments are connected by halo bridges appear to be of interest. The synthesis of such complexes is easy and can even be performed in situ.[3,4] Furthermore, due to the high intrinsic reactivity of halo-bridged complexes, they are well suited as catalyst precursors. In the following, we describe two chloro-bridged Rh–Ru complexes, which act as highly active catalyst precursors for atom-transfer radical additions (ATRAs) of polyhalogenated compounds to olefins (the "Kharasch reaction"). These catalysts were discovered in a parallel screening of bimetallic complexes.

Several transition-metal complexes are able to catalyze the anti-Markovnikov addition of polyhalogenated compounds to olefins.[5] Among these, Ru^{II}–phosphane complexes play a dominant role. For a long time, $[RuCl_2(PPh_3)_3]$ was considered to be the most active Ru-based ATRA catalyst,[5,6] and a variety of synthetically useful reactions were developed.[7] A drawback of this system, however, is the high catalyst loading (1–5 %) and the harsh reaction conditions required ($T > 100\,°C$). More recently, a number of new Ru^{II} catalysts with superior performance were developed.[8–10] So far, the pentamethylcyclopentadienyl (Cp*) complex $[Cp^*RuCl(PPh_3)_2]$[9] and its dicarbollide analogues $[(RR'S\text{-}C_2B_9RH_9)RuH(PPH_3)_2]$[10] show the highest activity, which allows the Kharasch addition of CCl_4 to styrene to be carried out at ambient temperature.[9]

The ruthenium-catalyzed Kharasch reaction is believed to proceed via a radical mechanism in the coordination sphere of the metal complex.[5] For reactions with $[RuCl_2(PPh_3)_3]$, the actual catalyst is presumably the fourteen-electron species $\{RuCl_2(PPh_3)_2\}$, which is generated by dissociation of PPh_3. This assumption is in agreement with the fact that the reaction is inhibited by an excess of PPh_3.[6] In a previous publication, we have reported that the $\{RuCl_2(PPh_3)_2\}$ fragment can be stabilized and solubilized using half-sandwich chloro complexes as labile ligands.[11] The resulting complexes $[L_nM(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (L_nM = (arene)Ru, Cp*Ir, Cp*Rh) can be obtained in quantitative yield by reaction of the dimeric acetone adduct $[(PPh_3)_2(CH_3COCH_3)Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (**1**) with chloro-bridged half-sandwich complexes (Scheme 1). More recently, we have found that structurally related complexes with chelating 1,4-bis(diphenylphosphanyl)butane (dppb) or 1,4-bis(dicyclohexylphosphanyl)butane (dcypb) ligands instead of the two PPh_3 ligands can be synthesized (also in quantitative yield) using the aqua complex $[(dppb)ClRu(\mu\text{-}Cl)_2(\mu\text{-}OH_2)RuCl(dppb)]$ (**2**) or the dinitrogen complex $[(dcypb)(N_2)Ru(\mu\text{-}Cl)_3RuCl(dcypb)]$ (**3**) instead of **1**.[4]

The reactions depicted in Scheme 1 are general, fast, and give rise to structurally defined products in quantitative yields. Therefore, they are ideally suited to generate a library of homo- and heterobimetallic complexes in a combinatorial fashion. To investigate whether compounds of this type are useful catalyst precursors for ATRA reactions, we have tested

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[+] X-ray structural analysis.

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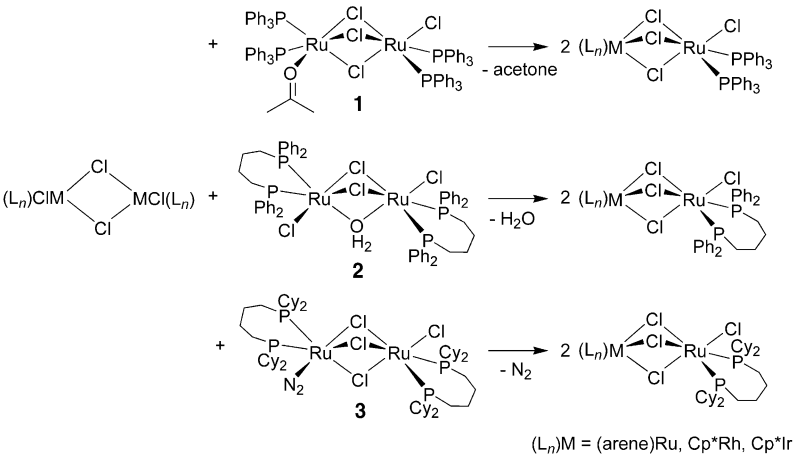

Scheme 1. Synthesis of bimetallic complexes containing $\{RuCl_2(PR_3)_2\}$ fragments.

66 different complexes in a parallel fashion. Assuming that a reaction similar to that depicted in Scheme 1 would occur with other chloro-bridged complexes of the late transition metals, we have prepared mixtures of **1**, **2**, or **3** with various dimeric $[\{L_nM(\mu\text{-}Cl)\}_2]$ complexes of Ru^{II}, Ru^{III}, Ru^{IV}, Rh^{I}, Rh^{III}, Ir^{I}, Ir^{III}, Pd^{II}, and Pt^{II}.[12] These reactions were carried out simultaneously on a small scale and the resulting products were immediately tested in a parallel fashion for catalytic activity without purification.[13] As a benchmark reaction we have employed the addition of CCl_4 to styrene, which was analyzed by gas chromatography using an autosampler (Figure 1).

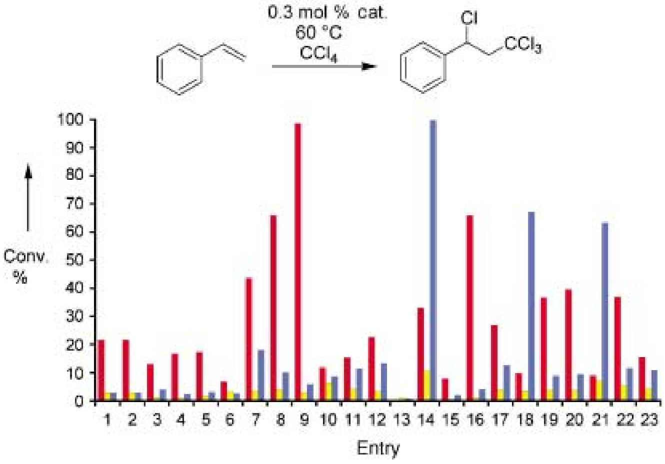

Figure 1. Parallel screening of catalyst activity using the addition of CCl_4 to styrene as a benchmark reaction. The catalysts were prepared in situ my mixing complex **1** (red), **2** (yellow), or **3** (blue) with: 1) $[\{(C_6H_6)RuCl(\mu\text{-}Cl)\}_2]$, 2) $[\{(C_6H_5CO_2Et)RuCl(\mu\text{-}Cl)\}_2]$, 3) $[\{(cymene)RuCl(\mu\text{-}Cl)\}_2]$, 4) $[\{(C_6Me_6)RuCl(\mu\text{-}Cl)\}_2]$, 5) $[\{(1,3,5\text{-}C_6Et_3H_3)RuCl(\mu\text{-}Cl)\}_2]$, 6) $[\{(1,3,5\text{-}C_6H_3iPr_3)RuCl(\mu\text{-}Cl)\}_2]$, 7) $[\{(C_{10}H_{16})RuCl(\mu\text{-}Cl)\}_2]$, 8) $[\{Cp^*RuCl(\mu\text{-}Cl)\}_2]$, 9) $[\{Cp^*RhCl(\mu\text{-}Cl)\}_2]$, 10) $[\{(ppy)_2Rh(\mu\text{-}Cl)\}_2]$, 11) $[\{(allyl)_2Rh(\mu\text{-}Cl)\}_2]$, 12) $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$, 13) $[\{(CO)_2Rh(\mu\text{-}Cl)\}_2]$, 14) $[\{(tpc)Rh(\mu\text{-}Cl)\}_2]$, 15) $[\{(cod)Ir(\mu\text{-}Cl)\}_2]$, 16) $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$, 17) $[\{(PEt_3)PdCl(\mu\text{-}Cl)\}_2]$, 18) $[\{(PEt_3)_2Pd(\mu\text{-}Cl)\}_2](BF_4)_2$, 19) $[\{(C_9H_{12}N)Pd(\mu\text{-}Cl)\}_2]$, 20) $[\{(allyl)Pd(\mu\text{-}Cl)\}_2]$, 21) $[\{(PEt_3)_2Pt(\mu\text{-}Cl)\}_2](BF_4)_2$, 22) $[\{(C_{11}H_{14}NO_2)Pd(\mu\text{-}Cl)\}_2]$, 23) no additional complex. Reaction conditions: styrene (1.4 mmol), CCl_4 (2.0 mmol), first complex (**1**, **2**, or **3**) (2.3 μmol), second complex (4.6 μmol), $CHCl_3$ (600 μL), 60 °C. The conversion after 2 h is based on the consumption of styrene as determined by GC. For the reactions 1, 10, and 21, some precipitation could be observed during the reaction.

For reactions with the $\{RuCl_2(PPh_3)_2\}$ complex **1**, several of the in situ generated homo- and heterobimetallic complexes display a substantial catalytic activity (Figure 1, red bars). The highest activity is observed for reactions with a mixture of **1** and the Rh^{III} complex $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (Figure 1, entry 9a; a = red, b = yellow, c = blue). The Rh^{I} complex $[\{(CO)_2Rh(\mu\text{-}Cl)\}_2]$, on the other hand, seems to inhibit the reaction completely (entry 13a). For mixtures containing the $\{RuCl_2(dppb)\}$ complex **2** (yellow bars), consistently low conversions were observed (1–11 %). This points to an intrinsic advantage of two monodentate PPh_3 ligands as compared to a chelating dppb co-ligand. Similarly, reactions with the $\{RuCl_2(dcypb)\}$ complex **3** gave low or moderate conversions with three notable exceptions: for mixtures with the cationic complexes $[\{(PEt_3)_2Pd(\mu\text{-}Cl)\}_2](BF_4)_2$ (entry 18c) and $[\{(PEt_3)_2Pt(\mu\text{-}Cl)\}_2](BF_4)_2$ (entry 21c) conversions of 67 % and 63 % were observed whereas a quantitative conversion was found for mixtures with the Rh^{I} complex $[\{(tpc)Rh(\mu\text{-}Cl)\}_2]$ (entry 14c; tpc = η^4-tetraphenylcyclopentadienone).

In a second set of experiments, we have tested the catalytic activity of all symmetrical complexes $[\{L_nM(\mu\text{-}Cl)\}_2]$ without the addition of the ruthenium complexes **1**–**3**. None of the complexes displayed any significant activity (conversion < 1 %). This indicates that the ruthenium–phosphane fragments are responsible for catalysis. The overall activity, however, is clearly modulated by the second metal fragment $\{L_nMCl\}$.

From the parallel screening, two promising catalyst precursors emerged. The first is formed by reaction of **1** with $[\{Cp^*RhCl(\mu\text{-}Cl)\}_2]$ and the second is formed by reaction of **3** with $[\{(tpc)Rh(\mu\text{-}Cl)\}_2]$. We have therefore repeated these reactions on a preparative scale from which we were able to isolate the heterometallic complexes $[Cp^*Rh(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (**4**) and $[\{(tcp)Rh(\mu\text{-}Cl)_3Ru(dcypb)\}_2(\mu\text{-}N_2)]$ (**5**) in good yield. Both compounds were characterized by single-crystal X-ray analysis (Figures 2 and 3).[14]

The $\{Cp^*Rh\}$ fragment in **4** is coordinated through three chloro-bridges to the Ru–phosphane fragment. The Ru–Cl bond length of the terminal chloro ligand is smaller than the Ru–Cl bond lengths found for the bridging chloro ligands. As expected, the angle between the sterically demanding PPh_3 groups is enlarged resulting in a distorted octahedral geometry around the Ru atom. The plane defined by the Cp* π ligand is almost parallel to that defined by the bridging chloro ligands.

Similar to what was found for complex **4**, the $\{(tcp)Rh\}$ fragment in **5** is coordinated through three chloro bridges to the Ru–phosphane fragment (Figure 3). Consequently, the Rh center exhibits a five-coordinate, electronically saturated configuration. This is in agreement with the known tendency of cyclopentadienone–rhodium complexes to form piano-stool-type complexes.[15] The ruthenium atom shows a dis-

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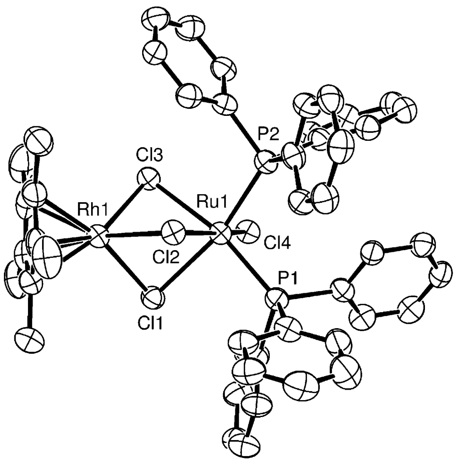


Figure 2. ORTEP drawing of the molecular structure of **4**. The hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [°]: Ru1-Cl4 = 2.375(2), Ru1-Cl2 = 2.436(2), Ru1-Cl3 = 2.399(2); P1-Ru1-P2 = 103.71(6), Cl4-Ru1-Cl2 = 169.42(6).

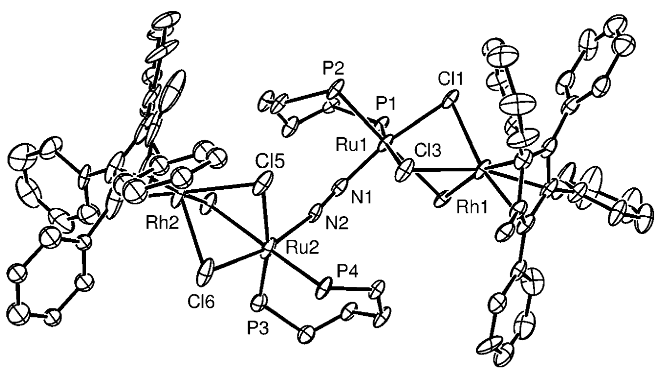


Figure 3. ORTEP drawing of the molecular structure of **5**. The hydrogen atoms, the cyclohexyl side chains, and the external solvent molecule are not shown for clarity. Selected bond lengths [Å] and angles [°]: Ru1-N1 = 1.963(10), Ru2-N2 = 1.985(9), N1-N2 = 1.118(12); P1-Ru1-P2 = 93.53(9), P3-Ru2-P4 = 94.14(11), N2-N1-Ru1 = 164.6(8), N1-N2-Ru2 = 164.2(8).

torted octahedral geometry with one coordination site being occupied by a dinitrogen ligand. The latter acts as an end-on bridging ligand that connects two heterobimetallic Rh^I–Ru^{II} complexes. The bond lengths and angles found for the Ru(μ^2-N_2)Ru moiety (Figure 3) are comparable to those observed for other ruthenium complexes with bridging N_2 ligands.[16]

With the isolated complexes **4** and **5**, we have performed a more detailed analysis of the catalytic performance using again the benchmark reaction between styrene and CCl_4. Apart from chloroform, toluene was employed as a solvent. The results are summarized in Table 1. The Rh^I–Ru^{II} complex **5** was found to display a very high activity surpassing not only that of the Rh^{III}–Ru^{II} complex **4** but also that of the previously described catalyst precursors [$RuCl_2(PPh_3)_3$] and [Cp*$RuCl(PPh_3)_2$] (entries 1–6). A surprising discovery was that for catalysts **4** and **5**, reactions performed in "wet" chloroform and toluene gave better results than those performed in thoroughly dried solvents (entries 7–12). This is in sharp contrast to reactions catalyzed by [$RuCl_2(PPh_3)_3$] or by the very sensitive[17] [Cp*$RuCl(PPh_3)_2$], for which traces of water were found to reduce the catalytic activity significantly (entries 11 and 12).

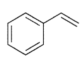
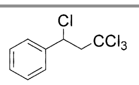
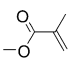
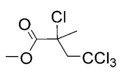
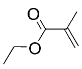
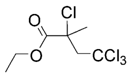
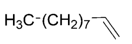
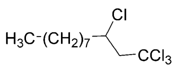
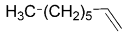
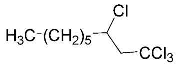
Table 1: Addition of CCl_4 to styrene, catalyzed by complex **4**, **5**, [$RuCl_2(PPh_3)_3$], or [Cp*$RuCl(PPh_3)_2$].[a]

Entry	Catalyst	Solvent	Conv. [%]
1	**4**	toluene	23
2	**4**	chloroform	20
3	**5**	toluene	78
4	**5**	chloroform	94
5	[$RuCl_2(PPh_3)_3$]	chloroform	14
6	[Cp*$RuCl(PPh_3)_2$]	chloroform	53
7	**4**	chloroform (saturated with H_2O)	37
8	**4**	toluene (saturated with H_2O)	36
9	**5**	toluene (saturated with H_2O)	76
10	**5**	chloroform (saturated with H_2O)	95
11	[$RuCl_2(PPh_3)_3$]	chloroform (saturated with H_2O)	7
12	[Cp*$RuCl(PPh_3)_2$]	chloroform (saturated with H_2O)	29

[a] Reaction conditions: cat./styrene/CCl_4 = 1:300:432; [cat.] = 4.59 mM, 60 °C. The conversion is based on the consumption of styrene and was determined after 1 h by GC.

Next, we investigated the influence of the CCl_4 concentration on the activity of the new catalysts using "wet" chloroform as the solvent. Both complexes were found to display the highest activities for total CCl_4 concentrations of around 5.5 M (catalyst/substrate/CCl_4 = 1:300:1200). Using these optimized conditions, the scope of the new heterometallic catalyst precursors **4** and **5** was tested in reactions with various olefinic substrates (Table 2). For styrene and methylacrylates, near-total conversion of the substrate is observed

Table 2: Atom-transfer radical additions catalyzed by the heterobimetallic complexes **4** and **5**.[a]

Entry	Cat.	Substrate	Product	*t* [h]	Conv. [%]	Yield [%]
1	**4**			4	88	86
2	**5**			1	99	98
3	**4**			4	99	84
4	**5**			1	98	93
5	**4**			4	99	79
6	**5**			1	98	92
7	**4**			10	97	88
8	**5**			24	80	75
9	**4**			10	98	90
10	**5**			24	80	74

[a] Reaction conditions: cat./styrene/CCl_4 = 1:300:1200; [cat.] = 4.59 mM; solvent: $CHCl_3$ saturated with H_2O; 60 °C. The conversion is based on the consumption of the substrate and the yield is based on the formation of product as determined by GC or by ^1H NMR spectroscopy.

after only 1 h for catalyst **5** and after 4 h for catalyst **4** (entries 1–6). The yields are slightly lower than the conversions due to the formation of oligomers, a problem generally encountered for these types of addition reactions.

Longer reaction times are required for 1-octene and 1-decene, two notoriously bad substrates for Kharasch reactions. It is interesting to note that for these substrates it is the Rh^{III}–Ru^{II} complex **4** that gives the better results: after 10 h, a yield of 88 % and 90 %, respectively, is found together with a nearly quantitative conversion (entry 7 and 9). These values are clearly superior to what is observed for other catalyst precursors. With [Cp*RuCl(PPh$_3$)$_2$], for example, a yield of 27 % and a conversion of 46 % was observed after 24 h under nearly identical conditions.[9]

The potential of the catalyst precursor **5** is further underlined by the high turnover frequencies (TOFs) and numbers (TONs) that can be achieved. For the addition of CCl$_4$ to styrene, for example, an initial TOF of 1200 h^{-1} and a total TON of 4500 has been determined (catalyst/substrate/CCl$_4$ = 1:6000:12 000). These are among the highest values that have been reported for an ATRA catalyst.[18] The unique tetrameric structure of **5** points to a possible explanation for its exceptionally high catalytic activity: As for the starting material **3**, the dinitrogen ligand is expected to be labile. Upon liberation of this ligand, an unsaturated 16-electron ruthenium complex would be generated, which is then stabilized by the sterically demanding {(tcp)Rh} fragment and the large dcypb ligand. For complex **4**, the mode of activation is less evident. A plausible mechanism involves the cleavage of one or several halo bridges, as was suggested for a chloro-bridged Rh^{III}–Ru^{II} metathesis catalyst.[19] It is clear, however, that both the {Cp*Rh^{III}} and the {Ru^{II}(PPh$_3$)$_2$} fragment are essential constituents of this new catalyst.

Aside from their high catalytic activity, complexes **4** and **5** offer some important advantages. Since they are obtained in reactions that are fast and quantitative, they can be generated in situ, prior to catalysis, without isolating the complexes. The corresponding starting materials are easily accessible, in particular for complex **4**. Of special interest is the fact that the catalysts display a good performance in organic solvents of moderate purity (saturated with water). Extensive purification of the solvents, as is required for other catalysts for the Kharasch reaction, is therefore not necessary. Current efforts in our laboratory are directed towards a deeper understanding of the mechanism of these new types of catalysts. Furthermore, we are investigating whether complexes **4** and **5** are useful catalysts for the closely related atom-transfer radical polymerization of olefins.[20]

Experimental Section

The complexes [(dppb)ClRu(μ-Cl)$_2$(μ-OH$_2$)RuCl(dppb)],[21] [(dcypb)(N$_2$)Ru(μ-Cl)$_3$RuCl(dcypb)],[22] [Cp*Rh(μ-Cl)$_3$RuCl(PPh$_3$)$_2$],[11] [{(C$_6$H$_5$CO$_2$Et)RuCl(μ-Cl)}$_2$],[23] [{(cymene)RuCl(μ-Cl)}$_2$],[24] [{(C$_6$H$_6$)RuCl(μ-Cl)}$_2$],[25] [{(C$_6$Me$_6$)RuCl(μ-Cl)}$_2$],[24] [{(1,3,5-C$_6$H$_3$Et$_3$)RuCl(μ-Cl)}$_2$],[26] [{(1,3,5-C$_6$H$_3$*i*Pr$_3$)RuCl(μ-Cl)}$_2$],[26] [{(η^3:η^3-C$_{10}$H$_{16}$)RuCl(μ-Cl)}$_2$],[27] [{Cp*RuCl(μ-Cl)}$_2$],[28] [{Cp*RhCl(μ-Cl)}$_2$],[29] [{Cp*IrCl(μ-Cl)}$_2$], [{(ppy)$_2$Rh(μ-Cl)}$_2$] (ppy = pyridin-2-yl-2-phenyl),[30] [{(allyl)$_2$Rh(μ-Cl)}$_2$] (allyl = η^3-C$_3$H$_5$),[31] [{(cod)Rh(μ-Cl)}$_2$] (cod = η^4-cycloocta-1,5-diene),[32] [{(CO)$_2$Rh(μ-Cl)}$_2$],[33] [{(tpc)Rh(μ-Cl)}$_2$] (tpc = η^4-tetraphenylcyclopentadienone),[34] [{(cod)Ir(μ-Cl)}$_2$],[35] [{(PEt$_3$)PdCl(μ-Cl)}$_2$],[36] [{(C$_9$H$_{12}$)Pd(μ-Cl)}$_2$] (C$_9$H$_{12}$ = *ortho*-metalated *N,N'*-dimethylbenzylamine),[37] [{(PEt$_3$)$_2$Pt(μ-Cl)}$_2$](BF$_4$)$_2$,[38] and [{(PEt$_3$)$_2$Pd(μ-Cl)}$_2$](BF$_4$)$_2$[38] were prepared according to literature procedures. The complex [{(allyl)Pd(μ-Cl)}$_2$] was purchased from Fluka. Complex **4** was prepared as described in ref. [11]. Crystals were obtained by slow diffusion of pentane into a solution of **4** in THF.

5: A mixture of [(dcypb)(N$_2$)Ru(μ-Cl)$_3$RuCl(dcypb)] (110 mg, 86 μmol) and [{(tpc)Rh(μ-Cl)}$_2$] (90 mg, 86 μmol) in CH$_2$Cl$_2$ (10 mL) was stirred until a homogeneous solution was obtained. The solution was then poured into hexane (100 mL) to precipitate a red powder, which was filtered off and washed with pentane (2 × 20 mL) and dried under a flow of dinitrogen for at least 5 h (yield: 87 %). Single crystals were obtained by slow diffusion of pentane into a solution of **5** in CH$_2$Cl$_2$. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 0.86–2.28$ (m, 104 H, dcypb), 7.11–7.82 ppm (m, 40 H, C$_{29}$H$_{20}$O); ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 14.24–40.21$ (dcypb), 67.71 (d, $^1J_{\text{C-Rh}} = 11$ Hz, tpc), 93.79 (d, $^1\text{J}_{\text{C-Rh}} = 13$ Hz, tpc), 127.20–133.18 ppm (tpc); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 42.44$ ppm; elemental analysis calcd (%) for C$_{114}$H$_{144}$N$_2$O$_2$Cl$_6$P$_4$Rh$_2$Ru$_2$·0.5 C$_6$H$_{14}$: C 59.49, H 6.44, N 1.19; found: C 59.76, H 6.50, N 1.09.

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[14] Crystal data for **4**: $C_{46}H_{45}Cl_4P_2RhRu$, $M_r = 1005.54$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.937(2)$, $b = 13.200(2)$, $c = 14.3916(14)$ Å, $\alpha = 81.696(12)$, $\beta = 77.383(14)$, $\gamma = 71.811(17)°$, $V = 2095.2(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.594$ g cm^{-3}, $\mu = 1.119$ mm^{-1}, $F(000) = 1016$, crystal dimensions $0.30 \times 0.25 \times 0.21$ mm^3. Data collection: mar345 IPDS, $T = 140(2)$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71070$ Å, $\theta = 3.54$–$25.02°$, $-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-17 \leq l \leq 16$, 12667 reflections collected, 6930 independent reflections, $R_{int} = 0.0619$, 5600 observed reflections $[I > 2\sigma(I)]$, empirical absorption correction, max./min. transmission: 0.563/0.101. Refinement: $N_{ref} = 6930$, $N_{par} = 488$, R_1 $[I > 2\sigma(I)] = 0.0637$, wR_2 (all data) = 0.1948, $S = 1.135$, the weighting scheme is $w^{-1} = [\sigma^2(F_o^2) + (0.1112P)^2 + 3.8732P]$ with $P = (F_o^2 + 2F_c^2)/3$, max. and average shift/error = 0.000, 0.000, largest difference peak/minimum: 1.059/–1.173 e Å^{-3}. Structure solution and refinement by SHELX97 (G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany), **1998**). H atoms were placed in calculated positions using the riding model. Crystal data for **5**: $C_{114}H_{144}Cl_6N_2O_2P_4Rh_2Ru_2 \cdot CH_2Cl_2$, $M_r = 2403.78$, monoclinic, space group $C2/c$ (No. 15), $a = 71.244(6)$, $b = 12.9605(11)$, $c = 24.9834(19)$ Å, $\beta = 94.136(11)$, $V = 23009(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.388$ g cm^{-3}, $\mu = 0.829$ mm^{-1}, $F(000) = 9920$, crystal dimensions $0.36 \times 0.25 \times 0.13$ mm^3. Data collection: Oxford Diffraction KM4/Sapphire CCD, $T = 140(2)$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\theta = 2.63$–$25.03°$, $-84 \leq h \leq 84$, $-13 \leq k \leq 13$, $-29 \leq l \leq 29$, 65671 reflections collected, 19222 independent reflections, $R_{int} = 0.1233$, 10703 observed reflections $[I > 2\sigma(I)]$, no absorption correction. Refinement: $N_{ref} = 19222$, $N_{par} = 1183$, R_1 $[I > 2\sigma(I)] = 0.0933$, wR_2 (all data) = 0.2712, $S = 1.055$, the weighting scheme is $w^{-1} = [\sigma^2(F_o^2) + (0.1120P)^2 + 391.8266P]$ with $P = (F_o^2 + 2F_c^2)/3$, max. and average shift/error = 0.001, 0.000, largest difference peak/minimum: 1.821/–1.636 e Å^{-3}. Structure solution and refinement by SHELX97. H atoms were placed in calculated positions using the riding model. Disorder problems dealing with two phenyl rings and with the CH_2Cl_2 group have been handled using the split model for the aromatic rings and keeping the carbon atoms isotropically defined. DELU and DFIX cards have been employed to achieve reasonable displacement parameters for the whole structure and to obtain reasonable geometrical data for the solvent molecule, respectively. CCDC-221541 and -221542 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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