Combinatorial Synthesis of Bimetallic Complexes with Three Halogeno Bridges

Sébastien Gauthier, Laurent Quebatte, Rosario Scopelliti, and Kay Severin*[a]

Abstract: Methods for the synthesis of bimetallic complexes in which two different metal fragments are connected by three chloro or bromo bridges are reported. The reactions are general, fast, and give rise to structurally defined products in quantitative yields. Therefore, they are ideally suited for generating a library of homo- and heterobimetallic complexes in a combinatorial fashion. This is of special interest for applications in homogeneous catalysis. Selected members of this library were synthesized and comprehensively characterized; single-crystal X-ray analyses were performed for 15 new bimetallic compounds.

Keywords: bimetallic complexes · bridging ligands · combinatorial chemistry · homogeneous catalysis

Introduction

The combination of diversity-oriented organic synthesis with fast screening assays has emerged as a powerful new tool for drug discovery.[1] Related concepts are increasingly being used to identify and optimize transition metal catalysts.[2] A prerequisite for this type of approach is the availability of a library of potential catalyst precursors. Most efforts to generate such libraries have focused on monometallic complexes, and structural diversity was obtained by variation of the ligands.[2] However, polynuclear complexes are also of interest because 1) the presence of two or more metal ions allows the diversity to be further increased and 2) the potentially superior performance of polynuclear catalysts as compared to their mononuclear counterparts.[3] To utilize bi- and oligometallic complexes in combinatorial catalysis, fast and reliable synthetic methods are required. In this context, bimetallic complexes in which two different metal fragments are connected by halogeno bridges are of special interest. In the last few years, several methods providing access to this class of compounds were developed.[4] Due to the presence of the labile halogeno bridges, the complexes generally show high intrinsic reactivity, and some catalytic applications were recently reported.[5,6] Chloro-bridged Rh^{III}–Ru^{II} complexes, for example, have been employed as highly efficient catalyst precursors for transfer hydrogenation,[5b] olefin metathesis,[5e] and atom-transfer radical additions (see below).[6]

So far, investigations of the syntheses and structures of heterobimetallic, halogeno-bridged complexes have focused primarily on compounds with two halogeno bridges.[4] These complexes can easily be obtained in metathesis reactions starting from the corresponding homodimeric compounds. Reactions of this kind were first described by Stone et al.[7] and Masters et al.[8] three decades ago, but detailed investigations highlighting the potential of this method were published only more recently.[9,10] Here we describe synthetic pathways for the generation of bimetallic complexes with three halogeno bridges in a combinatorial fashion. Given that the methods should be suited for screening assays, we sought reactions that are general, fast, and give rise to structurally defined products in quantitative yields.

From a retrosynthetic viewpoint it should be possible to synthesize bimetallic complexes with three halogeno bridges by combining a complex **A** with two halogeno ligands and one free coordination site with a complex **B** having one halogeno ligand and two free coordination sites (Scheme 1a). However, in reality, halogeno complexes with "free" coordination sites form adducts with solvent molecules or dimerize. In both cases, the resulting complexes are neither thermodynamically nor kinetically very stable and could still be suitable starting materials. This assumption is reinforced by the fact that dimeric complexes with two halogeno bridges undergo fast exchange reactions.[9,10] A priori, the reactions depicted in Scheme 1b could thus give rise to the desired products.

To validate this hypothesis, we synthesized complexes of types **A** (**1**–**5**) and **B** (**6**–**12**). We showed earlier that combination of the dimeric half-sandwich complexes **1**–**3** with rhe-

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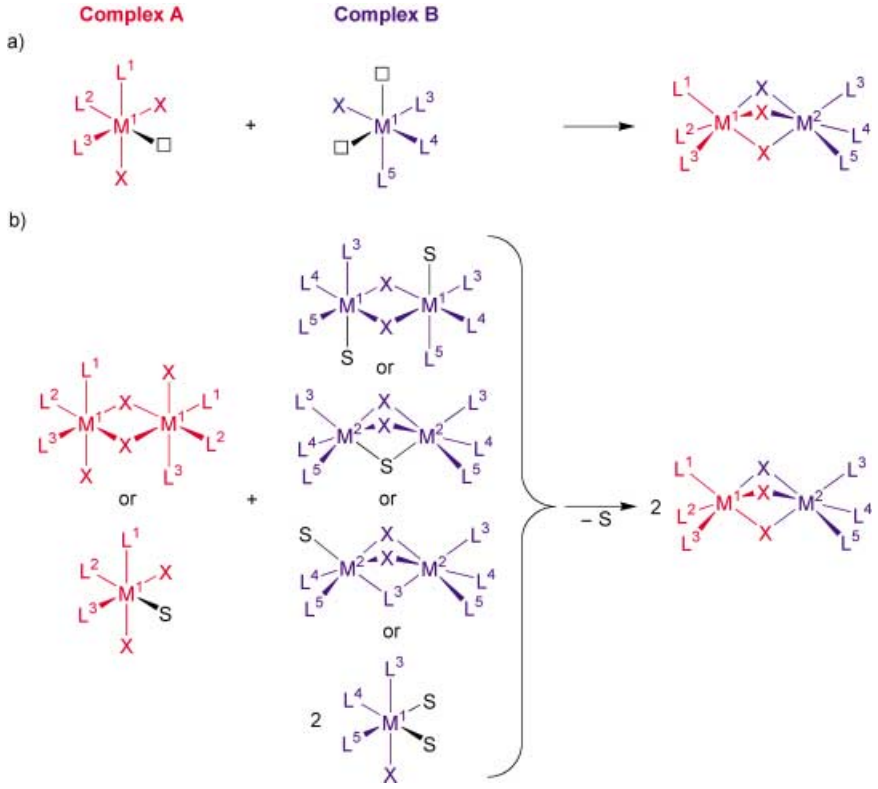


Scheme 1. General methods to synthesize bimetallic complexes with three halogeno bridges (S = solvent or labile ligand).

nium complex **6** (X = Br)[11] or ruthenium complex **7** (X = Cl)[5b] gives the corresponding heterobimetallic complexes in quantitative yield. We now demonstrate that the two types of complexes can be mixed in a truly combinatorial fashion to generate a library of homo- and heterobimetallic complexes.

Results and Discussion

Bimetallic complexes with {MX(allyl)(CO)$_2$} (M = Mo, W; X = Cl, Br) fragments: The acetonitrile ligands of molybdenum and tungsten complexes **8** and **9** are very labile and can easily be replaced. This is evidenced by extensive auto-ionization of **8** in various nonaqueous solvents to give the cation [Mo(allyl)(CO)$_2$(CH$_3$CN)$_3$]$^+$ and the bimetallic anion [(allyl)(CO)$_2$Mo(μ-Cl)$_3$Mo(CO)$_2$(allyl)]$^-$ with liberation of acetonitrile.[12] Furthermore, many substitution reactions of **8** and **9** with mono- and bidentate P- and N-donor ligands have been described.[13] Therefore, **8** and **9** seemed to be ideally suited for the generation of bimetallic halogeno-bridged complexes by using compounds of type **A** as reaction partners.

First, we investigated reactions with [{(arene)RuX$_2$}$_2$] complexes (arene = cymene, 1,3,5-C$_6$H$_3$*i*Pr$_3$; X = Cl, Br). Mixing two equivalents of **8** or **9** with one equivalent of [{(arene)RuX$_2$}$_2$] in chloroform gave **13**–**17** (Table 1). The reactions, which are entropically favored due to the liberation of two solvent molecules, were quantitative and fast (< 2 min). This was shown by in situ NMR experiments in CDCl$_3$. The reaction scheme is very general, since it tolerates substitution of the allyl ligand (**13** versus **14**), substitution of the halogeno ligand (**13** versus **15**), substitution of the arene ligand (**14** versus **16**), and use of Mo or W (**16** versus **17**).

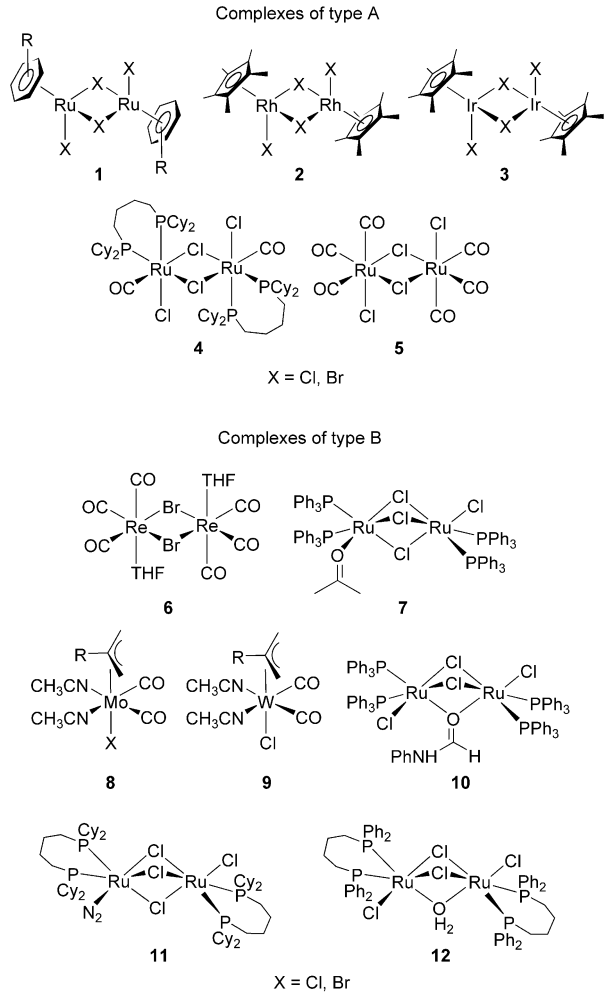
By using [{Cp*MX$_2$}$_2$] (M = Rh, Ir; X = Cl, Br) instead of [{(arene)RuX$_2$}$_2$], the heterobimetallic complexes **18**–**22** were obtained (Table 1). Reactions with [{Cp*RhX$_2$}$_2$] can be carried out in a similar fashion as for the [{(arene)RuX$_2$}$_2$] complexes, but it is advantageous to perform the reactions with [{Cp*IrCl$_2$}$_2$] in CH$_2$Cl$_2$ because the starting material is slightly more soluble in this solvent.

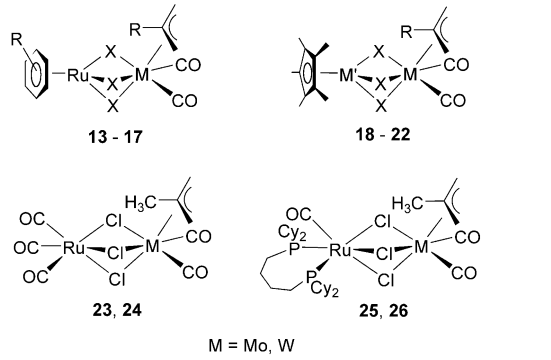
The reactions of [MCl(C$_4$H$_7$)(CO)$_2$(CH$_3$CN)$_2$] (M = Mo (**8**), W (**9**)] with the ruthenium carbonyl complexes [(dcypb)(CO)RuCl$_2$]$_2$ (**4**, dcypb = 1,4-bis(dicyclohexylphosphanyl)butane) and [{(CO)$_3$RuCl$_2$}$_2$] (**5**) gave heterobimetallic complexes **23**–**26** (Table 1). Again, the reactions were fast and quantitative, as evidenced by in situ ^{1}H NMR spectroscopy (CDCl$_3$). Interestingly, the heterobimetallic carbonyl complexes **23** and **24** have significantly higher solubility in nonpolar organic solvents than the starting materials **5**, **8**, and **9**. For example, **23** can be crystallized from hexane, whereas **5** and **8** have very low solubility in this solvent.

For the dcypb complexes **25** and **26**, two isomers are possible which differ in the relative positions of the CO and

Table 1. Composition and selected IR spectroscopic data for the MX(allyl)(CO)$_2$ (M = Mo, W; X = Cl, Br) complexes **13**–**26**.

Complex	Fragment A	Fragment B	ν_{M-CO} [cm^{-1}]
13	{(cymene)RuCl$_2$}	{MoCl(C$_3$H$_5$)(CO)$_2$}	1938, 1845
14	{(cymene)RuCl$_2$}	{MoCl(C$_4$H$_7$)(CO)$_2$}	1929, 1827
15	{(cymene)RuBr$_2$}	{MoBr(C$_3$H$_5$)(CO)$_2$}	1948, 1844
16	{(1,3,5-C$_6$H$_3$*i*Pr$_3$)RuCl$_2$}	{MoCl(C$_4$H$_7$)(CO)$_2$}	1940, 1865
17	{(1,3,5-C$_6$H$_3$*i*Pr$_3$)RuCl$_2$}	{WCl(C$_4$H$_7$)(CO)$_2$}	1934, 1853
18	{Cp*RhCl$_2$}	{MoCl(C$_4$H$_7$)(CO)$_2$}	1934, 1839
19	{Cp*RhBr$_2$}	{MoBr(C$_3$H$_5$)(CO)$_2$}	1933, 1843
20	{Cp*IrCl$_2$}	{MoCl(C$_3$H$_5$)(CO)$_2$}	1933, 1842
21	{Cp*IrCl$_2$}	{MoCl(C$_4$H$_7$)(CO)$_2$}	1938, 1844
22	{Cp*RhCl$_2$}	{WCl(C$_4$H$_7$)(CO)$_2$}	1925, 1823
23	{(CO)$_3$RuCl$_2$}	{MoCl(C$_4$H$_7$)(CO)$_2$}	2143, 2061, 1923, 1834
24	{(CO)$_3$RuCl$_2$}	{WCl(C$_4$H$_7$)(CO)$_2$}	2143, 2061, 1947, 1838
25	{(dcypb)(CO)RuCl$_2$}	{MoCl(C$_4$H$_7$)(CO)$_2$}	1936 (br), 1838
26	{(dcypb)(CO)RuCl$_2$}	{WCl(C$_4$H$_7$)(CO)$_2$}	1923 (br), 1828





allyl ligands. However, only one isomer is observed by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P; C_6D_6). Since one singlet is observed for the two phosphorus atoms in **25** and **26**, the two atoms must be chemically equivalent, that is, the isomer with C_s symmetry is formed. This was confirmed by X-ray crystallography (see below).

Investigations on reactions catalyzed by heterobimetallic, halogeno-bridged complexes have shown that the catalytic activity of one metal fragment is modulated by the other by both steric and electronic effects.[5] It was therefore of interest to determine the structural changes that occur on varying important parameters (e.g., nature of the metal, size and nature of the ligands, nature of the halogeno bridge). The bimetallic complexes obtained were thus comprehensively studied by single-crystal X-ray analyses.

Crystallographic data were obtained for **13**, **15**–**19**, **22**, **23**, and **25**. To best of our knowledge, they are the first structurally characterized heterobimetallic compounds with M′(μ-X)$_3$M units (M = Mo, W; X = Cl, Br; M′ ≠ M). The molecular structures of **15**, **22**, **23**, and **25** in the crystal are depicted in Figure 1 (for crystallographic details of **13** and **16**–**19**, see Table 2). As expected, the {(π-ligand)M′}, {(CO)$_3$Ru}, and {(dcypb)(CO)Ru} fragments are connected by three halogeno bridges to the {M(allyl)(CO)$_2$} fragments. The Mo–Cl and W–Cl distances involving the chloro ligands *trans* to the allyl ligand are generally shorter than the other two M–Cl distances involving the chloro ligands *trans* to the carbonyl ligands (Table 2). This corresponds to what has been observed for complexes with the bimetallic anions [(allyl)(CO)$_2$Mo(μ-Cl)$_3$Mo(CO)$_2$(allyl)]$^-$ and [(allyl)(CO)$_2$Mo(μ-Cl)$_3$Mo(CO)$_2$(allyl)]$^-$.[12a,14] The Ru–X and Rh–X bond lengths, in contrast, are all in the same range for a given complex. Substitution of the arene or allyl ligand and an exchange of Mo for W has only a small effect on the core structure of the binuclear complexes, as evidenced by the very similar structural parameters of the {(arene)RuCl$_2$} complexes **13**, **16**, and **17** (Table 2). For all complexes, a metal–metal bond can be excluded, because the Ru/Rh and the Mo/W atoms are 3.34–3.52 Å apart from each other. The shortest M···M distance is found in the Ru(CO)$_3$ complex **23** (Ru···Mo 3.343(1) Å). This is probably due to the *trans* influence of the CO ligands, which leads to slightly shorter Ru–Cl bond lengths relative to the (π-ligand)Ru complexes **13**, **16**, and **17**. As a consequence of the larger bromo ligand, **15** and **19** have the largest M···M distances (3.520(1) and 3.428(2) Å).

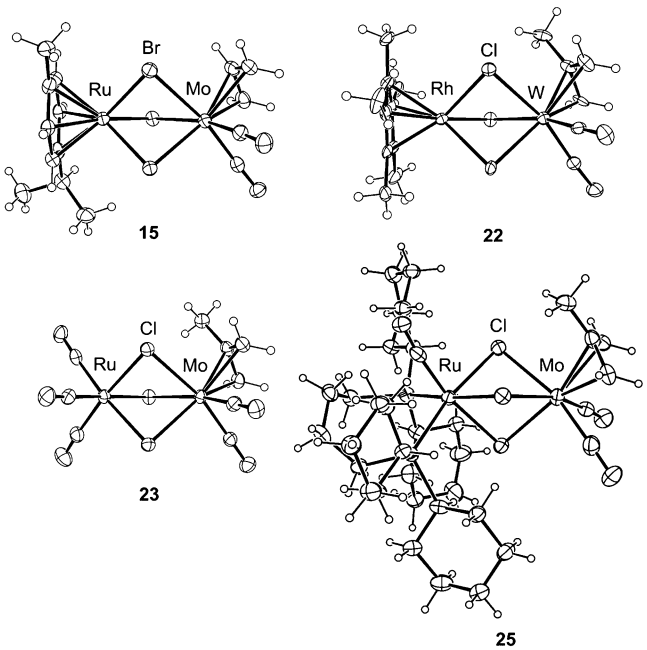
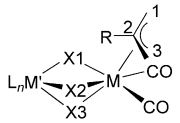


Figure 1. Molecular structures of complexes **15**, **22**, **23**, and **25** in the crystal (ORTEP plots).

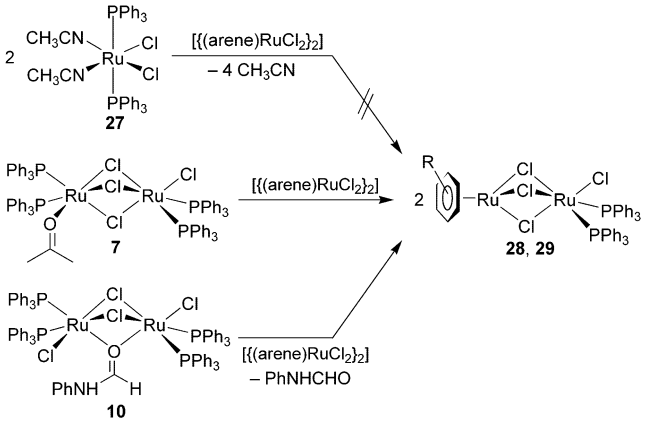
Table 2. Selected interatomic distances [Å] for the MX(allyl)$(CO)_2$ complexes **13**, **15**–**19**, **22**, **23**, and **25**.



Complex	M–X1	M–X2	M–X3	M′–X[a]	M–C1	M–C2	M–C3	M···M′
13	2.595(1)	2.619(1)	2.510(1)	2.44	2.308(4)	2.206(4)	2.328(4)	3.395(1)
15	2.764(1)	2.732(1)	2.649(1)	2.56	2.328(8)	2.211(8)	2.320(8)	3.520(1)
16	2.594(3)	2.595(3)	2.512(3)	2.42	2.305(13)	2.180(14)	2.307(12)	3.393(3)
17	2.572(6)	2.594(6)	2.504(6)	2.43	2.29(2)	2.17(3)	2.30(2)	3.403(6)
18	2.597(4)	2.597(4)	2.536(4)	2.43	2.290(15)	2.232(20)	2.290(15)	3.366(4)
19	2.753(1)	2.748(2)	2.667(2)	2.56	2.326(12)	2.177(10)	2.312(11)	3.482(2)
22	2.590(5)	2.590(5)	2.544(7)	2.46	2.318(19)	2.24(3)	2.318(19)	3.398(5)
23	2.623(1)	2.605(1)	2.569(1)	2.41	2.304(5)	2.229(4)	2.317(5)	3.343(1)
25	2.613(2)	2.598(2)	2.500(2)	2.47	2.309(10)	2.255(10)	2.311(9)	3.423(2)

[a] Average values.

Bimetallic complexes with {(arene)$RuCl_2$} and {Cp*MCl_2} fragments (M = Rh, Ir): Acetone complex **7** is well suited for the synthesis of bimetallic complexes containing {(arene)$RuCl_2$}, {Cp*$RhCl_2$}, and {Cp*$IrCl_2$} fragments.[5b] A drawback of this approach, however, is the low solubility of **7** in common organic solvents. The rate-limiting step for the formation of these complexes is dissolution of **7**, which requires 10–30 min and intensive stirring. For fast catalytic screening with bimetallic complexes generated in situ, this may be a disadvantage (e.g., the requirement for stirring may result in a technical problem). We therefore investigated whether alternative, more soluble complexes can be used instead of **7** (Scheme 2). Given the success of the reactions with the molybdenum and tungsten precursors $[MCl(C_4H_7)(CO)_2(CH_3CN)_2]$ (**8**, **9**), we first examined the reactivity of the ruthenium diacetonitrile complex **27**



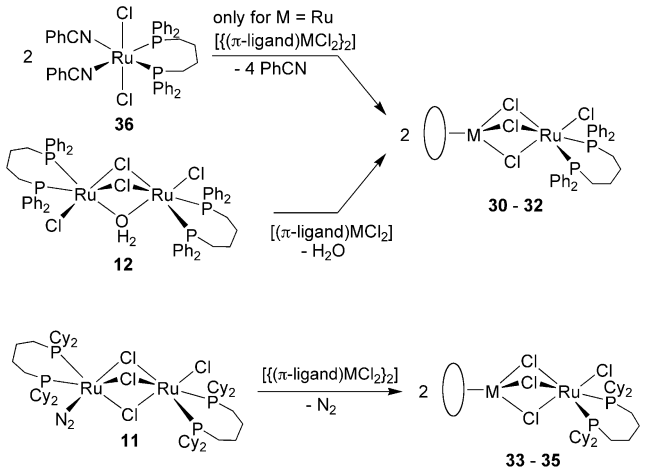
Scheme 2. Different methods to connect (arene)$RuCl_2$ complexes with the {$Ru(PPh_3)_2Cl_2$} fragment.

(Scheme 2). In contrast to the Mo and W complexes, the acetonitrile ligands in **27** are rather inert, although they are known to be partially lost on recrystallization of the complex.[15] When [{(cymene)$RuCl_2$}$_2$] and two equivalents of **27** were dissolved in CD_2Cl_2, more than 50% of the starting material could still be observed after 1 h according to the ^{31}P NMR spectrum of the mixture. After a longer time, new peaks were observed in the ^{31}P NMR spectrum, none of which corresponded to the desired product **28**. Complex **27** was therefore disregarded as a starting material.

We then investigated the reactivity of formanilide complex **10**, which can be obtained in crystalline form and good yield by reaction of $[RuCl_2(PPh_3)_3]$ with formanilide.[16] In contrast to **7**, **10** has moderate to good solubility in organic solvents such as dichloromethane, and its reactions with [{(cymene)$RuCl_2$}$_2$] and [{(1,3,5-$C_6H_3Et_3$)$RuCl_2$}$_2$] gave **28** and **29** (Scheme 2). As in the case of **7**, the reaction proceeds in quantitative yield with liberation of the O-donor ligand. Complex **10** therefore seems to be an ideal starting material for syntheses of bimetallic complexes containing the {$RuCl_2(PPh_3)_2$} fragment.

Given the importance of chelating phosphane ligands in ruthenium-catalyzed reactions, we were interested in methods which allow the synthesis of bimetallic complexes containing such fragments. Pregosin et al. recently reported a bimetallic complex in which a {(cymene)$RuCl_2$} fragment is connected by chloro bridges to a {(Binap*)$RuCl_2$} fragment (Binap* = alkyl-substituted 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl).[17] We have shown that [(cymene)Ru-(μ-Cl)$_3$Ru(dppb)Cl] (**31**, dppb = 1,4-bis(diphenylphosphanyl)butane) can be obtained by reaction of [$RuCl_2$-(dppb)(PPh_3)] with [{(cymene)$RuCl_2$}$_2$].[5b] This method has the disadvantage that [(cymene)$RuCl_2(PPh_3)$] is formed as a side product which must be separated by fractional crystallization.

Compounds **36** and **12** can be regarded as solvent-stabilized $RuCl_2$(dppb) complexes. The benzonitrile ligands of **36** are labile: in solution, **36** dimerizes with liberation of PhCN.[18] However, as was observed for **27**, the reaction of [{(arene)$RuCl_2$}$_2$] with two equivalents of **36** in $CDCl_3$ gives a number of unidentified side products. When the reactions were performed in benzene under reflux, on the other hand, the desired products (e.g., **30**) were formed in nearly quantitative yield after 1 h (Scheme 3). Unfortunately, similar reactions with [{Cp*$RhCl_2$}$_2$] and [{Cp*$IrCl_2$}$_2$] gave unidentified side products. This strongly limits the versatility of **36** as a starting material. However, bimetallic complex **12** proved to be ideally suited for this purpose. Reactions with [{(arene)$RuCl_2$}$_2$] or [{Cp*MCl_2}$_2$] (M = Rh, Ir) gave **30**–**32** rapidly



Scheme 3. Synthesis of bimetallic complexes with {Ru(dppb)Cl_2} and {Ru(dcypb)Cl_2} fragments.

(< 2 min) and in quantitative yield. In solution, **12** is known to form the electronically unsaturated dimer [Cl(dppb)Ru(μ-Cl)$_2$Ru(dppb)Cl] by liberation of the weakly bound water ligand.[19] This dimer likely undergoes a fast metathesis reaction with the chloro-bridged half-sandwich complexes. The driving force for shifting the metathesis equilibrium completely towards the products **30**–**32** is the formation of electronically saturated complexes with three chloro bridges.

In reactions with chloro-bridged half-sandwich complexes of Ru, Rh, and Ir, dinitrogen complex **11** displayed a reactivity similar to that of **12**: bimetallic complexes **33**–**35** were formed without side products under release of dinitrogen (Scheme 3, Table 3). Although **11** is reported to decompose in halogenated solvents,[20] **33**–**35** can be prepared and analyzed in CH_2Cl_2 and $CDCl_3$, respectively.

The structures of complexes **29**, **30**, **31**, and **35** in the crystal are depicted in Figure 2 (for structural data of **28** see Table 4). The {(π-ligand)M} fragments are coordinated through three chloro bridges to the {RuCl(PRR$_2$)$_2$} fragments. The Ru–Cl bonds of the bridging chloro ligands (2.49–2.54 Å) are longer than the Ru–Cl bond of the terminal chloro ligand (2.36–2.40 Å). In the PPh_3 complexes **28** and **29**, the octahedral geometry around the Ru atom is slightly distorted due to an enlarged angle between the sterically demanding PPh_3 groups (P1-Ru1-P2 98.90, 99.49°). In the complexes with chelating dppb (**30** and **31**) and dcypb ligands (**35**), however, the P1-Ru1-P2 angle is closer to what is expected for an octahedral geometry (Table 4). In all com-

Table 3. Composition and ^{31}P NMR spectroscopic data ($CDCl_3$) for the (arene)$RuCl_2$ and Cp*MCl_2 (M = Rh, Ir) complexes **28**–**35**.

Complex	Fragment A	Fragment B	δ [ppm]
28	{(cymene)$RuCl_2$}	{$(PPh_3)_2RuCl_2$}	50.3[a,b]
29	{(1,3,5-C_6H_3iPr$_3$)$RuCl_2$}	{$(PPh_3)_2RuCl_2$}	49.8[b]
30	{(1,3,5-$C_6H_3Et_3$)$RuCl_2$}	{(dppb)$RuCl_2$}	54.3
31	{Cp*$RhCl_2$}	{(dppb)$RuCl_2$}	54.5
32	{Cp*$IrCl_2$}	{(dppb)$RuCl_2$}	56.5
33	{(cymene)$RuCl_2$}	{(dcypb)$RuCl_2$}	51.6
34	{Cp*$RhCl_2$}	{(dcypb)$RuCl_2$}	50.7
35	{Cp*$IrCl_2$}	{(dcypb)$RuCl_2$}	53.1

[a] From reference [11]. [b] In CD_2Cl_2.

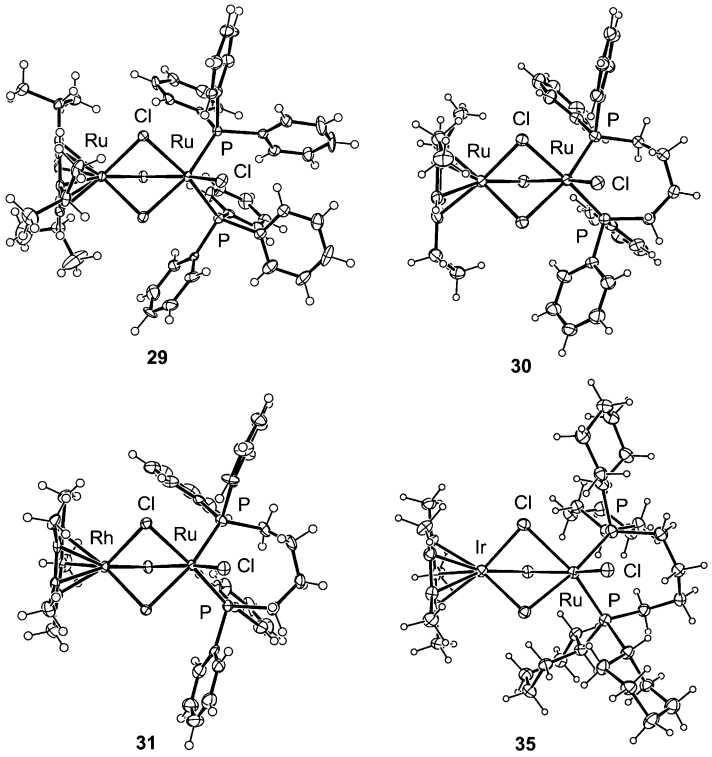
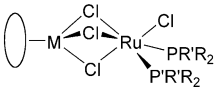


Figure 2. Molecular structures of complexes **29**–**31** and **35** in the crystal (ORTEP plots).

Table 4. Selected interatomic distances [Å] and angles [°] for **28**–**31** and **35**.

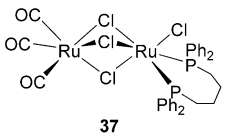


Complex	Ru–Cl_{br}[a]	Ru-–Cl_t	Ru–P	Ru–P′	P-Ru-P′	P-Ru-Cl_t[a]	M···Ru
28	2.49	2.364(3)	2.283(3)	2.292(3)	98.90(12)	91.68	3.331(3)
29	2.50	2.389(1)	2.275(2)	2.295(2)	99.49(5)	91.45	3.360(2)
30	2.50	2.381(1)	2.240(1)	2.269(1)	93.97(5)	91.74	3.326(1)
31	2.50	2.399(1)	2.258(1)	2.252(1)	93.65(5)	93.25	3.273(1)
35	2.54	2.395(2)	2.273(2)	2.275(2)	92.95(8)	92.95	3.357(2)

[a] Average values; br = bridging, t = terminal.

plexes, the plane defined by the arene π ligand is almost parallel to that defined by the bridging chloro ligands.

Bimetallic complexes with {(CO)L_2RuX_2} (L = CO, PR_3) fragments: Finally, we investigated whether ruthenium carbonyl complexes **4** and **5** can be combined with ruthenium–phosphane complexes **10**–**12**. Trichloro-bridged complexes **37**–**40** were obtained simply by mixing equal amounts of the respective starting materials. Again, entropy appears to be a driving force for the reactions, since weakly coordinated ligands such as water or dinitrogen are released in all cases.



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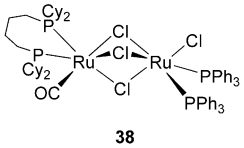

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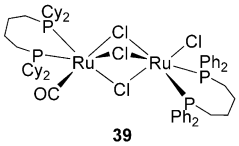

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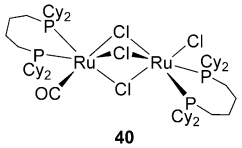
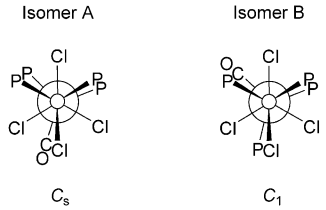


40

For **38**–**40**, two isomers are possible (Scheme 4). Contrary to what was observed for **25** and **26**, only C_1-symmetric isomer B was formed in all cases. This was evidence by the ^{31}P NMR spectra (C_6D_6) of **38**–**40**, which display four doublets corresponding to the four chemically distinct P atoms. The same stereochemistry was found for the structurally related PPh_3 complexes [$(PPh_3)_2$ClRu(μ-Cl)$_3$Ru(PF_3)(PPh_3)$_2$][21] and [$(PPh_3)_2$ClRu(μ-Cl)$_3$Ru(CE)(PPh_3)$_2$] (E = O, S),[22] for some bimetallic dppb complexes [(dppb)ClRu(μ-Cl)$_3$Ru(L)(dppb)] (L = H_2, C_2H_4, pyridine),[19] and for the starting material **11**.[20]



Scheme 4. Schematic representation of the two possible isomers for complexes of the type [$(PR_3)_2$ClRu(μ-Cl)$_3$Ru(CO)(PR_3)$_2$].

The molecular structure of **40** is displayed in Figure 3. The geometry around both ruthenium atoms can be described as slightly distorted octahedral with P-Ru-P angles of 95.23(8)° for the {RuCl(dcypb)} fragment and 93.79(9)° for the {Ru(CO)(dcypb)} fragment. The Ru–Cl and Ru–P distances are within the expected ranges. A structurally related alkylidene complex having a CHCH=CMe_2 ligand instead of the CO ligand was recently described by Fogg et al.[23]

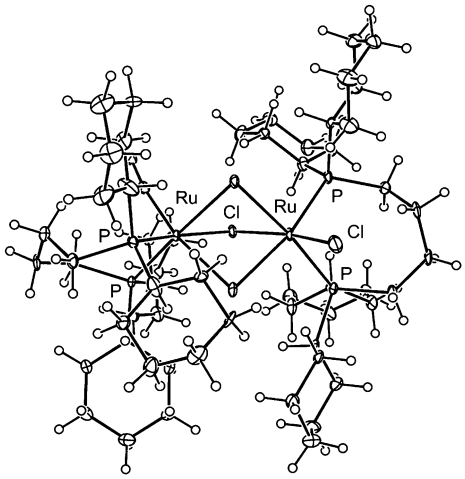
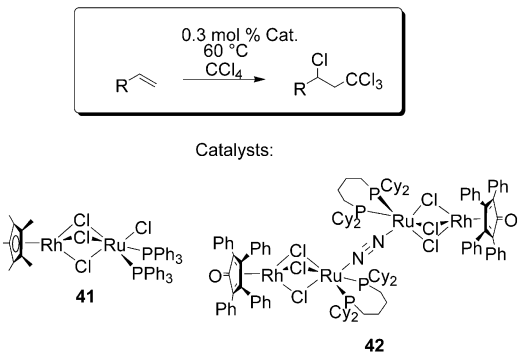


Figure 3. Molecular structure of complex **40** in the crystal (ORTEP plot).

Conclusion

We have presented methods for the synthesis of homo- and heterobimetallic complexes in a combinatorial fashion. The underlying reactions are general, fast, and give defined products with substantial structural diversity in quantitative yield. Although only selected members of the library were synthesized, many more could be generated by using complexes of types **A** and **B** as starting materials. Furthermore, structurally related complexes such as [{$(PR_3)_2$(CO)RuCl$_2$}$_2$] (analogous to **4**, type **A**) are expected to display a similar reactivity which would allow the diversity to be expanded even further. For applications in the field of combinatorial catalysis, it is also of importance that the bimetallic complexes can be synthesized in situ without prior purification, which considerably facilitates screening assays.

A first application in combinatorial catalysis was recently reported by us.[6] A library of 66 catalyst precursors was generated in situ by mixing chloro-bridged complexes of Ru^{II}, Ru^{III}, Ru^{IV}, Rh^{I}, Rh^{III}, Ir^{I}, Ir^{III}, Pd^{II}, and Pt^{II} with the Ru^{II}–phosphane complexes **7**, **11**, and **12**. Using the addition of CCl_4 to styrene as a benchmark reaction for atom-transfer radical additions (ATRA), we identified two chloro-bridged Rh–Ru complexes which show an exceptionally high activity (**41** and **42**, Scheme 5). With an initial TOF of 1200 h^{-1} and



Scheme 5. Atom-transfer radical addition of CCl_4 to olefins catalyzed by the Rh^{III}–Ru^{II} complex **41** or the Rh^{I}–Ru^{II} complex **42**.

a maximum TON of 4500, they are among the best ATRA catalysts described so far. Furthermore, these new catalysts tolerate the use of water-containing solvents and give excellent yields for difficult substrates such as octene. Both catalysts precursors contain the $Rh(\mu\text{-}Cl)_3Ru$ structural motif, and the investigations described here provide the foundation to explain the formation of these heterometallic complexes.

The above-mentioned application clearly demonstrates the potential of halogeno-bridged heterometallic complexes in homogeneous catalysis. Note, however, that this class of compounds is less suited for catalytic reactions with substrates that act as strong donor ligands (e.g., CO), because cleavage of the halogeno bridge is expected. Despite this limitation, we believe that libraries of homo- and heterobimetallic halogeno-bridged complexes will increasingly be used for the discovery of new transition-metal catalysts.

Experimental Section

General: All complexes were synthesized under an atmosphere of dry dinitrogen or argon by using standard Schlenk techniques. $[MoX(C_3H_4R)(CO)_2(CH_3CN)_2]$ (X = Cl, Br; R = H, CH_3), $[WX(C_3H_4R)(CO)_2(CH_3CN)_2]$ (X = Cl, Br; R = H, CH_3),[24] $[\{Cp^*RhCl_2\}_2]$,[25] $[\{Cp^*RhBr_2\}_2]$,[11] $[\{Cp^*IrCl_2\}_2]$,[25] $[\{(cymene)RuCl_2\}_2]$,[26] $[\{(cymene)RuBr_2\}_2]$,[11] $[\{(1,3,5\text{-}C_6H_3R_3)RuCl_2\}_2]$ (R = Me, Et, *i*Pr),[27] $[\{(dcypb)(CO)RuCl_2\}_2]$,[28] $[RuCl_2(CH_3CN)_2(PPh_3)_2]$,[29] $[RuCl_2(PhCN)_2(dppb)]$,[18] [(dppb)ClRu-(μ-Cl)$_2$(μ-OH$_2$)RuCl(dppb)],[19] [(dcypb)(N_2)Ru(μ-Cl)$_3$RuCl(dcypb)],[20] $[(PPh_3)_2ClRu(\mu\text{-}Cl)_2(\mu\text{-}PhNHCHO\text{-}O,O)RuCl(PPh_3)_2]$,[16] and $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(acetone)(PPh_3)_2]$[5b] were prepared according to literature procedures. $[\{(CO)_3RuCl_2\}_2]$ and 1,4-bis(diphenylphosphanyl)butane (dppb) were purchased from Acros, and 1,4-bis(dicyclohexylphosphanyl)-butane (dcypb) was purchased from Aldrich. The ^1H and ^{13}C spectra were recorded on a Bruker Advance DPX 400 or a Bruker Advance 200 spectrometer using the residual protonated solvents as internal standards. All spectra were recorded at room temperature.

[(cymene)Ru(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_3$H$_5$)] (13): $[\{(cymene)RuCl_2\}_2]$ (25 mg, 41 μmol) and $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(CH_3CN)_2]$ (25.4 mg, 82 μmol) in degassed $CHCl_3$ (4 mL) were stirred for 30 min. After evaporation of the solvent under reduced pressure the product was washed with pentane and dried under vacuum (yield of isolated compound: 92%). Orange crystals were obtained by slow diffusion of pentane into a solution of **14** in benzene. IR: $\tilde{\nu}$ = 1938 (CO), 1845 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.92 (d, ^3J = 10 Hz, 2H; CH_2, allyl), 1.32 (d, ^3J = 7 Hz, 6H; $CH(CH_3)_2$), 2.24 (s, 3H; CH_3), 2.85 (sept, ^3J = 7 Hz, 1H; $CH(CH_3)_2$), 3.50 (d, ^3J = 6 Hz, 2H; CH_2, allyl), 3.67 (m, 1H; CH, allyl), 5.31 (d, ^3J = 6 Hz, 2H; CH, cymene), 5.53 (d, ^3J = 6 Hz, 2H; CH, cymene); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.8, 22.2 (CH_3), 31.2 ($CH(CH_3)_2$), 54.2 (CH_2, allyl), 74.1 (CH, allyl), 78.1, 79.5 (CH, cymene), 96.8, 101.2 (C, cymene), 228.2 (CO); elemental analysis (%) calcd for $C_{15}H_{19}Cl_3MoO_2Ru\cdot H_2O$: C 32.60, H 3.83; found: C 32.63, H 3.56.

[(cymene)Ru(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_4$H$_7$)] (14): The synthesis was performed analogously to that of complex **13** using $[MoCl(\eta^3\text{-}C_4H_7)(CO)_2(CH_3CN)_2]$ (yield of isolated compound: 90%). IR: $\tilde{\nu}$ = 1929 (CO), 1827 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.82 (s, 2H; CH_2, allyl), 1.29 (d, ^3J = 7 Hz, 6H; $CH(CH_3)_2$), 1.98 (s, 3H; CH_3, allyl), 2.23 (s, 3H; CH_3, cymene), 2.82 (sept, ^3J = 7 Hz, 1H; $CH(CH_3)_2$), 3.16 (s, 2H; CH_2, allyl), 5.31 (d, ^3J = 6 Hz, 2H; CH, cymene), 5.51 (d, ^3J = 6 Hz, 2H; CH, cymene); ^{13}C NMR (101 MHz, C_6D_6/CD_2Cl_2 9:1): δ = 18.2, 21.9, 22.9 (CH_3), 31.0 ($CH(CH_3)_2$), 53.2 (CH_2, allyl), 78.1, 79.5 (CH, cymene), 84.5 (C, allyl), 95.9, 100.3 (C, cymene), 229.1 (CO); elemental analysis (%) calcd for $C_{16}H_{21}Cl_3MoO_2Ru$: C 35.02, H 3.86; found: C 34.72, H 3.64.

[(cymene)Ru(μ-Br)$_3$Mo(CO)$_2$(η^3-C$_3$H$_5$)] (15): The synthesis was performed analogously to that of complex **13** using $[\{(cymene)RuBr_2\}_2]$ and $[MoBr(\eta^3\text{-}C_3H_5)(CO)_2(CH_3CN)_2]$ (yield of isolated compound: 88%). Red crystals were obtained by slow diffusion of pentane into a solution of **15** in benzene. IR: $\tilde{\nu}$ = 1948 (CO), 1844 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.91 (d, ^3J = 10 Hz, 2H; CH_2, allyl), 1.29 (d, ^3J = 7 Hz, 6H; $CH(CH_3)_2$), 2.26 (s, 3H; CH_3), 2.88 (sept, ^3J = 7 Hz, 1H; $CH(CH_3)_2$), 3.57 (d, ^3J = 6 Hz, 2H; CH_2, allyl), 3.90 (m, 1H; CH, allyl), 5.27 (d, ^3J = 6 Hz, 2H; CH, cymene), 5.48 (d, ^3J = 6 Hz, 2H; CH, cymene); ^{13}C NMR (101 MHz, C_6D_6/CD_2Cl_2 9:1): δ = 18.8, 22.1 (CH_3), 31.1 ($CH(CH_3)_2$), 52.5 (CH_2, allyl), 73.8 (CH, allyl), 78.4, 78.6 (CH, cymene), 95.8, 101.5 (C, cymene), 228.1 (CO); elemental analysis (%) calcd for $C_{15}H_{19}Br_3MoO_2Ru$: C 26.97, H 2.87; found: C 27.14, H 2.83

[(1,3,5-C$_6$H$_3$*i*Pr$_3$)Ru(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_4$H$_7$)] (16): The synthesis was performed analogously to that of complex **13** using $[\{(1,3,5\text{-}C_6H_3iPr_3)RuCl_2\}_2]$ and $[Mo(\eta^3\text{-}C_4H_7)(CO)_2(CH_3CN)_2Cl]$ (yield of isolated compound: 85%). Orange crystals were obtained by slow diffusion of pentane into a solution of **16** in benzene. IR: $\tilde{\nu}$ = 1940 (CO), 1865 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.78 (s, 2H; CH_2, allyl), 1.30 (d, ^3J = 7 Hz, 18H; $CH(CH_3)_2$), 1.97 (s, 3H; CH_3, allyl), 2.84 (sept, ^3J = 7 Hz, 3H; $CH(CH_3)_2$), 3.12 (s, 2H; CH_2, allyl), 5.27 (s, 3H; C_6H_3); ^{13}C NMR (101 MHz, C_6D_6/CD_2Cl_2 9:1): δ = 22.1 (CH_3, *i*Pr), 22.7 (CH_3, allyl), 31.6 ($CH(CH_3)_2$), 53.2 (CH_2, allyl), 75.2 (CH, arene), 84.5 (C, allyl), 103.1 (C, arene), 229.1 (CO); elemental analysis (%) calcd for $C_{21}H_{31}Cl_3MoO_2Ru\times H_2O$: C 39.60, H 5.22; found: C 39.91, H 4.98.

[(1,3,5-*i*Pr$_3$C$_6$H$_3$)Ru(μ-Cl)$_3$W(CO)$_2$(η^3-C$_4$H$_7$)] (17): The synthesis was performed analogously to that of complex **13** using $[\{(1,3,5\text{-}C_6H_3iPr_3)RuCl_2\}_2]$ and $[WCl(\eta^3\text{-}C_3H_4(CH_3))(CO)_2(CH_3CN)_2]$ (yield of isolated compound: 88%). Red crystals were obtained by slow diffusion of pentane into a solution of **17** in benzene. IR: $\tilde{\nu}$ = 1934 (CO), 1853 cm^{-1} (CO); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 2H; CH_2, allyl), 1.31 (d, ^3J = 7 Hz, 18H; $CH(CH_3)_2$), 2.13 (s, 3H; CH_3, allyl), 2.85 (sept, ^3J = 7 Hz, 3H; $CH(CH_3)_2$), 2.94 (s, 2H; CH_2, allyl), 5.30 ppm (s, 3H; C_6H_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.5 (CH_3, allyl), 22.3 (CH_3, *i*Pr), 31.5 ($CH(CH_3)_2$), 46.0 (CH_2, allyl), 74.4 (CH, arene), 75.3 (C, allyl), 103.7 (C, arene), 220.2 ppm (CO); elemental analysis (%) calcd for $C_{21}H_{31}Cl_3O_2RuW\cdot{}^1/_3\,CHCl_3$: C 34.32, H 4.23; found: C 34.56, H 4.17.

[Cp*Rh(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_4$H$_7$)] (18): The synthesis was performed analogously to that of complex **13** using $[\{Cp^*RhCl_2\}_2]$ and $[MoCl(\eta^3\text{-}C_4H_7)(CO)_2(CH_3CN)_2]$ (yield of isolated compound: 90%). Red crystals were obtained by slow diffusion of pentane into a solution of **18** in benzene. IR: $\tilde{\nu}$ = 1934 (CO), 1839 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (s, 2H; CH_2, allyl), 1.67 (s, 15H; Cp*), 2.08 (s, 3H; CH_3, allyl), 3.18 ppm (s, 2H; CH_2, allyl); ^{13}C NMR (101 MHz, C_6D_6/CD_2Cl_2 9:1): δ = 8.8 (Cp*), 22.7 (CH_3, allyl), 53.8 (CH_2, allyl), 84.2 (C, allyl), 94.2 (d, $^1J_{Rh,C}$ = 9 Hz, $C_5(CH_3)_5$), 228.9 ppm (CO); elemental analysis (%) calcd for $C_{16}H_{22}Cl_3MoO_2Rh$: C 34.84, H 4.02; found: C 34.93, H 4.03.

[Cp*Rh(μ-Br)$_3$Mo(CO)$_2$(η^3-C$_3$H$_5$)] (19): The synthesis was performed analogously to that of complex **13** using $[\{Cp^*RhBr_2\}_2]$ and $[MoBr(\eta^3\text{-}C_3H_5)(CO)_2(CH_3CN)_2]$ (yield of isolated compound: 89%). Red crystals were obtained by slow diffusion of pentane into a solution of **19** in benzene. IR: $\tilde{\nu}$ = 1933 (CO), 1843 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 (d, ^3J = 10 Hz, 2H; CH_2, allyl), 1.74 (s, 15H; Cp*), 3.61 (d, ^3J = 7 Hz, 2H; CH_2, allyl), 4.02 ppm (m, 1H; CH, allyl); ^{13}C NMR (101 MHz, C_6D_6/[D$_6$]acetone 9:1): δ = 9.6 (Cp*), 53.1 (CH_2, allyl), 73.4 (C, allyl), 95.9 (d, $^1J_{Rh,C}$ = 9 Hz, $C_5(CH_3)_5$), 228.1 ppm (CO); elemental analysis (%) calcd for $C_{15}H_{20}Br_3MoO_2Rh\cdot CHCl_3$: C 24.32, H 2.68; found: C 24.89, H 2.87.

[Cp*Ir(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_3$H$_5$)] (20): The synthesis was performed analogously to that of complex **13** using $[\{Cp^*IrCl_2\}_2]$ (25 mg, 32 μmol), $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(CH_3CN)_2]$ (19.5 mg, 63 μmol), and CH_2Cl_2 (8 mL) (yield of isolated compound: 94%). IR: $\tilde{\nu}$ = 1933 (CO), 1842 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.93 (d, ^3J = 10 Hz, 2H; CH_2, allyl), 1.64 (s, 15H; Cp*), 3.57 (d, ^3J = 7 Hz, 2H; CH_2, allyl), 3.97 ppm (m, 1H; CH, allyl); ^{13}C NMR (101 MHz, $C_6D_6/CDCl_3$ 9:1): δ = 9.0 (Cp*), 54.8 (CH_2, allyl), 74.8 (CH, allyl), 99.7 ($C_5(CH_3)_5$), 229.1 ppm (CO); elemental analysis (%) calcd for $C_{15}H_{20}Cl_3IrMoO_2\cdot H_2O$: C 27.94, H 3.44; found: C 27.45, H 2.99.

[Cp*Ir(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_4$H$_7$)] (21): The synthesis was performed analogously to that of complex **20** using $[MoCl(\eta^3\text{-}C_4H_7)(CO)_2(CH_3CN)_2]$ (yield of isolated compound: 85%). IR: $\tilde{\nu}$ = 1938 (CO), 1844 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.85 (s, 2H; CH_2, allyl), 1.6 (s, 15H; Cp*), 2.09 (s, 3H; CH_3, allyl), 3.21 ppm (s, 2H; CH_2, allyl); ^{13}C NMR

(101 MHz, C_6D_6/$CDCl_3$ 9:1): $\delta = 8.9$ (Cp*), 23.2 (CH_3, allyl), 53.9 (CH_2, allyl), 85.7 (CH, allyl), 99.6 ($C_5(CH_3)_5$), 229.7 ppm (CO); elemental analysis (%) calcd for $C_{16}H_{22}Cl_3IrMoO_2$: C 29.99, H 3.46; found: C 29.56, H 3.11.

[Cp*Rh(μ-Cl)$_3$W(CO)$_2$(η^3-C$_4$H$_7$)] (22): The synthesis was performed analogously to that of complex **13** using [{Cp*RhCl$_2$}$_2$] and [WCl(η^3-C_4H_7)(CO)$_2$(CH_3CN)$_2$] (yield of isolated compound: 90%). Red crystals were obtained by slow diffusion of pentane into a solution of **22** in benzene. IR: $\tilde{\nu} = 1925$ (CO), 1823 cm^{-1} (CO); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.37$ (s, 2H; CH_2, allyl), 1.69 (s, 15H; Cp*), 2.24 (s, 3H; CH_3, allyl), 2.99 ppm (s, 2H; CH_2, allyl); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 9.4$ (Cp*), 21.4 (CH_3, allyl), 46.8 (CH_2, allyl), 77.2 (C, allyl), 95.0 (d, $^1J_{Rh,C} = 9$ Hz, $C_5(CH_3)_5$), 219.7 ppm (CO); elemental analysis (%) calcd for $C_{16}H_{22}Cl_3O_2RhW$: C 30.05, H 3.47; found: C 29.79, H 3.24.

[(CO)$_3$Ru(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_4$H$_7$)] (23): [{$(CO)_3RuCl_2$}$_2$] (80 mg, 156 μmol) and [MoCl(η^3-C_4H_7)$(CO)_2(CH_3CN)_2$] (101 mg, 312 μmol) in degassed CH_2Cl_2 (4 mL) were stirred for 30 min. After removal of the solvent under reduced pressure, the product was heated to reflux in hexane (10 mL). After 30 min, heating was stopped and the solution was placed in a refrigerator (5 °C). After one day, orange crystals had formed (yield of isolated compound: 88%). IR: $\tilde{\nu} = 1834$ (CO), 1923 (CO), 2061 (CO), 2143 cm^{-1} (CO); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.88$ (s, 2H; CH_2), 1.99 (s, 3H; CH_3), 3.22 ppm (s, 2H; CH_2); ^{13}C NMR (101 MHz, C_6D_6): $\delta = 22.3$ (CH_3), 53.6 (CH_2), 85.7 (C), 181.7 (CO, Ru), 227.8 ppm (CO, Mo); elemental analysis (%) calcd for $C_9H_7Cl_3MoO_5Ru{\cdot}CH_3CN$: C 24.49, H 1.87, N 2.60; found: C 24.86, H 1.95, N 2.95.

[(CO)$_3$Ru(μ-Cl)$_3$W(CO)$_2$(η^3-C$_4$H$_7$)] (24): The synthesis was performed analogously to that of complex **23** using [WCl(η^3-C_4H_7)$(CO)_2(CH_3CN)_2$] (yield of isolated compound: 90%). IR: $\tilde{\nu} = 1838$ (CO), 1947 (CO), 2061 (CO), 2143 cm^{-1} (CO); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.59$ (s, 2H; CH_2), 2.17 (s, 3H; CH_3), 3.12 ppm (s, 2H; CH_2); ^{13}C NMR (101 MHz, C_6D_6): $\delta = 21.4$ (CH_3), 46.3 (CH_2), 76.5 (C), 181.6 (CO, Ru), 218.3 ppm (CO, W); elemental analysis (%) calcd for $C_9H_7Cl_3O_5RuW{\cdot}CH_3CN$: C 21.06, H 1.61, N 2.23; found: C 21.38, H 1.76, N 2.73.

[(dcypb)(CO)Ru(μ-Cl)$_3$Mo(CO)$_2$(η^3-C$_4$H$_7$)] (25): [{(dcypb)(CO)RuCl$_2$}$_2$] (40 mg, 31 μmol) and [MoCl(η^3-C_4H_7)$(CO)_2(CH_3CN)_2$] (20 mg, 61 μmol) in degassed C_6H_6 (8 mL) were stirred for 30 min. After evaporation of the solvent under reduced pressure, the product was washed with pentane and dried under vacuum (yield of isolated compound: 92%). Yellow crystals were obtained by slow diffusion of pentane into a solution of **25** in benzene. IR: $\tilde{\nu} = 1838$ (CO), 1936 cm^{-1} (br, CO); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.10$ (s, 2H; CH_2), 1.50–2.33 (m, 52H; dcypb), 2.42 (s, 3H; CH_3), 3.46 ppm (s, 2H; CH_2); ^{13}C NMR (101 MHz, C_6D_6): $\delta = 26.9$ (CH_3), 27–44.5 (m, dcypb), 57.1 (CH_2, allyl), 88.2 (CH, allyl), 197.3 (CO), 228.2 ppm (CO); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 45.6$ ppm (s); elemental analysis (%) calcd for $C_{35}H_{59}Cl_3MoO_3P_2Ru{\cdot}{}^2/_3\,C_6H_6$: C 45.34, H 6.15; found: C 45.81, H 5.73.

[(dcypb)(CO)Ru(μ-Cl)$_3$W(CO)$_2$(η^3-C$_4$H$_7$)] (26): The synthesis was performed analogously to that of complex **25** using [WCl(η^3-C_4H_7)$(CO)_2(CH_3CN)_2$] (yield of isolated compound: 94%). IR: $\tilde{\nu} = 1828$ (CO), 1923 cm^{-1} (br, CO); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.72$ (s, 2H; CH_2), 1.11–1.67 (m, 36H; dcypb), 2.62 (s, 3H; CH_3), 1.80–2.40 (m, 16H; dcypb), 3.36 ppm (s, 2H; CH_2); ^{13}C NMR (101 MHz, C_6D_6): $\delta = \delta = 25.8$ (CH_3, allyl), 27–44.7 (m, dcypb), 49.9 (CH_2, allyl), 78.9 (CH, allyl), 195.1 (CO), 224.5 ppm (CO); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 46.8$ ppm (s); elemental analysis (%) calcd for $C_{35}H_{59}Cl_3O_3P_2RuW{\cdot}H_2O$: C 42.08, H 6.15; found: C 42.15, H 6.51.

[(cymene)Ru(μ-Cl)$_3$Ru(PPh$_3$)$_2$Cl] (28): Method A: [{(cymene)RuCl$_2$}$_2$] (18 mg, 30 μmol) and [$(PPh_3)_2$ClRu(μ-Cl)$_2$(μ-PhNHCHO-*O*,*O*)-RuCl$(PPh_3)_2$] (45 mg, 30 μmol) in degassed CH_2Cl_2 (8 mL) were stirred for 30 min. After evaporation of the solvent under reduced pressure, the product was washed with pentane and dried under vacuum (yield of isolated compound: 95%). Method B: [$(PPh_3)_2$ClRu(μ-Cl)$_3$Ru(acetone)$(PPh_3)_2$] (50 mg, 33 μmol) and [{(cymene)RuCl$_2$}$_2$] (20 mg, 33 μmol)

Table 5. Crystallographic data for complexes **13**, and **15**–**18**.

	13	**15**	**16**	**17**	**18**
empirical formula	$C_{15}H_{19}Cl_3MoO_2Ru$	$C_{15}H_{19}Br_3MoO_2Ru$	$C_{21}H_{31}Cl_3MoO_2Ru$	$C_{21}H_{31}Cl_3WO_2Ru$	$C_{16}H_{22}Cl_3MoO_2Rh$
M [g mol^{-1}]	534.66	668.04	618.82	706.73	551.54
crystal size [mm]	0.25×0.22×0.16	0.30×0.25×0.18	0.22×0.15×0.13	0.16×0.10×0.08	0.15×0.10×0.08
crystal system	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pnma$
a [Å]	7.8477(6)	7.8988(6)	10.723(4)	10.663(3)	19.651(10)
b [Å]	12.265(3)	12.4468(11)	14.432(5)	14.2887(17)	12.183(8)
c [Å]	18.756(4)	19.0832(18)	15.800(5)	15.809(5)	8.334(3)
α [°]	90	90	89.60(3)	89.656(16)	90
β [°]	93.596(11)	92.332(7)	87.46(3)	87.12(3)	90
γ [°]	90	90	89.41(3)	89.321(17)	90
V [Å^3]	1801.7(6)	1874.6(3)	2442.6(14)	2405.5(11)	1995.2(17)
Z	4	4	4	4	4
ρ [g cm^{-3}]	1.971	2.367	1.683	1.951	1.836
T [K]	140(2)	140(2)	293(2)	140(2)	293(2)
absorption coefficient [mm^{-1}]	1.981	7.871	1.474	5.754	1.862
Θ range [°]	3.32–25.02	3.44–25.03	3.27 to 25.03	3.29 to 25.02	3.62–25.02
index ranges					
h	−8 to 8	−9 to 9	−12 to 12	−12 to 12	−23 to 23
k	−14 to 14	−14 to 14	−16 to 17	−16 to 16	−14 to 14
l	−20 to 22	−22 to 22	−18 to 18	−18 to 18	−9 to 9
reflections collected	10053	10832	14879	14605	11232
independent reflections	3056 (R_{int} = 0.0386)	3221 (R_{int} = 0.0546)	8102 (R_{int} = 0.0519)	7965 (R_{int} = 0.0807)	1837 (R_{int} = 0.1596)
absorption correction	empirical	empirical	empirical	empirical	empirical
max./min. transmission	0.7110/0.2560	0.8200/0.4520	0.7160/0.2630	0.574/0.109	0.6070/0.1360
data/restraints/parameters	3056/0/200	3221/0/199	8102/0/515	7965/0/505	1837/57/116
GOF on F^2	1.116	1.095	1.036	1.066	1.093
final R indices [$I > 2\sigma(I)$]					
$R1$	0.0343	0.0388	0.0662	0.1016	0.0807
$wR2$	0.0820	0.0784	0.1597	0.2737	0.2249
R indices (all data)					
$R1$	0.0413	0.0664	0.0923	0.1118	0.1135
$wR2$	0.0926	0.0851	0.1700	0.2788	0.2576
largest diff. peak/hole [e Å^{-3}]	0.632/−0.594	0.684/−0.725	1.214/−0.848	2.857/−3.005	0.974/−0.717

in degassed CH_2Cl_2 (5 mL) were stirred for 30 min at room temperature. The solvent was then removed under reduced pressure and the product washed with Et_2O (10 mL) and dried under vacuum (yield of isolated compound: 93%). Crystals were obtained by slow diffusion of pentane into a solution of **28** in THF. The spectroscopic and analytical data were identical to those previously published for this compound.[5b]

[(1,3,5-C_6H_3*i*Pr_3)Ru(μ-Cl)$_3$Ru(PPh$_3$)$_2$Cl] (29): [$(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru$(acetone)$(PPh_3)_2$] (151 mg, 100 μmol) and [{(1,3,5-C_6H_3*i*Pr_3)$RuCl_2$}$_2$] (75 mg, 100 μmol) in degassed CH_2Cl_2 (10 mL) were stirred for 30 min at room temperature. The solvent volume was then reduced to one half and the concentrated solution was poured into pentane (50 mL) to precipitate of the complex. The product was collected by filtration, washed with Et_2O, and dried under vacuum (yield of isolated compound: 87%). Crystals were obtained by slow diffusion of pentane into a solution of **29** in C_6H_6/CD_2Cl_2 (1:1). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.25$ (d, $^3J = 6.9$ Hz, 18H; $CH(CH_3)_2$), 2.80 (sept, $^3J = 6.9$, 3H; $CH(CH_3)_2$), 5.27 (s, 3H; CH), 7.00–7.32 ppm (m, 30H; Ph); ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 22.51$ ($CH(CH_3)_2$), 31.47 ($CH(CH_3)_2$), 75.1 (CH), 102.5 (C), 136.8–166.7 ppm (Ph); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 49.8$; elemental analysis (%) calcd for $C_{51}H_{54}Cl_4P_2Ru_2$ (1072.87): C 57.09, H 5.07; found: C 57.26, H 5.06.

[(1,3,5-$C_6H_3Et_3$)Ru(μ-Cl)$_3$Ru(dppb)Cl] (30): [{(1,3,5-$C_6H_3Et_3$)$RuCl_2$}$_2$] (25 mg, 41 μmol) and [(dppb)ClRu(μ-Cl)$_2$(μ-OH_2)RuCl(dppb)] (50 mg, 41 μmol) in degassed $CHCl_3$ (4 mL) were stirred for 30 min. After evaporation of the solvent under reduced pressure, the product was dried under vacuum (yield of isolated compound: 92%). Red crystals were obtained by slow diffusion of pentane into a solution of **30** in benzene. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.18$ (t, $^3J = 7$ Hz, 9H; CH_2CH_3), 1.25 (m, 2H; CH_2), 1.82 (m, 2H; CH_2), 2.08 (m, 2H; CH_2), 2.41 (q, $^3J = 7$ Hz, 6H; CH_2CH_3), 3.19 (m, 2H; CH_2), 5.11 (s, 3H; C_6H_3), 7.24–7.46 ppm (m, 20H; Ph); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 13.6$ (CH_3, Et), 22.9 (CH_2, dppb), 26.2 (CH_2, Et), 30.1–30.5 (m, CH_2, dppb), 76.5 (CH, arene), 99.5 (C, arene), 127.3–133.8 ppm (m, Ph); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta =$ 54.3 ppm (s); elemental analysis (%) calcd for $C_{40}H_{46}Cl_4P_2Ru_2 \cdot {}^1/_4CHCl_3$: C 50.22, H 4.84; found: C 50.60, H 5.07.

[Cp*Rh(μ-Cl)$_3$Ru(dppb)Cl] (31): The synthesis was performed analogously to that of complex **30** using [{Cp*$RhCl_2$}$_2$] (yield of isolated compound: 90%). Red crystals were obtained by slow diffusion of pentane into a solution of **31** in benzene. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (m, 2H; CH_2), 1.55 (s, 15H; Cp*), 1.89 (m, 2H; CH_2), 2.11 (m, 2H; CH_2), 3.25 (m, 2H; CH_2), 7.20–7.56 ppm (m, 20H; Ph); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 9.1$ (Cp*), 22.6 (CH_2, dppb), 30.1–30.5 (m, CH_2, dppb), 93.1 (d, $^1J_{Rh,C} = 9$ Hz, $C_5(CH_3)_5$), 126.9–133.6 ppm (m, Ph); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 54.5$ ppm (s); elemental analysis (%) calcd for $C_{38}H_{43}Cl_4P_2RhRu \cdot {}^1/_2\,CHCl_3$: C 47.81, H 4.53; found: C 47.80, H 4.29.

[Cp*Ir(μ-Cl)$_3$Ru(dppb)Cl] (32): The synthesis was performed analogously to that of complex **30** using [{Cp*$IrCl_2$}$_2$] (yield of isolated compound: 94%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.32$ (m, 2H; CH_2), 1.50 (s, 15H; Cp*), 1.92 (m, 2H; CH_2), 2.13 (m, 2H; CH_2), 3.28 (m, 2H; CH_2), 7.21–7.34 ppm (m, 20H; Ph); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 9.0$ (Cp*), 22.6 (CH_2, dppb), 30.0–30.3 (m, CH_2, dppb), 84.6 ($C_5(CH_3)_5$), 127.0–133.9 ppm (m, Ph); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 56.5$ ppm (s); elemental analysis (%) calcd for $C_{38}H_{43}Cl_4IrP_2Ru \cdot {}^1/_2CHCl_3$: C 43.77, H 4.15; found: C 43.60, H 4.36.

[(cymene)Ru(μ-Cl)$_3$Ru(dcypb)Cl] (33): [{(cymene)$RuCl_2$}$_2$] (10 mg, 16 μmol) and [(dcypb)(N_2)Ru(μ-Cl)$_3$RuCl(dcypb)] (20 mg, 16 μmol) in degassed CH_2Cl_2 (4 mL) were stirred for 30 min. After evaporation of the solvent under reduced pressure the product was dried under vacuum (yield of isolated compound: 92%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 1.10–1.40 (m, 14H; dcypb), 1.32 (d, $^3J = 7$ Hz, 6H; $CH(CH_3)_2$), 1.50–2.00 (m, 30H; dcypb), 2.10–2.35 (m, 5H; dcypb), 2.28 (s, 3H; CH_3), 2.45 (m, 2H; dcypb), 2.96 (sept, $^3J = 7$ Hz, 1H; $CH(CH_3)_2$), 5.28 (d, $^3J = 6$ Hz, 2H; CH, cymene), 5.41 ppm (d, $^3J = 6$ Hz, 2H; CH, cymene); ^{13}C NMR

Table 6. Crystallographic data for **19**, **22**, **23**, **25**, and **28**.

	19	**22**	**23**	**25**	**28**
empirical formula	$C_{15}H_{20}Br_3MoO_2Rh$	$C_{16}H_{22}Cl_3O_2RhW$	$C_9H_7Cl_3MoO_5Ru$	$C_{35}H_{59}Cl_3MoO_3P_2Ru$	$C_{46}H_{44}Cl_4P_2Ru_2$
M [g mol^{-1}]	670.89	639.45	498.51	893.12	1002.69
crystal size [mm]	0.19×0.16×0.13	0.15×0.10×0.08	0.30×0.25×0.15	0.23×0.16×0.10	0.19×0.12×0.10
crystal system	monoclinic	orthorhombic	triclinic	orthorhombic	triclinic
space group	$P2_1/n$	*Pnma*	$P\bar{1}$	*Pna*2(1)	$P\bar{1}$
a [Å]	14.708(7)	19.778(3)	6.8700(5)	22.605(7)	10.072(3)
b [Å]	9.9648(12)	11.7753(2)	14.749(3)	16.399(5)	12.099(5)
c [Å]	15.177(6)	8.6027(15)	15.157(3)	10.1964(10)	18.801(10)
α [°]	90	90	80.876(18)	90	91.17(4)
β [°]	118.23(4)	90	78.573(11)	90	100.77(4)
γ [°]	90	90	89.817(11)	90	109.93(4)
V [Å^3]	1959.8(12)	2003.5(5)	1485.6(5)	3779.8(16)	2107.2(16)
Z	4	4	4	4	2
ρ [g cm^{-3}]	2.274	2.120	2.229	1.569	1.580
T [K]	293(2)	140(2)	140(2)	140(2)	140(2)
absorption coefficient [mm^{-1}]	7.601	6.965	2.408	1.062	1.079
Θ range [°]	3.75–25.02	3.58–25.02	3.31–25.03	2.96–25.02	3.29–25.02
index ranges					
h	−17 to 17	−23 to 23	−7 to 7	−26 to 26	−11 to 11
k	−10 to 10	−12 to 12	−17 to 17	−19 to 19	−14 to 14
l	−18 to 17	−10 to 10	−18 to 18	−12 to 11	−22 to 21
reflections collected	11157	11690	9648	23455	12838
independent reflections	3267 ($R_{int} = 0.0414$)	1779 ($R_{int} = 0.1583$)	4913 ($R_{int} = 0.0316$)	6583 ($R_{int} = 0.0823$)	6981 ($R_{int} = 0.0654$)
absorption correction	empirical	empirical	empirical	empirical	empirical
max./min. transmission	0.6480/0.1760	0.7870/0.3840	0.7000/0.2400	0.6470/0.1750	0.5100/0.0670
data/restraints/parameters	3267/0/200	1779/57/115	4913/0/344	6583/1/407	6981/0/488
GOF on F^2	1.126	1.164	1.112	1.106	0.966
final R indices [$I > 2\sigma(I)$]					
$R1$	0.0486	0.0879	0.0389	0.0518	0.0781
$wR2$	0.1389	0.1743	0.1081	0.1235	0.2036
R indices (all data)					
$R1$	0.0675	0.1190	0.0430	0.0667	0.1283
$wR2$	0.1568	0.1865	0.1140	0.1358	0.2486
largest diff. peak/hole [e Å^{-3}]	0.853/−0.952	2.456/−2.479	0.734/−0.968	0.751/−0.773	1.166/−2.061

(101 MHz, $CDCl_3$): $\delta = 22.2$, 23.4 (CH_3), 26.6–28.9 (m, dcypb), 30.0 ($CH(CH_3)_2$), 37.6–37.8 (m, dcypb), 42.1–42.3 (m, dcypb), 78.2, 78.7 (CH, cymene), 94.8, 100.9 ppm (C, cymene); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta =$ 51.6 (s); elemental analysis (%) calcd for $C_{38}H_{66}Cl_4P_2Ru_2$: C 49.14, H 7.16; found: C 48.86, H 7.16.

[Cp*Rh(μ-Cl)$_3$Ru(dcypb)Cl] (34): The synthesis was performed analogously to that of complex **33** using [{Cp*$RhCl_2$}$_2$] (yield of isolated compound: 88%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.10$–1.50 (m, 25H; dcypb), 1.74 (s, 15H; Cp*), 1.85–2.10 (m, 11H; dcypb), 2.25–2.35 (m, 4H; dcypb), 2.45 ppm (m, 2H; dcypb); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 9.2$ (Cp*), 23.4–30.0 (m, dcypb), 37.6–37.9 (m, dcypb), 41.7–41.9 (m, dcypb), 92.8 ppm (d, $^1J_{Rh,C} = 9$ Hz, $C_5(CH_3)_5$); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta =$ 50.7 ppm (s); elemental analysis (%) calcd for $C_{38}H_{67}Cl_4P_2RhRu \cdot {}^1/_2\,CH_2Cl_2 \cdot {}^1/_2\,H_2O$: C 47.03, H 7.07; found: C 46.87, H 6.64.

[Cp*Ir(μ-Cl)$_3$Ru(dcypb)Cl] (35): The synthesis was performed analogously to that of complex **33** using [{Cp*$IrCl_2$}$_2$] (yield of isolated compound: 90%). Orange crystals were obtained by slow diffusion of pentane into a solution of **35** in benzene. ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 1.10–1.50 (m, 25H; dcypb), 1.60–2.10 (m, 11H; dcypb), 1.66 (s, 15H; Cp*), 2.20–2.40 (m, 4H; dcypb), 2.45 ppm (m, 2H; dcypb); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 9.1$ (Cp*), 21.8–29.9 (m, dcypb), 37.6–37.9 (m, dcypb), 41.7–42.0 (m, dcypb), 84.5 ppm (Cp*); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 53.1$ ppm (s); elemental analysis (%) calcd for $C_{38}H_{67}Cl_4IrP_2Ru$: C 44.70, H 6.61; found: C 44.81, H 6.60.

[(CO)$_3$Ru(μ-Cl)$_3$Ru(dppb)Cl] (37): [{$(CO)_3RuCl_2$}$_2$] (12 mg, 23 μmol) and [(dppb)ClRu(μ-Cl)$_2$(μ-OH_2)RuCl(dppb)] (28 mg, 23 μmol) in degassed CH_2Cl_2 (4 mL) were stirred for 30 min (yield of isolated compound: 87%). IR: $\tilde{\nu} = 1991$ (br, CO), 2055 (CO), 2131 cm^{-1} (CO); ^1H NMR (400 MHz, C_6D_6): $\delta = 1.13$ (m, 2H; CH_2), 1.96 (m, 4H; CH_2), 3.30 (m, 2H; CH_2), 6.99–8.07 ppm (m, 20H; Ph); ^{13}C NMR (101 MHz, C_6D_6): $\delta =$ 24.9–36.1 (m, CH_2, dppb), 132.8–138.8 (m, CH_2, dppb), 197.1 (CO), 197.4 ppm (CO); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 56.1$ ppm (s); elemental analysis (%) calcd for $C_{31}H_{28}Cl_4O_3P_2Ru_2 \cdot 2\,H_2O$: C 41.81, H 3.62; found: C 42.13, H 3.44.

[Cl(PPh$_3$)$_2$Ru(μ-Cl)$_3$Ru(dcypb)CO] (38): [{(dcypb)(CO)$RuCl_2$}$_2$] (34 mg, 26 μmol) and [$(PPh_3)_2$ClRu(μ-Cl)$_2$(μ-PhNHCHO-*O*,*O*)RuCl$(PPh_3)_2$] (40 mg, 26 μmol) in degassed CH_2Cl_2 (4 mL) were stirred for 30 min. After evaporation of the solvent under reduced pressure the product was washed with pentane and dried under vacuum (yield of isolated compound: 90%). IR: $\tilde{\nu} = 1941$ cm^{-1} (CO); ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.99–2.56 (m, 52H; dcypb), 6.99–7.15 (m, 30H; Ph); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta =$ 19.5–40.7 (m, dcypb), 126.3–136.6 (m, Ph), 201.4 ppm (t, $^2J_{C,P} = 15$ Hz; CO); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 46.4$ (d, $^2J_{P,P} =$ 36 Hz), 48.3 (d, $^2J_{P,P} = 36$ Hz), 49.2 (d, $^2J_{P,P} = 24$ Hz), 49.7 ppm (d, $^2J_{P,P} =$ 24 Hz); elemental analysis (%) calcd for $C_{65}H_{82}Cl_4OP_4Ru_2$: C 57.95, H 6.14; found: C 57.73, H 6.49.

[Cl(dppb)Ru(μ-Cl)$_3$Ru(dcypb)CO] (39): The synthesis was performed analogously to that of complex **37** using [(dppb)ClRu(μ-H_2O)-(μ-Cl)$_2$RuCl(dppb)] (yield of isolated compound: 88%). IR: $\tilde{\nu} =$ 1949 cm^{-1} (s) (CO); ^1H NMR (400 MHz, C_6D_6): $\delta = 0.80$–3.20 (m, 60H; dcypb and CH_2 of dppb), 6.50–8.20 ppm (m, 20H; dcypb); ^{13}C NMR (101 MHz, C_6D_6): $\delta =$ 24.3–44.4 (m, dcypb and CH_2 of dppb), 130.8–147.6 (m, Ph), 206.3 ppm (t, $^2J_{C,P} = 15$ Hz; CO); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 43.7$ (d, $^2J_{P,P} = 24$ Hz), 47.4 (d, $^2J_{P,P} = 24$ Hz), 53.3 (d, $^2J_{P,P} = 44$ Hz), 55.1 ppm (d, $^2J_{P,P} = 44$ Hz); elemental analysis (%) calcd for $C_{57}H_{80}Cl_4O$-$P_4Ru_2 \cdot {}^1/_2\,CH_2Cl_2$: C 53.47 H 6.32; found: C 53.59 H 5.98.

[Cl(dcypb)Ru(μ-Cl)$_3$Ru(dcypb)CO] (40): [{(dcypb)(CO)$RuCl_2$}$_2$] (26 mg, 20 μmol) and [(dcypb)N_2Ru(μ-Cl)$_3$RuCl(dcypb)] (25 mg, 20 μmol) in degassed C_6H_6 (8 mL) were stirred for 30 min under reflux. After evaporation of the solvent under reduced pressure the product was washed with pentane and dried under vacuum (yield of isolated compound: 92%). Orange crystals were obtained by slow diffusion of pentane into a solution of **40** in benzene. IR: $\tilde{\nu} = 1942$ cm^{-1} (CO); ^1H NMR (400 MHz,

Table 7. Crystallographic data for **29**, **30**, **31**, **35**, and **40**.

	29·CH_2Cl_2	**30**·C_6H_6	**31**·2.5 C_6H_6	**35**·2.5 C_6H_6	**40**·0.5 C_6H_6·0.5 C_5H_{12}
empirical formula	$C_{52}H_{56}Cl_6P_2Ru_2$	$C_{46}H_{52}Cl_4P_2Ru_2$	$C_{53}H_{58}Cl_4P_2RhRu$	$C_{53}H_{82}Cl_4IrP_2Ru$	$C_{62.5}H_{113}Cl_4OP_4Ru_2$
M [g mol^{-1}]	1157.75	1010.76	1102.71	1216.20	1348.35
crystal size [mm]	0.23×0.17×0.13	0.25×0.16×0.11	0.35×0.12×0.11	0.18×0.14×0.12	0.19×0.14×0.13
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	*Cc*	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.0300(12)	10.7446(19)	11.4513(6)	11.859(2)	13.4435(15)
b [Å]	17.2480(10)	24.885(5)	12.1954(9)	14.423(6)	13.8876(13)
c [Å]	22.9595(16)	15.985(3)	34.9857(17)	17.631(5)	18.8314(15)
α [°]	90	90	90	70.53(3)	92.278(7)
β [°]	101.182(7)	102.339(15)	92.668(4)	86.50(2)	107.829(9)
γ [°]	90	90	90	72.42(3)	93.664(8)
V [Å^3]	5062.0(7)	4175.4(13)	4880.6(5)	2707.7(15)	3333.6(5)
Z	4	4	4	2	2
ρ [g cm^{-3}]	1.519	1.608	1.501	1.492	1.343
T [K]	140(2)	140(2)	140(2)	140(2)	140(2)
absorption coefficient [mm^{-1}]	1.012	1.090	0.968	3.023	0.747
Θ range [°]	2.98–25.03	2.90–25.03	2.95–25.02	2.73–25.03	3.04–25.03
index ranges					
h	−15 to 15	−12 to 12	−12 to 12	−13 to 13	−16 to 16
k	−20 to 20	−29 to 29	−14 to 14	−17 to 17	−16 to 16
l	−27 to 27	−19 to 17	−41 to 41	−20 to 20	−22 to 18
reflections collected	14799	24440	28019	17606	19624
independent reflections	7693 ($R_{int} = 0.0420$)	7356 ($R_{int} = 0.0432$)	8158 ($R_{int} = 0.0586$)	8973 ($R_{int} = 0.0544$)	10286 ($R_{int} = 0.0877$)
absorption correction	empirical	empirical	semi-empirical	empirical	empirical
max./min. transmission	0.8770/0.5930	0.7540/0.3230	0.8921/0.8141	0.7120/0.2570	0.704/0.246
data/restraints/parameters	7693/2/559	7356/0/488	8158/0/550	8973/0/551	10286/289/745
GOF on F^2	0.948	1.086	0.961	1.088	1.151
final R indices [$I > 2\sigma(I)$]					
$R1$	0.0337	0.0451	0.0395	0.0476	0.0888
$wR2$	0.0677	0.1184	0.0830	0.1220	0.2308
R indices (all data)					
$R1$	0.0424	0.0569	0.0743	0.0621	0.1072
$wR2$	0.0706	0.1327	0.0976	0.1344	0.2392
largest diff. peak/hole [e Å^{-3}]	0.560/−0.854	0.940/−1.059	0.862/−0.752	1.938/−1.941	2.430/−1.570

C_6D_6): $\delta = 1.00$–2.15 (m, 46H; dcypb), 2.20–2.60 (m, 4H; dcypb), 2.70–2.90 (m, 2H; dcypb); ^{13}C NMR (101 MHz, C_6D_6): $\delta = 19.5$–47.6 (m, dcypb), 206.3 ppm (t, $^2J_{C,P} = 15$ Hz, CO); ^{31}P NMR (162 MHz, C_6D_6): $\delta =$ 43.3 (d, $^2J_{P,P} = 24$ Hz), 44.1 (d, $^2J_{P,P} = 39$ Hz), 50.7 (d, $^2J_{P,P} = 24$ Hz), 59.8 (d, $^2J_{P,P} = 39$ Hz); elemental analysis (%) calcd for $C_{57}H_{106}Cl_4OP_4Ru_2 \cdot H_2O$: C 53.02, H 8.27; found: C 52.79, H 8.43.

X-ray crystallography: Details of the crystals, data collection, and structure refinement are listed in Tables 5, 6, and 7. Diffraction data were collected with $Mo_{K\alpha}$ radiation on an Oxford Diffraction diffractometer with a kappa geometry, equipped with a Sapphire CCD detector (**15**, **22**, **29**, **31**, **40**) or mar345 imaging plate detector (**13**, **16**, **17**, **18**, **19**, **23**, **25**, **28**, **30**, **35**). Data reduction and cell refinement were performed with CrysAlis RED 1.6.9.[30] Absorption correction was applied to all data sets. For **31** a semiempirical method (MULTI-SCAN)[31] was employed, whereas an empirical method (DIFABS)[32] was used for the other structures. Structures were solved with ab initio direct methods.[33] All structures were refined by full-matrix least-squares methods on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the riding model with $U_{iso} = aU_{eq}(C)$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others, and C is the parent carbon atom). Space group determination, structure refinement, and geometrical calculations for all structures were performed with the SHELXTL software package, release 5.1.[34] Graphical representations of the molecular structures in the crystal were generated with the program ORTEP.[35] CCDC 214256–214270 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/const/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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