Syntheses and Structures of Homo- and Heterobimetallic Complexes Containing a (Cyclopentadienone)rhodium(I) Fragment

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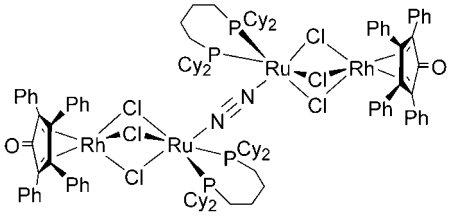
Dedicated to Professor *André E. Merbach* on the occasion of his 65th birthday

The reaction of $[RhCl(\eta^4\text{-}Ph_2R_2C_4CO)]_2$ (R = Ph, 2-naphthyl) with the dimeric complexes $[RuCl_2(p\text{-cymene})]_2$ *p*-cymene = 1-methyl-4-(1-methylethyl)benzene, $[RuCl_2(1,3,5\text{-}Et_3C_6H_3)]_2$, $[MCl_2(Cp^*)]_2$ (M = Rh, Ir; Cp* = 1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl), $[RuCl_2(CO)_3]_2$, $[RuCl_2(dcypb)(CO)]_2$ (dcypb = butane-1,4-diylbis[dicyclohexylphosphine]), [(dppb)ClRu(μ-Cl)$_2$(μ-OH$_2$)RuCl(dppb)] (dppb = butane-1,4-diylbis[diphenylphosphine]), and [(dcypb)(N$_2$)Ru(μ-Cl)$_3$RuCl(dcypb)] was investigated. In all cases, mixed, chloro-bridged complexes were formed in quantitative yield (see **5**–**8**, **9**–**16**, **18**, **19**, **21**, and **22**). The six new complexes **5**, **8**, **9**, **13**, **15**, and **22** were characterized by single-crystal X-ray analysis (*Figs. 1–3*).

1. Introduction. – Complexes in which a metal fragment A is connected by two or three halogeno bridges to a different metal fragment B [1] have emerged as a promising new class of catalysts. They have been used for olefin metathesis reactions [2], for *Oppenauer*-type oxidations [3], for atom-transfer radical additions [4], and for atom-transfer radical polymerizations [5]. Two of the recently described catalysts are **1** and **2**. Complex **1** was identified as a potent and robust catalyst for the addition of CCl_4 to olefins [4b], and complex **2** can be used to oxidize primary and secondary alcohols by using acetone as the solvent and oxidation agent [3a]. Since both complexes contain a $Rh^I(\eta^4\text{-}Ph_4C_4CO)$ fragment, we were interested to develop a general synthetic route which provides access to homo- and heterobimetallic complexes containing this fragment. In the following, the results of these studies are reported.



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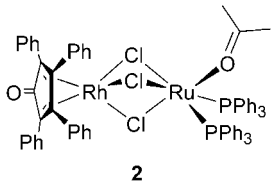

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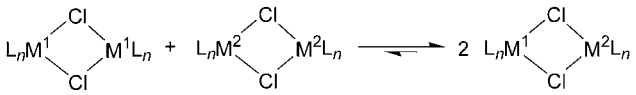
2. Results and Discussion. – For the synthesis of mixed complexes with two halogeno bridges, metathesis reactions with the corresponding homobimetallic complexes were found to be very useful (*Scheme 1*). Reactions of this kind were first

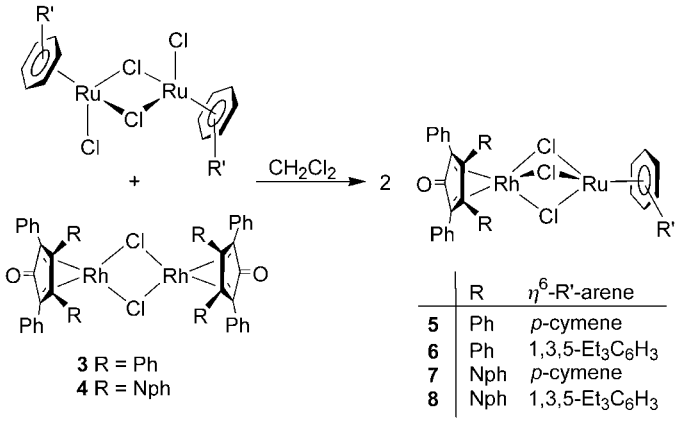
described by *Stone* and co-workers [6] and *Masters* and co-workers [7], but more-detailed investigations which demonstrate the potential of this method have been published only recently [8][9].

Scheme 1. *Metathesis Reaction for the Synthesis of Mixed Chloro-Bridged Complexes*



To investigate whether a metathesis reaction of this kind is suited to synthesize mixed complexes containing a $Rh^I(\eta^4\text{-}Ph_2R_2C_4CO)$ fragment and a Ru^{II}(arene) fragment, we first carried out reactions between the dimeric complexes **3** and **4** and the complexes $[RuCl_2(p\text{-cymene})]_2$ (*p*-cymene = 1-methyl-4-(1-methylethyl)benzene) and $[RuCl_2(1,3,5\text{-}Et_3C_6H_3)]_2$ (*Scheme 2*). *In situ* ^{1}H-NMR experiments ($CDCl_3$) showed in all cases the fast and quantitative formation of a new complex, *i.e.*, of **5**–**8**.

Scheme 2. *Synthesis of the Heterobimetallic Rh/Ru Complexes* **5**–**8**. Nph = 2-naphthyl.



	R	η^6-R'-arene
5	Ph	*p*-cymene
6	Ph	1,3,5-$Et_3C_6H_3$
7	Nph	*p*-cymene
8	Nph	1,3,5-$Et_3C_6H_3$

The formation of heterobimetallic Rh^I/Ru^{II} complexes was confirmed by the results of single-crystal X-ray analyses of **5** and **8** (*Fig. 1*). Contrary to what is found for the two starting materials, the products display three and not two chloro bridges, resulting in a five-coordinated, electronically saturated configuration at the Rh-center. It should be noted that (cyclopentadienone)rhodium complexes have a tendency to form piano-stool-type complexes [10], a fact that is also evident from the molecular structures of **1** and **2**. The formation of this additional chloro bridge probably contributes to the driving force for the reaction. The M–Cl and the M–C bond distances are very similar for **5** and **8** (*Table 1*). With 2.412(3) Å (**5**) and 2.434(5) Å (**8**), the C-atoms of the carbonyl group are further apart from the Rh-atom than the olefinic C-atoms, indicating a η^4-coordination of the cyclopentadienone ligands. The phenyl and the 2-naphthyl groups adopt a 'propeller' conformation with angles between 27.3° and 54.3° between their normals and the normal to the mean plane through atoms C(2), C(3), C(4), and C(5).

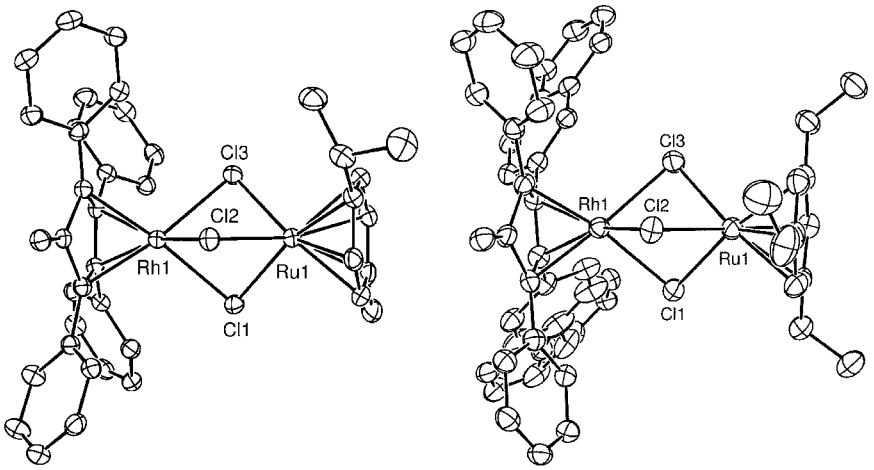
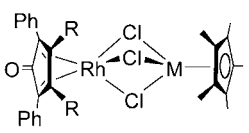
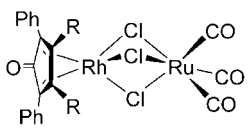


Fig. 1. *ORTEP* [11] *Representation of the molecular structure of* **5** *and* **8** *in the crystal.* The H-atoms are not shown for clarity.

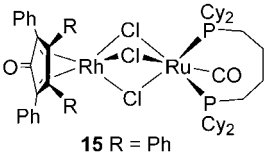
The homodimeric complexes $[MCl_2(Cp^*)]_2$ (M = Rh, Ir; Cp* = 1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl), $[RuCl_2(CO)_3]_2$, and $[RuCl_2(dcypb)(CO)]_2$ (dcypb = butane-1,4-diylbis[dicyclohexylphosphine] react with the rhodium compounds **3** and **4** in a similar fashion as it was found for the $[RuCl_2(arene)]_2$ complexes. This was evidenced by the synthesis of the mixed complexes **9**–**16**, which were obtained in excellent yields in chloro bridge metatheses reactions.



	R	M
9	Ph	Rh
10	Ph	Ir
11	Nph	Rh
12	Nph	Ir



13 R = Ph
14 R = Nph

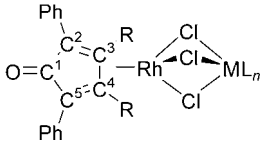


15 R = Ph
16 R = Nph

A single-crystal X-ray analysis was carried out for one complex of each class. The geometries that were determined resemble those of **5** and **8**: a η^4-bound (cyclopentadienone)rhodium fragment is connected *via* three chloro bridges to a $Rh^{III}(Cp^*)$ fragment (see **9**), a $Ru^{II}(CO)_3$ fragment (see **13**), or a Ru^{II}(dcypb)(CO) fragment (see **15**) (*Fig. 2*). A summary of selected bond lengths is given in *Table 1.*

The bis(phosphine)ruthenium catalysts **1** and **2** were obtained by reaction of **3** with the dinitrogen complex **17** [4b] or the acetone complex $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(acetone)(PPh_3)_2]$ [3a]. In both complexes, a $RuCl_2$(phosphine)$_2$ fragment is stabilized by coordination to a $RhCl(\eta^4\text{-}Ph_4C_4CO)$ fragment, but for complex **2**, the electronic

Table 1. *Selected Bond Lengths* [Å] *for the Complexes* **5**, **8**, **9**, **13**, **15**, *and* **22**

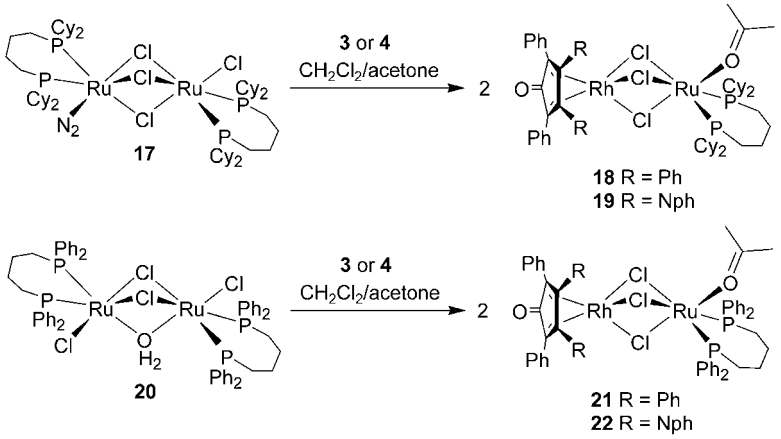


	Rh–Cl[a])	M–Cl[a])	Rh–C(1)	Rh–C(2)	Rh–C(3)	Rh–C(4)	Rh–C(5)
5	2.500	2.438	2.412(3)	2.156(4)	2.110(4)	2.109(4)	2.143(4)
8	2.483	2.433	2.434(5)	2.123(5)	2.114(5)	2.097(5)	2.138(5)
9	2.486	2.446	2.401(3)	2.147(3)	2.099(3)	2.106(3)	2.160(3)
13	2.523	2.417	2.424(5)	2.145(5)	2.116(4)	2.108(4)	2.137(5)
15	2.474	2.496	2.371(8)	2.143(7)	2.113(7)	2.099(7)	2.120(6)
22	2.488	2.470	2.420(5)	2.159(5)	2.101(5)	2.126(5)	2.127(4)

[a]) Averaged values are given.

saturation of the Ru-center is achieved by coordination to a weakly bound acetone ligand and not by dimerization *via* a dinitrogen bridge. The dinitrogen bridge, however, can be replaced by an acetone ligand. This was confirmed by the synthesis of the heterobimetallic complexes **18** and **19** in CH_2Cl_2/acetone 9 : 1 as the solvent (*Scheme 3*). Furthermore, it is possible to make the analogous dppb complexes **21** and **22** by using the aqua complex **20** instead of the dinitrogen complex **17** (dppb = butane-1,4-diylbis[diphenylphosphine].

Scheme 3. *Synthesis of the Heterobimetallic Rh/Ru Complexes* **18**, **19**, **21**, *and* **22**



In solution, the presence of excess acetone is crucial for the stability of the dppb complexes **21** and **22**. When they were dissolved in plain $CDCl_3$ or C_6D_6, several new peaks were immediately observed by ^{31}P-NMR. In the presence of 10% (D_6)acetone, however, the complexes were stable, as evidenced by a single peak in the ^{31}P-NMR spectrum at δ *ca.* 47. This behavior is in contrast to what was found for the dcypb complexes **18** and **19**, for which no immediate decomposition in C_6D_6 was observed.

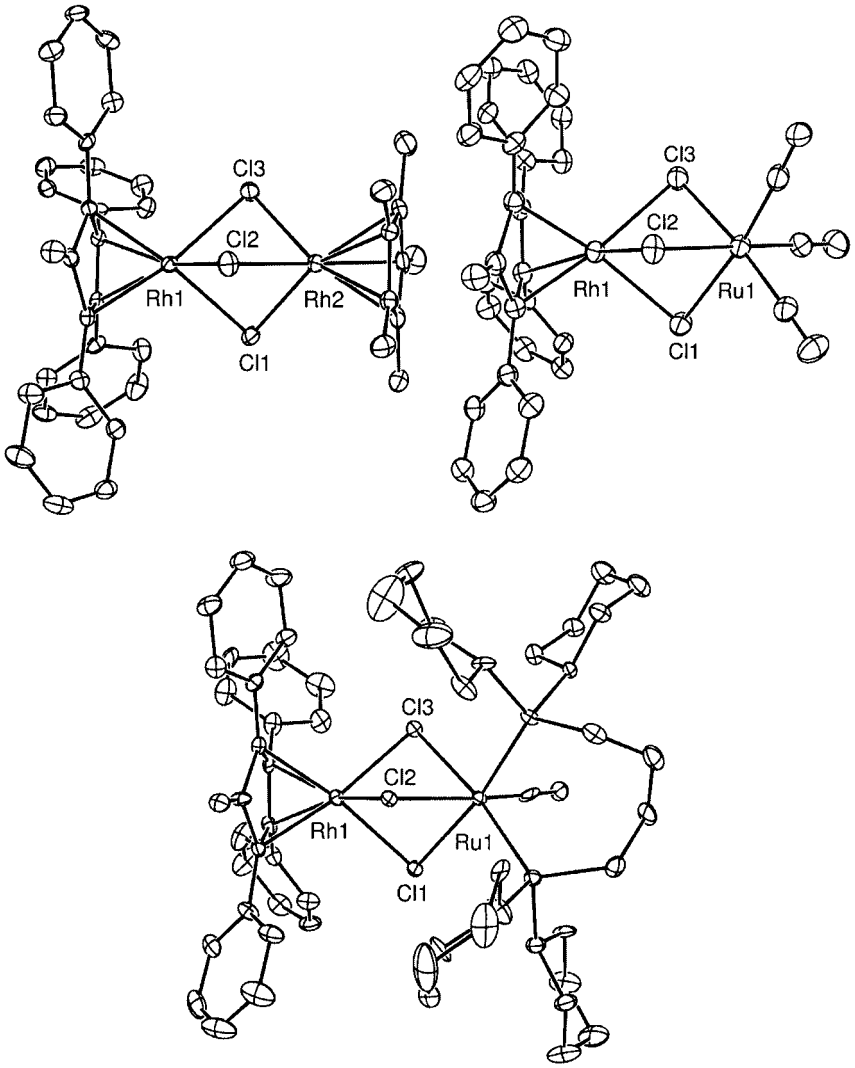


Fig. 2. *ORTEP* [11] *Representation of the molecular structure of* **9**, **13**, *and* **15** *in the crystal.* The H-atoms are not shown for clarity.

This difference could be explained by the reduced steric demand of the dppb ligand as compared to the dcypb ligand, which makes the labile acetone ligand more accessible.

For complex **22**, we were able to obtain single crystals, which were suited for crystallographic analysis. As expected, its structure is similar to that of complex **2**: a $RuCl_2$(dppb) fragment is connected *via* three chloro bridges to a RhCl[η^4-$Ph_2(Nph)_2C_4CO$] fragment with the remaining coordination site at the Ru-atom being occupied by an acetone ligand (*Fig. 3*, *Table 1*). The resulting octahedral Ru-center is

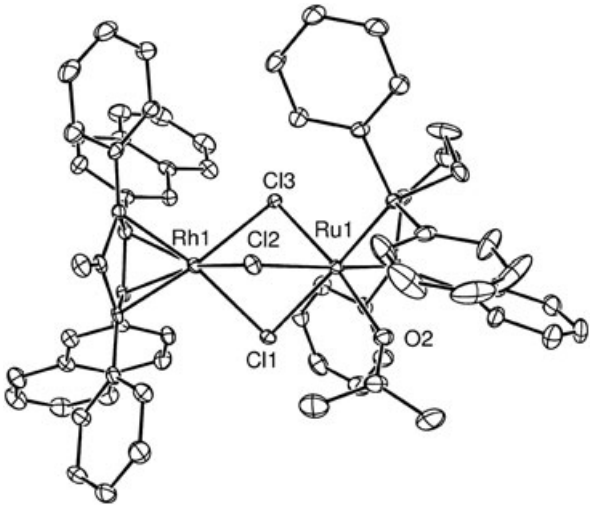
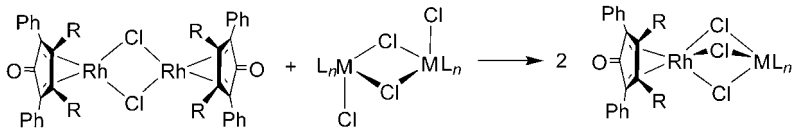


Fig. 3. *ORTEP* [11] *Representation of the molecular structure of* **22** *in the crystal.* The H-atoms are not shown for clarity.

slightly distorted as a result of the two sterically demanding phosphine ligands (P(1)–Ru(1)–P(2) = 93.50°).

3. Conclusions. – Mixed, chloro-bridged complexes containing a $Rh^{I}(\eta^4\text{-}Ph_2R_2C_4CO)$ fragment were obtained in metathesis reactions of the homodimeric complexes **3** or **4** with complexes of the general formula $[L_nClM(\mu\text{-}Cl)_2MClL_n]$ (*Scheme 4*) or with the bis[phosphine]ruthenium complexes **17** and **20**. These reactions give access to complexes containing various organometallic fragments such as $RuCl_2$(arene), $RuCl_2(CO)_3$, $RuCl_2$(dcypb)(CO), $RuCl_2$(dcypb)(acetone), $RuCl_2$(dppb)-(acetone), $RhCl_2$(Cp*), and $IrCl_2$(Cp*). Crystallographic data revealed that the mixed complexes all contain a triple chloro bridge. The additional M–Cl interactions found for the products are likely to be responsible for the fact that the metathesis reaction is shifted completely towards the mixed complexes (for less-biased chloro bridge metathesis reactions, see [7][9a]). All reactions described above were completed within minutes and proceeded with excellent yields. The latter point is of interest for applications in homogeneous catalysis because the mixed complexes can be prepared *in situ* prior to the reaction.

Scheme 4. *General Synthesis of Mixed, Chloro-Bridged Complexes Containing a* $Rh^{I}(\eta^4\text{-}Ph_2R_2C_4CO)$ *Fragment*



(R = Ph, Nph)

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Experimental Part

General. The synthesis of all complexes was performed under dry N_2 or Ar by using standard *Schlenk* techniques. The complexes $[RhCl(\eta^4\text{-}Ph_4C_4CO)]_2$ (**3**) [12], $[RuCl_2(p\text{-cymene})]_2$ [13], $[RuCl_2(1,3,5\text{-}Et_3C_6H_3)]_2$ [14], $[RhCl_2(Cp^*)]_2$ [15], $[IrCl_2(Cp^*)]_2$ [15], $[RuCl_2(dcypb)(CO)]_2$ [16], $[(dcypb)(N_2)Ru(\mu\text{-}Cl)_3RuCl(dcypb)]$ (**17**) [17], and $[(dppb)ClRu(\mu\text{-}Cl)_2(\mu\text{-}OH_2)RuCl(dppb)]$ (**20**) [18] were prepared according to literature procedures. $[RuCl_2(CO)_3]_2$ and 1,4-bis(diphenylphosphino)butane (= butane-1,4-diylbis[diphenylphosphine]; dppb) were purchased from *Acros*, and 1,4-bis(dicyclohexylphosphino)butane (= butane-1,4-diylbis[dicyclohexylphosphine]; dcypb) was purchased from *Aldrich*. CC = Column chromatography. IR spectra: ν in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker Avance-DPX-400* or *Bruker Advance-200* spectrometer; residual protonated solvents as internal standards; δ in ppm, J in Hz. All spectra were recorded at r.t.

Di-μ-chlorobis[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]dirhodium ([RhCl{η⁴-Ph₂(Nph)₂C₄CO}]₂; **4**). A soln. of 3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one (1.45 g, 3 mmol) and $[RhCl(C_2H_4)]_2$ (0.50 g, 1.25 mmol) in THF (50 ml) was heated under reflux for 24 h. The soln. was concentrated to 5 ml and then subjected to CC (silica gel, $CHCl_3$/MeOH 98 : 2): **4** (0.85 g, 55%). Dark red powder. IR: 1648 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.03 – 7.65 (*m*, 48 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 68.36 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 94.31 (*d*, ^1J(Rh,C) = 12, *C*−Nph); 125.83 – 132.77 (*m*, Ph, Nph); 165.31 (CO). Anal. calc. for $C_{74}H_{48}Cl_2O_2Rh_2 \cdot 1/5\ CHCl_3$: C 70.19, H 3.83; found: C 70.09, H 4.18.

Tri-μ-chloro[η⁶-1-methyl-4-(1-methylethyl)benzene][[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}ruthenium [(p-cymene)Ru(μ-Cl)₃Rh(η⁴-Ph₄C₄CO)]; **5**). $[RuCl_2(p\text{-cymene})]_2$ (65 mg, 106 μmol) and $[RhCl_2(\eta^4\text{-}Ph_4C_4CO)]_2$ (111 mg, 106 μmol) in degassed CH_2Cl_2 (8 ml) were stirred for 30 min. After evaporation, the product was washed with pentane and dried under vacuum: **5** (92%). Red crystals were obtained by slow diffusion of pentane into a soln. of **5** in CH_2Cl_2. IR: 1647 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.31 (*d*, ^3J = 7, *Me*$_2$CH); 2.19 (*s*, Me); 2.86 (*sept.*, ^3J = 7, Me$_2$C*H*); 5.27 (*d*, ^3J = 6, 2 arom. H (cym.)); 5.53 (*d*, ^3J = 6, 2 arom. H (cym.)); 7.06 – 7.67 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 18.93, 22.22 (Me); 31.33 (Me$_2$*C*H); 68.07 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 77.75, 80.29 (CH (cym.)); 93.89 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 96.88, 100.24 (C (cym.)); 127.21 – 131.67 (Ph); 165.50 (CO). Anal. calc. for $C_{39}H_{34}Cl_3ORhRu$: C 56.50, H 4.13; found C 56.82, H 4.11.

Tri-μ-chloro{[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}(η⁶-1,3,5-triethylbenzene)-ruthenium ([(1,3,5-Et₃C₆H₃)Ru(μ-Cl)₃Rh(η⁴-Ph₄C₄CO)]; **6**). As described for **5**, with $[RuCl_2(1,3,5\text{-}Et_3C_6H_3)]_2$ and $[RhCl(\eta^4\text{-}Ph_4C_4CO)]_2$: **6** (95%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **6** in benzene. IR: 1647 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.26 (*t*, ^3J = 7, 3 *Me*CH$_2$); 2.58 (*q*, ^3J = 7, 3 MeC*H*$_2$); 5.11 (*s*, C_6H_3); 7.06 – 7.69 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 13.63 (*Me*CH$_2$); 26.41 (MeCH$_2$); 68.00 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 73.29 (arom. CH); 93.71 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 103.38 (arom. C); 127.10 – 131.74 (Ph); 165.28 (CO). Anal. calc. for $C_{41}H_{38}Cl_3ORhRu$: C 57.46, H 4.47; found: C 57.65, H 4.33.

Tri-μ-chloro{[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}[η⁶-1-methyl-4-(1-methylethyl)benzene]ruthenium [(p-cymene)Ru(μ-Cl)₃Rh{η⁴-Ph₂(Nph)₂C₄CO}]; **7**). As described for **5**, with $[RuCl_2(p\text{-cymene})]_2$ and $[RhCl\{\eta^4\text{-}Ph_2(Nph)_2C_4CO\}]_2$: **7** (94%). IR: 1636 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.31 (*d*, ^3J = 7, *Me*$_2$CH); 2.18 (*s*, Me); 2.86 (*sept.*, ^3J = 7, Me$_2$C*H*); 5.28 (*d*, ^3J = 6, 2 arom. H (cym.)); 5.54 (*d*, ^3J = 6, 2 arom. H (cym.); 7.07 – 7.65 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 18.95, 22.22 (Me); 31.32 (Me$_2$*C*H); 68.51 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 77.67, 80.29 (CH (cym.)); 93.57 (*d*, ^1J(Rh,C) = 12, *C*−Nph); 96.91, 100.13 (C (cym.)); 125.95 – 132.77 (Ph, Nph); 165.55 (CO). Anal. calc. for $C_{47}H_{38}Cl_3ORhRu$: C 60.76, H 4.12; found: C 60.99, H 4.43.

Tri-μ-chloro{[2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}(η⁶-1,3,5-triethylbenzene)ruthenium ([(1,3,5-Et₃C₆H₃)Ru(μ-Cl)₃Rh{η⁴-Ph₂(Nph)₂C₄CO}]; **8**). As described for **5**, with $[RuCl_2(1,3,5\text{-}Et_3C_6H_3)]_2$ and $[RhCl\{\eta^4\text{-}Ph_2(Nph)_2C_4CO\}]_2$: **8** (95%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **8** in CH_2Cl_2. IR: 1661 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.26 (*t*, ^3J = 7, 3 *Me*CH$_2$); 2.59 (*q*, ^3J = 7, MeC*H*$_2$); 5.12 (*s*, C_6H_3); 7.10 – 7.48 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 13.72 (*Me*CH$_2$); 26.45 (MeCH$_2$); 68.46 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 73.14 (arom. CH); 93.39 (*d*, ^1J(Rh,C) = 12, *C*−Nph); 103.53 (arom. C); 125.88 – 132.74 (Ph, Nph); 165.32 (CO). Anal. calc. for $C_{49}H_{42}Cl_3ORhRu$: C 61.48, H 4.42; found: C 61.17, H 4.34.

Tri-μ-chloro(η⁵-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]dirhodium ([(Cp)Rh(μ-Cl)₃Rh(η⁴-Ph₄C₄CO)]*; **9**). As described for **5**, with $[RhCl_2(Cp^*)]_2$ and

[RhCl(η^4-Ph_4C_4CO)]$_2$: **9** (95%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **9** in CH_2Cl_2. IR: 1645 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.66 (*s*, 15 H, Cp*); 7.08–7.75 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 9.40 (Cp*); 67.90 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 93.47 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 94.29 (*d*, ^1J(Rh,C) = 9, Me_5C_5); 127.08–131.85 (Ph); 165.15 (CO). Anal. calc. for $C_{39}H_{35}Cl_3ORh_2$: C 56.31, H 4.24; found: C 56.85, H 4.08.

Tri-μ-chloro(η^5-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl){[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}iridium ([(Cp)Ir(μ-Cl)$_3$Rh(η^4-Ph$_4$C$_4$CO)]*; **10**). As described for **5**, with [$IrCl_2$(Cp*)]$_2$ and [RhCl(η^4-Ph_4C_4CO)]$_2$: **10** (94%). IR: 1650 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.62 (*s*, 15 H, Cp*); 7.09–7.76 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 9.34 (Cp*); 68.41 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 85.66 (*s*, Me_5C_5); 93.58 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 127.24–131.57 (Ph); 164.99 (CO). Anal. calc. for $C_{39}H_{35}Cl_3IrORh$: C 50.85, H 3.83; found: C 50.92, H 3.93.

Tri-μ-chloro[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one](η^5-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)dirhodium ([(Cp)Rh(μ-Cl)$_3$Rh{η^4-Ph$_2$(Nph)$_2$C$_4$CO}]*; **11**). As described for **5**, with [$RhCl_2$(Cp*)]$_2$ and [RhCl{η^4-$Ph_2(Nph)_2C_4CO$}]$_2$: **11** (95%). IR: 1647 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.67 (*s*, 15 H, Cp*); 7.11–7.80 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 9.42 (Cp*); 68.36 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 93.20 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 94.31 (*d*, ^1J(Rh,C) = 9, Me_5C_5); 125.83–132.77 (Ph, Nph); 165.31 (CO). Anal. calc. for $C_{47}H_{39}Cl_3ORh_2$: C 60.57, H 4.22; found: C 60.96, H 4.53.

Tri-μ-chloro{[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}(η^5-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)iridium ([(Cp)Ir(μ-Cl)$_3$Rh{η^4-Ph$_2$(Nph)$_2$C$_4$CO)]*; **12**). As described for **5**, with [$IrCl_2$(Cp*)]$_2$ and [RhCl{η^4-$Ph_2(Nph)_2C_4CO$}]$_2$: **12** (94%). IR: 1650 (CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.64 (*s*, 15 H, Cp*); 7.10–7.78 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 9.37 (Cp*); 68.89 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 85.69 (*s*, Me_5C_5); 93.35 (*d*, ^1J(Rh,C) = 12, *C*–Nph); 125.94–132.83 (Ph, Nph); 165.17 (CO). Anal. calc. for $C_{47}H_{39}Cl_3OIrRh$: C 55.27, H 3.85; found: C 55.43, H 3.47.

Tricarbonyltri-μ-chloro{[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}ruthenium ([(CO)$_3$Ru(μ-Cl)$_3$Rh(η^4-Ph$_4$C$_4$CO)]; **13**). As described for **5**, with [$RuCl_2(CO)_3$]$_2$ and [RhCl(η^4-Ph_4C_4CO)]$_2$: **13** (93%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **13** in CH_2Cl_2. IR: 1645 (CO), 2003 (M–CO), 2063 (M–CO), 2140 (M–CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.14–7.73 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 69.31 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 94.80 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 127.97–131.32 (Ph); 165.18 (CO); 182.97 (CO–Ru). Anal. calc. for $C_{32}H_{20}Cl_3O_4RhRu$: C 49.35, H 2.59; found: C 49.34, H 2.86.

Tricarbonyltri-μ-chloro{[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}ruthenium ([(CO)$_3$Ru(μ-Cl)$_3$Rh{η^4-Ph$_2$(Nph)$_2$C$_4$CO)]; **14**). As described for **5**, with [$RuCl_2(CO)_3$]$_2$ and [RhCl{η^4-$Ph_2(Nph)_2C_4CO$}]$_2$: **14** (91%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **14** in CH_2Cl_2. IR: 1645 (CO), 2008 (M–CO), 2061 (M–CO), 2138 (M–CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.18–7.77 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 69.73 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 94.61 (*d*, ^1J(Rh,C) = 12, *C*–Nph); 126.36–133.00 (Ph, Nph); 165.38 (CO); 182.98 (M–CO). Anal. calc. for $C_{40}H_{24}Cl_3O_4RhRu$: C 54.66, H 2.75; found: C 54.28, H 2.25.

[Butane-1,4-diylbis[dicyclohexylphosphine-κP]]carbonyltri-μ-chloro{[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}rhutenium ([(dcypb)(CO)Ru(μ-Cl)$_3$Rh(η^4-Ph$_4$C$_4$CO)]; **15**). As described for **5**, with [$RuCl_2$(dcypb)(CO)]$_2$ and [RhCl(η^4-Ph_4C_4CO)]$_2$: **15** (90%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **15** in CH_2Cl_2. IR: 1643 (CO), 1948 (br., M–CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.18–2.11 (*m*, 52 H, dcypb); 7.08–7.83 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, $CDCl_3$): 20.70–40.05 (*m*, dcypb); 67.27 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 93.25 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 126.68–132.42 (Ph); 164.81 (CO); 201.56 (*t*, ^2J(C,P) = 15, CO). ^{31}P-NMR (162 MHz, $CDCl_3$): 45.99 (*s*). Anal. calc. for $C_{58}H_{72}Cl_3O_2P_2RhRu$: C 59.36, H 6.18; found: C 58.97, H 6.24.

[Butane-1,4-diylbis[dicyclohexylphosphine-κP]]carbonyltri-μ-chloro{[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}ruthenium ([(dcypb)(CO)Ru(μ-Cl)$_3$Rh{η^4-Ph$_2$(Nph)$_2$C$_4$CO)]; **16**). As described for **5**, with [$RuCl_2$(dcypb)(CO)]$_2$ and [RhCl{η^4-$Ph_2(Nph)_2C_4CO$}]$_2$: **16** (90%). IR: 1638 (CO), 1949 (br., M–CO). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.22–2.19 (*m*, 52 H, dcypb); 7.15–8.06 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, $CDCl_3$): 20.74–25.94 (*m*, dcypb); 26.18–29.09 (*m*, dcypb); 37.20–40.75 (*m*, dcypb); 67.68 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 92.91 (*d*, ^1J(Rh,C) = 12, *C*–Nph); 125.69–132.61 (Ph, Nph); 164.98 (CO); 201.55 (*t*, ^2J(C,P) = 15, M–CO). ^{31}P-NMR (162 MHz, $CDCl_3$): 46.31 (*s*). Anal. calc. for $C_{66}H_{76}Cl_3O_2P_2RhRu$: C 62.24, H 6.01; found: C 62.24, H 6.08.

[Butane-1,4-diylbis[dicyclohexylphosphine-κP]]tri-μ-chloro(propan-2-one){[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}ruthenium ([(dcypb)(Me$_2$CO)Ru(μ-Cl)$_3$Rh(η^4-Ph$_4$C$_4$CO)]; **18**). A soln. of [(dcypb)(N_2)Ru(μ-Cl)$_3$RuCl(dcypb)] (70 mg, 55 μmol) and [RhCl(η^4-Ph_4C_4CO)]$_2$ (58 mg, 55 μmol) in CH_2Cl_2/Me_2CO 9:1 (10 ml) was stirred for 30 min. After evaporation, the product was washed with pentane and

dried under vacuum: **18** (90%). IR: 1646 (br., Me_2CO). ^{1}H-NMR (400 MHz, (D_6)acetone): 1.21–2.24 (*m*, 52 H, dcypb); 7.07–7.90 (*m*, 20 H, Ph). ^{13}C-NMR (101 MHz, (D_6)acetone): 23.42–25.93 (*m*, dcypb); 28.79–30.44 (*m*, dcypb); 39.84–43.47 (*m*, dcypb); 69.23 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 95.46 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 129.05–134.63 (*m*, Ph); 168.77 (CO). ^{31}P-NMR (162 MHz, (D_6)acetone): 42.88 (*s*). Anal. calc. for $C_{60}H_{78}Cl_3O_2P_2RhRu \cdot 3/2\ H_2O$: C 58.56, H 6.63; found: C 58.24, H 6.99.

[Butane-1,4-diylbis[dicyclohexylphosphine-κP]]tri-μ-chloro{[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}(propan-2-one)ruthenium ([(dcypb)(Me$_2$CO)Ru(μ-Cl)$_3$Rh{η^4-Ph$_2$(Nph)$_2$C$_4$CO}]; **19**). As described for **18**, with [(dcypb)(N_2)Ru(μ-Cl)$_3$RuCl(dcypb)] and [RhCl{η^4-$Ph_2(Nph)_2C_4CO$)]$_2$: **19** (95%). IR: 1646 (br., CO, Me_2CO). ^{1}H-NMR (400 MHz, (D_6)acetone): 1.21–2.26 (*m*, 52 H, dcypb); 7.09–7.92 (*m*, 24 H, Ph, Nph). ^{13}C-NMR (101 MHz, (D_6)acetone): 21.39–28.68 (*m*, dcypb); 37.78–39.29 (*m*, dcypb); 40.36–41.55 (*m*, dcypb); 67.67 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 94.15 (*d*, ^1J(Rh,C) = 12, *C*−Nph); 126.73–133.37 (*m*, Ph, Nph); 166.87 (CO). ^{31}P-NMR (162 MHz, (D_6)acetone): 43.17 (*s*). Anal. calc. for $C_{68}H_{82}Cl_3O_2P_2RhRu \cdot 1/2\ H_2O$: C 62.22, H 6.37; found: C 62.08, H 6.33.

[Butane-1,4-diylbis[diphenylphosphine-κP]]tri-μ-chloro(propan-2-one){[(2,3,4,5-η)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one]rhodium}ruthenium ([(dppb)(Me$_2$CO)Ru(μ-Cl)$_3$Rh(η^4-Ph$_4$C$_4$CO)]; **21**). As described for **18**, with [(dppb)ClRu(μ-Cl)$_2$(μ-OH_2)RuCl(dppb)] and [RhCl(η^4-Ph_4C_4CO)]$_2$: **21** (97%). IR: 1644 (br., CO, Me_2CO). ^{1}H-NMR (400 MHz, (D_6)acetone): 1.57 (*m*, CH_2); 1.81 (*m*, CH_2); 2.53 (*m*, CH_2); 2.86 (*m*, CH_2); 7.14–7.92 (*m*, 40 H, Ph). ^{13}C-NMR (101 MHz, (D_6)acetone): 23.71 (*s*, CH_2 (dppb)); 31.77–32.08 (*m*, CH_2 (dppb)); 66.82 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 93.83 (*d*, ^1J(Rh,C) = 12, *C*−Ph); 127.16–139.94 (*m*, Ph); 166.73 (CO); 227.10 (Me_2CO). ^{31}P-NMR (162 MHz, (D_6)acetone): 47.59 (*s*). Anal. calc. for $C_{60}H_{54}Cl_3O_2P_2RhRu \cdot 2\ H_2O$: C 59.29, H 4.81; found: C 59.09, H 4.95.

[Butane-1,4-diylbisdiphenylphosphine-κP]]tri-μ-chloro{[(2,3,4,5-η)-3,4-dinaphthalen-2-yl-2,5-diphenylcyclopenta-2,4-dien-1-one]rhodium}(propan-2-one)ruthenium ([(dppb)(Me$_2$CO)Ru(μ-Cl)$_3$Rh{η^4-Ph$_2$(Nph)$_2$-

Table 2. *Crystallographic Data for the Complexes* **5** *and* **8**

	5	**8** · CH_2Cl_2
Empirical formula	$C_{39}H_{34}Cl_3ORhRu$	$C_{50}H_{44}Cl_5ORhRu$
Molar mass [g mol^{-1}]	828.99	1042.08
Crystal size [mm]	0.13 × 0.12 × 0.11	0.15 × 0.14 × 0.12
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.1058(9)	12.458(3)
b [Å]	11.771(3)	13.679(3)
c [Å]	13.387(3)	15.190(2)
α [°]	78.40(2)	115.542(18)
β [°]	81.021(12)	105.835(17)
γ [°]	88.492(12)	97.518(19)
Volume [Å^3]	1693.2(6)	2152.9(8)
Z	2	2
Density [g cm^{-3}]	1.626	1.608
Temperature [K]	140(2)	140(2)
Absorption coefficient [nm^{-1}]	1.201	1.083
Θ range [°]	2.97–25.03	3.01–25.03
Index ranges	−12 → 11, −14 → 14, −15 → 15	−14 → 14, −16 → 16, −17 → 18
Reflections collected	10966	14025
Independent reflections	5597 (R_{int} = 0.0295)	7141 (R_{int} = 0.0366)
Absorption correction	semi-empirical	semi-empirical
Max. and min. transmission	0.9168 and 0.8131	0.9468 and 0.8180
Data/restraints/parameters	5597/0/407	7141/6/581
Goodness-of-fit on F^2	1.119	1.136
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0354, wR_2 = 0.0966	R_1 = 0.0479, wR_2 = 0.1331
R indices (all data)	R_1 = 0.0428, wR_2 = 0.1047	R_1 = 0.0560, wR_2 = 0.1427
Largest diff. peak/hole [eÅ^{-3}]	0.606/−0.659	1.504/−0.719

C_4CO)]; **22**). As described for **18**, with [(dppb)ClRu(μ-Cl)$_2$(μ-OH$_2$)RuCl(dppb)] and [RhCl{η^4-Ph$_2$(Nph)$_2$C$_4$CO)]$_2$: **22** (90%). Orange crystals were obtained by slow diffusion of pentane into a soln. of **22** in CH_2Cl_2/acetone. IR: 1643 (br., CO, Me_2CO). ^{1}H-NMR (400 MHz, (D_6)acetone): 1.53 (*m*, CH_2); 1.79 (*m*, CH_2); 2.53 (*m*, CH_2); 2.91 (*m*, CH_2); 7.13–8.25 (*m*, 44 H, Ph, Nph). ^{13}C-NMR (101 MHz, (D_6)acetone): 23.66 (*s*, CH_2 (dppb)); 31.71–32.02 (*m*, CH_2 (dppb)); 67.22 (*d*, ^1J(Rh,C) = 12, *C*–Ph); 93.89 (*d*, ^1J(Rh,C) = 12, *C*–Nph); 126.76–133.93 (*m*, Ph, Nph); 166.87 (CO). ^{31}P-NMR (162 MHz, (D_6)acetone): 47.64 (*s*). Anal. calc. for $C_{68}H_{58}Cl_3O_2P_2RhRu$: C 63.83, H 4.57; found: C 63.32, H 4.25.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement are listed in the *Tables 2–4*. Diffraction data were collected by using the MoK_α radiation on different equipment: *Oxford-Diffraction* diffractometer with a kappa geometry and equipped with a *Sapphire-CCD* detector (for **9**, **15**, and **22**) or a *mar345-imaging-plate* detector (for **5**, **8**, and **13**). Data reduction and cell refinement were performed with CrysAlis RED 1.6.9 [19]. Absorption correction was applied to all data sets by using a semi-empirical method (MULTI-SCAN) [20]. Structure solutions were determined with *ab initio* direct methods [21]. All structures were refined by full-matrix least-squares on F^2 with all non-H-atoms anisotropically defined. The H-atoms were placed in calculated positions by using the 'riding model' with $U_{iso} = a \cdot U_{eq}$(C) (where *a* is 1.5 for Me H-atoms and 1.2 for others, C is the parent C-atom). Space-group determination, structure refinement, and geometrical calculations were carried out with all structures by the SHELXTL software package, release 5.1 [22]. CCDC-254057–CCDC-254062 contain supplementary crystallographic data for **5**, **8**, **9**, **13**, **15**, and **22**. 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).

Table 3. *Crystallographic Data for the Complexes* **9** *and* **13**

	9 · CH_2Cl_2	**13**
Empirical formula	$C_{40}H_{37}Cl_5ORh_2$	$C_{32}H_{20}Cl_3O_4RhRu$
Molar mass [g mol^{-1}]	916.77	778.81
Crystal size [mm]	0.16 × 0.13 × 0.10	0.16 × 0.10 × 0.10
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.3109(5)	10.177(3)
b [Å]	12.6523(11)	10.353(4)
c [Å]	15.8881(10)	16.081(4)
α [°]	80.926(6)	94.32(3)
β [°]	81.670(5)	95.67(2)
γ [°]	66.784(6)	118.49(3)
Volume [Å^3]	1872.7(2)	1467.3(8)
Z	2	2
Density [g cm^{-3}]	1.626	1.763
Temperature [K]	140(2)	140(2)
Absorption coefficient [nm^{-1}]	1.269	1.387
Θ range [°]	3.23–25.03	3.18–25.02
Index ranges	$-12 \rightarrow 12$, $-14 \rightarrow 15$, $-18 \rightarrow 18$	$-12 \rightarrow 12$, $-11 \rightarrow 11$, $-19 \rightarrow 19$
Reflections collected	11363	9579
Independent reflections	5775 ($R_{int} = 0.0297$)	4865 ($R_{int} = 0.0522$)
Absorption correction	semi-empirical	semi-empirical
Max. and min. transmission	0.8724 and 0.7533	0.9764 and 0.7011
Data/restraints/parameters	5775/0/443	4865/0/371
Goodness-of-fit on F^2	0.936	1.165
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0246$, $wR_2 = 0.0526$	$R_1 = 0.0518$, $wR_2 = 0.1391$
R indices (all data)	$R_1 = 0.0370$, $wR_2 = 0.0549$	$R_1 = 0.0603$, $wR_2 = 0.1551$
Largest diff. peak/hole [eÅ^{-3}]	0.519/−0.589	1.573/−1.629

Table 4. *Crystallographic Data for the Complexes* **15** *and* **22**

	15 · 2 CH_2Cl_2	**22** · 3 acetone
Empirical formula	$C_{60}H_{76}Cl_7O_2P_2RhRu$	$C_{77}H_{76}Cl_3O_5P_2RhRu$
Molar mass [g mol^{-1}]	1343.28	1453.65
Crystal size [mm]	$0.22 \times 0.18 \times 0.17$	$0.20 \times 0.14 \times 0.13$
Crystal system	monoclinic	triclinic
Space group	*Cc*	$P\bar{1}$
a [Å]	21.8005(14)	12.8812(9)
b [Å]	17.5088(15)	13.9637(8)
c [Å]	16.7048(14)	20.4804(14)
α [°]	90	74.782(5)
β [°]	105.911(6)	72.973(6)
γ [°]	90	86.223(5)
Volume [Å^3]	6132.0(8)	3398.6(4)
Z	4	2
Density [g cm^{-3}]	1.455	1.421
Temperature [K]	140(2)	140(2)
Absorption coefficient [nm^{-1}]	0.913	0.681
Θ range [°]	3.14 – 25.03	3.16 – 25.03
Index ranges	$-25 \rightarrow 25$, $-20 \rightarrow 20$, $-17 \rightarrow 19$	$-14 \rightarrow 14$, $-16 \rightarrow 16$, $-24 \rightarrow 24$
Reflections collected	17986	20176
Independent reflections	9852 ($R_{int} = 0.0440$)	10509 ($R_{int} = 0.0376$)
Absorption correction	semi-empirical	semi-empirical
Max. and min. transmission	0.8773 and 0.7968	0.9326 and 0.8260
Data/restraints/parameters	9852/8/670	10509/8/766
Goodness-of-fit on F^2	0.932	0.987
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0448$, $wR_2 = 0.0916$	$R_1 = 0.0455$, $wR_2 = 0.1216$
R indices (all data)	$R_1 = 0.0582$, $wR_2 = 0.0954$	$R_1 = 0.0629$, $wR_2 = 0.1299$
Largest diff. peak/hole [eÅ^{-3}]	1.041/ – 0.704	1.277/ – 1.071

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