Heterobimetallic and Mixed-Valence Chloro-Bridged Complexes with Orthometalated Rhodium(III) and Iridium(III) Fragments☆

Kurt Polborn and Kay Severin*

Institut für Anorganische Chemie der Ludwig-Maximilians-Universität,
Meiserstraße 1, D-80333 München, Germany
Fax.: (internat.) + 49(0)89/5902–214
E-mail: kse@anorg.chemie.uni-muenchen.de

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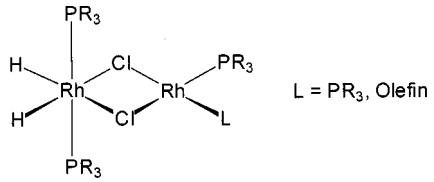
The synthesis and characterization of heterobimetallic and mixed-valence complexes in which orthometalated $[(ppy)_2MCl]$ (M = Rh, Ir; ppy = 2-phenylpyridine anion) and $[(bzq)_2RhCl]$ (bzq = benzo[*h*]quinoline anion) fragments are linked via chloro-bridges with rhodium(I), iridium(I), palladium(II), and platinum(II) fragments is reported. These complexes are formed in nearly quantitative yields by metathesis reactions from the respective homodimeric compounds. The structures of $[(ppy)_2Rh(\mu\text{-}Cl)_2Rh(cod)]$ (cod = η^4-1,5-cyclooctadiene) and $[(ppy)_2Rh(\mu\text{-}Cl)_2Pt(PBu_3)\text{-}Cl]$ were determined by X-ray structure analyses.

Introduction

Dichloro-bridged complexes of rhodium and iridium play an important role as starting materials in organometallic chemistry and catalysis. Subsequent functionalization of these complexes is easily possible through bridge-splitting reactions with various donor ligands.[1] Generally, the two metal fragments are symmetrically linked by halide ligands. Dinuclear complexes in which rhodium or iridium complexes are *asymmetrically joined* with a different transition metal fragment, on the other hand, are rare.[2][3][4][5][6][7] Among the more prominent examples are the mixed-valence hydrido complexes shown below. They are produced in catalytic hydrogenation[3] and dehydrogenation[4] reactions with rhodium(I) phosphine complexes. At present there is no general methodology available for the synthesis of such heterodimeric or mixed-valence complexes. Furthermore the reactivity of these compounds is virtually unexplored.



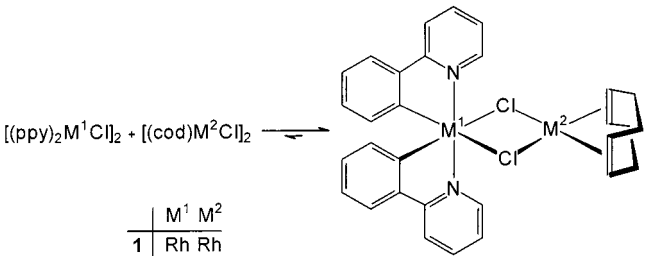
L = PR_3, Olefin

Here we describe the synthesis and characterization of new dinuclear, chloro-bridged complexes containing Rh^{III} or Ir^{III} fragments together with Rh^{I}, Ir^{I}, Pd^{II}, and Pt^{II} fragments. They are obtained by metathesis reactions of $[(cod)MCl]_2$ (M = Rh, Ir) or $[(R_3P)MCl_2]_2$ (M = Pd, Pt; R = Et, *n*-Bu) with the orthometalated Rh^{III} and Ir^{III} complexes $[(bzq)_2RhCl]_2$ or $[(ppy)_2MCl]_2$ (M = Rh, Ir). The latter compounds have found considerable attention since they are powerful photoreducing agents.[8][9]

Dinuclear Rh^{III}-Rh^{I}, Rh^{III}-Ir^{I}, and Ir^{III}-Ir^{I} Complexes

The dinuclear complexes **1**–**3** were obtained in nearly quatitative yield when a suspension of $[(ppy)_2MCl]_2$ (M = Rh, Ir) in dichloromethane was stirred with equivalent amounts of $[(cod)MCl]_2$ (M = Rh, Ir) (Scheme 1). Upon completion of the reactions clear yellow solutions were formed indicating a strongly enhanced solubility of the heterodimeric products with respect to the homodimeric Rh^{III} and Ir^{III} complexes. Yellow powders were obtained after removal of the solvent. Other Rh^{III}-Rh^{I} complexes containing Rh^{III} fragments with orthometalated ligands (e.g. the tridentate *o*,*o*′-$(Me_2NCH_2)C_6H_3$) were described by van Koten[5], Bruce[6], and Mills.[7]

Scheme 1



	M^1	M^2
1	Rh	Rh
2	Rh	Ir
3	Ir	Ir

1–**3**

The ^1H and ^{13}C NMR spectra ($CDCl_3$) of racemic **1**–**3** are in accordance with the structures shown in Scheme 1. For the two phenylpyridyl ligands one set of signals is observed. The ^1H NMR spectra of the cyclooctadiene ligand reflect the reduced symmetry of **1**–**3** as compared to $[(cod)MCl]_2$: the vinylic proton signals appear as two well separated groups at δ 3.8 and 4.0.

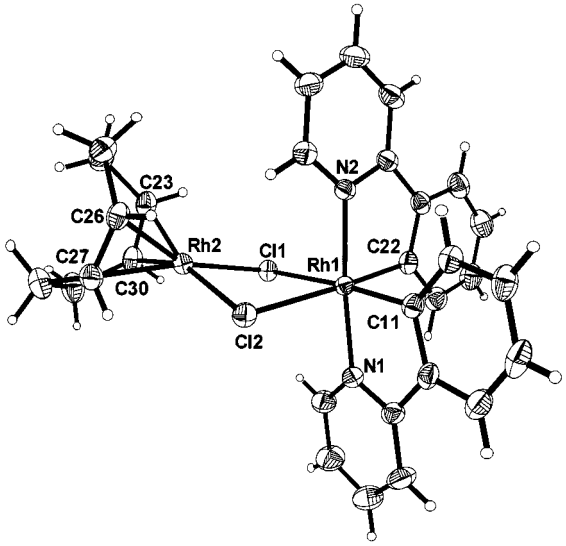
Minor amounts of starting material can be detected in the ^1H NMR spectra of **1**–**3** indicating a dynamic equilib-

  1434–1948/98/0808–1187 $ 17.50+.50/0

rium between homo- and heterodimeric complexes (K_{eq} > 100). Similar equilibria were observed in solutions of $[(R_3P)PtCl_2]_2$ together with $[(R_3P)PdCl_2]_2$.[10] In these cases, however, the amount of heterodinuclear Pd-Pt complexes present in solution were close to what is expected for a statistical distribution. Quantitative formation of heterodimeric complexes, on the other hand, was also observed in reactions of $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ with various chloro-bridged complexes.[11]

The molecular structure of **1** was confirmed by single crystal X-ray analysis (Figure 1). The Rh^{III} center is coordinated in a slightly distorted octahedral fashion with the two N-donor groups adopting a *trans* configuration. The Rh(μ-Cl)$_2$Rh unit is markedly non-planar with a dihedral angle between the normals to the planes defined by Rh1, Cl1, Cl2 and Rh2, Cl1, Cl2, of 24.14°. Folded Rh(μ-Cl)$_2$Rh units are also found for $[(CO)_2RhCl]_2$,[12] $[(PMe_2Ph)(CO)RhCl]_2$,[13] $[(C_6H_{10})_2RhCl]_2$,[14] $[(PhN{=}NC_6H_4)_2(CO)_2Rh_2]$,[7] $[(CO)_2(cod)Rh_2]$,[2a] and for **5** (Figure 2). According to a recent theoretical and structural analysis of square-planar complexes of the general formula $[L_2M(\mu\text{-}Cl)_2ML_2]$ the main driving force for bending are attractive metal−metal interactions[15] but for **1** direct Rh−Rh interactions are unlikely due to a Rh−Rh bond length of 3.60 A. The Rh2−Cl bond lengths are very close to that in the homodimeric complex $[(cod)RhCl]_2$.[16] Significantly longer are the Rh1−Cl bond lengths (2.55 and 2.57 A), presumably due to the strong σ-donor character of the coordinating carbons in *trans* position.

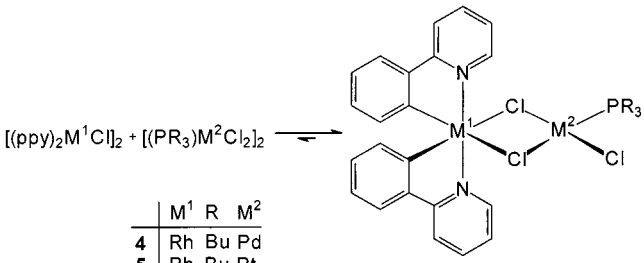
Figure 1. Molecular structure of complex **1**. Selected bond lengths [A] and angles [°]: Rh2−C26 2.104(4), Rh2−C27 2.120(4), Rh2−Cl2 2.407(1), Rh2−Cl1 2.410(2), Rh1−C11 1.980(4), Rh1−C22 1.982(4), Rh1−N2 2.046(3), Rh1−N1 2.043(4), Rh1−Cl1 2.553(1), Rh1−Cl2 2.569(2), N1−Rh1−Cl1 95.56(11), N1−Rh1−Cl2 86.42(11), Cl1−Rh1−Cl2 81.36(5), N1−Rh1−N2 174.66(14), Cl2−Rh2−Cl1 87.74(5)



Dinuclear Rh^{III}-Pd^{II}, Rh^{III}-Pt^{II}, and Ir^{III}-Pt^{II} Complexes

Similar as for **1**−**3** the heterobimetallic complexes **4**−**8** are obtained by metathesis reactions of $[(ppy)_2MCl]_2$ (M = Rh, Ir) with the respective chloro-bridged palladium or platinum phosphine complex (Scheme 2). The yields are quantitative for the platinum complexes **5**, **7**, and **8**. ^{1}H NMR spectra ($CDCl_3$) of the palladium complexes **4** and **6** show very small amounts of homodimeric starting material (K_{eq} > 100). The dynamic nature of these metathesis reactions as well as the higher stability of Rh^{III}-Pt^{II} complexes in comparison to the corresponding Rh^{III}-Pd^{II} complexes was confirmed by a direct competition experiment: if one equivalent of $[(ppy)_2Rh(\mu\text{-}Cl)_2Pd(PBu_3)Cl]_2$ (**4**) was mixed with 0.5 equivalents of $[(Bu_3P)PtCl_2]_2$ in dichloromethane the immediate formation of $[(ppy)_2Rh(\mu\text{-}Cl)_2Pt(PBu_3)Cl]_2$ (**5**) together with $[(Bu_3P)PdCl_2]_2$ was observed by ^{31}P NMR spectroscopy. The ratio between **5** and **4**, which was estimated by integration of the respective ^{31}P NMR signals, was 3:1.

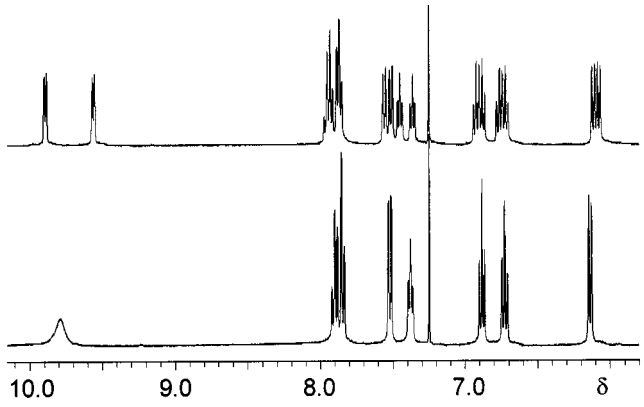
Scheme 2



	M^1	R	M^2
4	Rh	Bu	Pd
5	Rh	Bu	Pt
6	Rh	Et	Pd
7	Ir	Bu	Pt
8	Ir	Et	Pt

The ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) of **4**−**6** are strongly temperature dependent. At temperatures below 250 K the phenylpyridyl ligands show two distinct sets of signals in accordance with the structure depicted in Scheme 2. At room temperature, however, only one set of signals can be observed (Figure 2).

Figure 2. Aromatic region of the ^{1}H NMR spectra of complex **5** at 233 K (top) and at 328 K (bottom) in $CDCl_3$

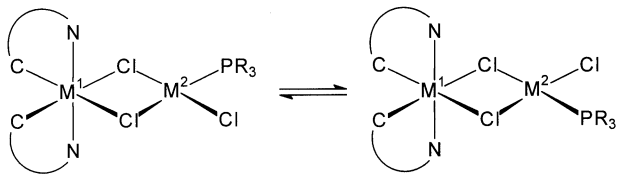


The fluctional process most probably consists of a "*cis-trans*" isomerisation as shown in Scheme 3. Plausible intermediates are solvent stabilized complexes with only one chloride bridge. From the coalescence temperature T_c and the difference in chemical shift Δν of selected signals a $\Delta G^{\#}$ value of 59 (±1) kJ mol^{-1} was calculated for **5**.[17] A similar

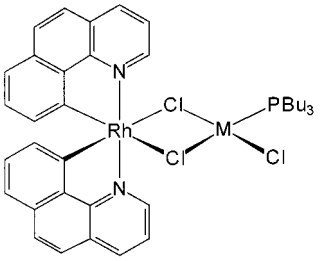
dynamic behaviour was previously observed for mixtures of *cis*- and *trans*-$[(Ph_3P)(CO)RhCl]_2$.[18] In contrast to the rhodium complexes **4**−**6** the iridium complexes **7** and **8** exhibit no fluxional behavior at room temperature. Coalescence effects are observed at temperatures above 325 K. For **7** a $\Delta G^{\#}$ value of 69 (±1) kJ mol^{-1} was calculated.

When the ^{1}H NMR spectra of **5** and **7** are recorded in $CDCl_3$ containing 20% CD_3OD only minor changes in the coalescence temperature can be observed. Interestingly this more polar solvent mixture disfavors the formation of the heterobimetallic complexes: significant amounts ($K_{eq} \approx 10$) of the homodimeric starting materials are present in solution as judged by integration of selected ^{1}H NMR signals. NMR experiments in neat CD_3OD were not performed due to the very low solubility of the complexes in this solvent. Other polar solvents like dimethyl sulfoxide or acetonitrile were likewise omitted because they are known to react with chloro-bridged complexes to yield the respective monomeric species.

Scheme 3



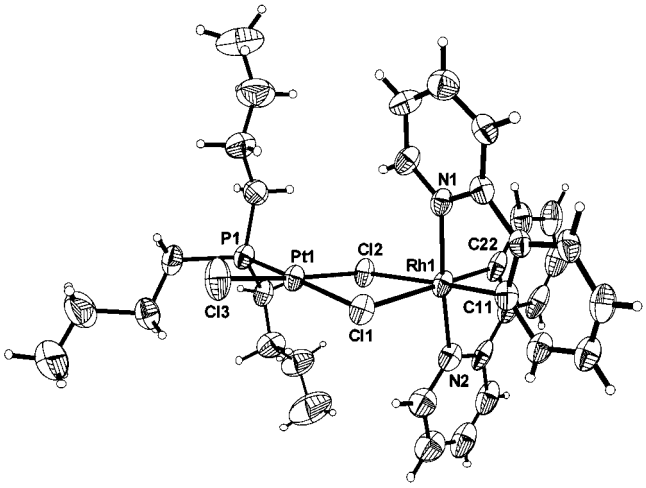
In analogy to **4**−**8** the Rh^{III}-Pd^{II} complex **9** and the Rh^{III}-Pt^{II} complex **10** containing two metalated benzoquinoline ligands were synthesized. Again, the NMR spectra ($CDCl_3$) exhibit dynamic behavior with a coalescence temperature close to what was observed for the rhodium complexes **4**−**6**.



	M
9	Pd
10	Pt

The structural assignments for **4**−**10** are supported by a single crystal X-ray analysis of **5** (Figure 3). There are two independent molecules in the unit cell, the metric parameters of which are very similar. As in **1**, the two metal centers are bridged by a slightly bent dichloro-bridge with the dihedral angle of the folded Rh(μ-Cl)$_2$Pt unit beeing 13.2°. Furthermore, the dichloro bridge is highly asymmetric with four distinct M−Cl bond lengths between 2.31 (Pt1−Cl2) and 2.54 A (Rh1−Cl2). Metal-metal interactions are unlikely due to a Rh−Pt bond length of 3.61 A. The configuration and the bond lengths of the octahedral Rh^{III} fragment are similar to that observed for **1**.

Figure 3. Molecular structure of complex **5**. Selected bond lengths [A] and angles [°]: Pt1−P1 2.216(3), Pt1−Cl1 2.407(2), Pt1−Cl2 2.313(2), Pt1−Cl3 2.270(3), Rh1−C11 1.975(9), Rh1−C22 1.995(11), Rh1−N2 2.036(8), Rh1−N1 2.038(8), Rh1−Cl1 2.528(3), Rh1−Cl2 2.540(2); N1−Rh1−Cl1 85.8(2), N1−Rh1−Cl2 96.8(2), Cl1−Rh1−Cl2 80.52(8), N1−Rh1−N2 175.2(3), Cl1−Pt1−Cl2 87.85(8), Cl3−Pt1−Cl2 174.70(10)



Conclusions

The present study establishes that heterobimetallic and mixed-valence complexes containing orthometalated Rh^{III} and Ir^{III} fragments can be obtained in nearly quantitative yields by metathesis reactions of $[(N-C)_2MCl]_2$ (M = Rh, Ir) with various dichloro-bridged complexes of the late transition metals. It is conceivable that this synthetic scheme is not restricted to the cyclooctadiene and phosphine complexes described here. Indeed, preliminary experiments have shown that chloro-bridged, orthometalated Pd^{II} and Pt^{II} complexes undergo similar disproportion reactions. It remains to be seen, how general the concept of chloro-bridge metathesis is appliciable for the synthesis of new, heterometallic complexes. Studies along these lines will be reported shortly.

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Experimental Section

General: All solvents were of analytical grade quality, obtained commercially and used without further purification. Reactions with $[(cod)IrCl]_2$ were performed with degassed solvents under an inert atmosphere. The complexes $[(R_3P)MCl_2]_2$ (M = Pd, Pt; R = Et, *n*-Bu),[18] $[(ppy)_2MCl]_2$ (M = Rh, Ir),[8b] $[(bzq)_2RhCl]_2$,[8b] $[(cod)RhCl]_2$,[20] and $[(cod)IrCl]_2$[21] were prepared as described in the literature. − IR: Perkin-Elmer 841, Nicolet 520. − NMR: JEOL EX 400,GSX 270. The NMR spectra were recorded at room temperature − exceptions are indicated. Due to the low solubility of **6** and **8** ^{13}C NMR spectra were not recorded.

General Procedure for the Synthesis of **1**−**10**: 10 ml of dichloromethane were added to 0.1 mmol of $[(ppy)_2MCl]_2$ (M = Rh, Ir) or

$[(bzq)_2RhCl]_2$ and 0.1 mmol of the respective chloro-bridged complex $[(cod)RhCl]_2$ (M = Rh, Ir) or $[(R_3P)MCl_2]_2$ (M = Pd, Pt). After 1 h clear yellow or orange solutions were observed. The products were isolated after evaporation of the solvent under reduced pressure and dried in vacuo at 50°C.

[(ppy)$_2$Rh(μ-Cl)$_2$Rh(cod)] (**1**): Yellow powder. Crystals can be obtained by slow diffusion of diethyl ether in a solution of **1** in chloroform. M. p. 255−258°C (dec.). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.61−1.74 (m, 4 H, CH_2, cod), 2.27−2.53 (m, 4 H, CH_2, cod), 3.98−4.03 (m, 2 H, CH, cod), 4.14−4.19 (m, 2 H, CH, cod), 6.14 (d, ^3J = 8.0 Hz, 2 H, CH, ppy), 6.72 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 6.85 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 7.43 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 7.51 (d, ^3J = 7.7 Hz, 2 H, CH, ppy), 7.83−7.94 (m, 4 H, CH, ppy), 9.94 (d, ^3J = 5.6 Hz, 2 H, NCH, ppy). − ^{13}C NMR (68 MHz, $CDCl_3$): δ = 30.81, 31.07 (CH_2, cod), 78.13, 78.33, 78.55, 78.75 (CH, cod), 118.83, 122.12, 122.62, 123.81, 129.37, 132.65, 137.39, 143.73, 151.87, 164.71 (CH, ppy), 164.64 (d, $^1J_{RhC}$ = 37.4 Hz, RhC). − $C_{30}H_{28}Cl_2N_2Rh_2{\cdot}CHCl_3$ (812.67): calcd. C 45.82, H 3.59, N 3.45; found C 45.16, H 3.82, N 3.14.

[(ppy)$_2$Rh(μ-Cl)$_2$Ir(cod)] (**2**): Yellow powder, m.p. 209−213°C (dec.). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.22−1.35 (m, 4 H, CH_2, cod), 2.02−2.24 (m, 4 H, CH_2, cod), 3.75−3.81 (m, 2 H, CH, cod), 3.90−3.96 (m, 2 H, CH, cod), 6.13 (d, ^3J = 8.0 Hz, 2 H, CH, ppy), 6.72 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 6.87 (t, ^3J = 7.5 Hz, 2 H, CH, ppy), 7.39 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 7.51 (d, ^3J = 7.7 Hz, 2 H, CH, ppy), 7.82−7.94 (m, 4 H, CH, ppy), 9.77 (d, ^3J = 5.6 Hz, 2 H, NCH, ppy). − ^{13}C NMR (68 MHz, $CDCl_3$): δ = 31.62, 31.82 (CH_2, cod), 61.35, 61.79 (CH, cod), 118.82, 122.18, 122.84, 123.87, 129.45, 132.67, 137.54, 143.73, 151.92, 164.48 (CH, ppy), 163.99 (d, $^1J_{RhC}$ = 37.7 Hz, RhC). − $C_{30}H_{28}Cl_2IrN_2Rh{\cdot}CH_2Cl_2$ (867.54): calcd. C 42.92, H 3.49, N 3.23; found C 43.25, H 3.55, N 3.23.

[(ppy)$_2$Ir(μ-Cl)$_2$Ir(cod)] (**3**): Orange powder, m.p. 194−197°C (dec.). − ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.21−1.34 (m, 4 H, CH_2, cod), 1.99−2.23 (m, 4 H, CH_2, cod), 3.68−3.74 (m, 2 H, CH, cod), 3.88−3.94 (m, 2 H, CH, cod), 6.06 (d, ^3J = 7.7 Hz, 2 H, CH, ppy), 6.62 (t, ^3J = 7.7 Hz, 2 H, CH, ppy), 6.79 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 7.36−7.52 (m, 4 H, CH, ppy), 7.83−7.90 (m, 4 H, CH, ppy), 9.76 (d, ^3J = 5.9 Hz, 2 H, NCH, ppy). − ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 37.21, 37.55 (CH_2, cod), 62.06, 62.35 (CH, cod), 118.72, 121.86, 122.50, 123.93, 129.34, 131.45, 137.76, 142.79, 144.13, 151.37, 167.34 (CH, ppy). − $C_{30}H_{28}Cl_2Ir_2N_2{\cdot}1/2\ CH_2Cl_2$ (914.38): calcd. C 40.06, H 3.20, N 3.06; found C 39.58, H 2.86, N 2.96.

[(ppy)$_2$Rh(μ-Cl)$_2$Pd(PBu$_3$)Cl] (**4**): Orange powder, m.p. 265−268°C (dec.). − ^{1}H NMR (270 MHz, $CDCl_3$, 35°C): δ = 0.90 (t, ^3J = 7.3 Hz, 9 H, CH_3, PBu_3), 1.35−1.79 (m, 18 H, CH_2, PBu_3), 6.13 (d, ^3J = 7.8 Hz, 2 H, CH, ppy), 6.72 (dt, ^3J = 7.4 Hz, ^5J = 1.3 Hz, 2 H, CH, ppy), 6.86 (dt, ^3J = 7.5 Hz, ^5J = 1.3 Hz, 2 H, CH, ppy), 7.37 (t, br, ^3J = 5.6 Hz, 2 H, CH, ppy), 7.51 (dd, ^3J = 7.7 Hz, ^5J = 1.0 Hz, 2 H, CH, ppy), 7.82−7.93 (m, 4 H, CH, ppy), 9.81 (s, br, 2 H, NCH, ppy). − ^{13}C NMR (68 MHz, $CDCl_3$, 35°C): δ = 13.72 (CH_3, PBu_3), 23.32 (d, $^1J_{PC}$ = 32.0 Hz, PCH_2), 24.11 (d, $^2J_{PC}$ = 14.8 Hz, PCH_2CH_2), 26.04 (d, $^3J_{PC}$ = 2.8 Hz, $PCH_2CH_2CH_2$), 118.81, 122.23, 122.72, 123.74, 129.37, 132.64, 137.56, 143.75, 151.68, 164.75 (CH, ppy), 164.77 (d, $^1J_{RhC}$ = 37.0 Hz, RhC). − ^{31}P NMR (109 MHz, CH_2Cl_2): δ = 33.51. − $C_{34}H_{43}Cl_3N_2PPdRh{\cdot}1/3\ CH_2Cl_2$ (854.71): calcd. C 48.25, H 5.15, N 3.28; found C 48.27, H 5.17, N 3.24.

[(ppy)$_2$Rh(μ-Cl)$_2$Pt(PBu$_3$)Cl] (**5**): Yellow powder. Crystals can be obatined by slow diffusion of diethyl ether in a solution of **5** in dichloromethane. M.p. 255−257°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.4 Hz, 9 H, CH_3, PBu_3), 1.33−1.74 (m, 18 H, CH_2, PBu_3), 6.12 (d, ^3J = 7.7 Hz, 2 H, CH, ppy), 6.73 (t, ^3J = 7.1 Hz, 2 H, CH, ppy), 6.89 (t, ^3J = 7.7 Hz, 2 H, CH, ppy), 7.39 (s, br, 2 H, CH, ppy), 7.52 (d, ^3J = 7.4 Hz, 2 H, CH, ppy), 7.85−7.94 (m, 4 H, CH, ppy), 9.75 (d, br, 2 H, NCH, ppy). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.87 (CH_3, PBu_3), 21.50 (d, $^1J_{PC}$ = 39.6 Hz, PCH_2), 24.05 (d, $^2J_{PC}$ = 14.3 Hz, PCH_2CH_2), 25.72 (d, $^3J_{PC}$ = 2.8 Hz, $PCH_2CH_2CH_2$), 118.94, 122.42, 122.94, 123.87, 129.47, 132.61, 137.60, 143.83, 151.80, 164.45 (CH, ppy), 164.51 (d, $^1J_{RhC}$ = 37.8 Hz, RhC). − ^{31}P NMR (162 MHz, $CDCl_3$): δ = −2.80 ($^1J_{PtP}$ = 3489 Hz). − $C_{34}H_{43}Cl_3N_2PPtRh$ (915.06): calcd. C 44.63, H 4.74, N 3.06; found C 44.23, H 4.57, N 2.96.

[(ppy)$_2$Rh(μ-Cl)$_2$Pd(PEt$_3$)Cl] (**6**): Yellow powder, m.p. 288−291°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (dt, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 18.0 Hz, 9 H, CH_3, PEt_3), 1.75−1.84 (m, 6 H, CH_2, PEt_3), 6.14 (d, ^3J = 8.2 Hz, 2 H, CH, ppy), 6.73 (t, ^3J = 7.4 Hz, 2 H, CH, ppy), 6.87 (t, ^3J = 7.5 Hz, 2 H, CH, ppy), 7.40 (s, br, 2 H, CH, ppy), 7.53 (d, ^3J = 6.7 Hz, 2 H, CH, ppy), 7.85−7.94 (m, 4 H, CH, ppy), 9.81 (s, br, 2 H, NCH, ppy). − ^{31}P NMR (109 MHz, CH_2Cl_2): δ = 40.43. − $C_{28}H_{31}Cl_3N_2PPdRh$ (742.23): calcd. C 45.31, H 4.21, N 3.77; found C 45.31, H 3.86, N 3.76.

[(ppy)$_2$Ir(μ-Cl)$_2$Pt(PBu$_3$)Cl] (**7**): Yellow powder; m.p. 253−255°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 6.7 Hz, 9 H, CH_3, PBu_3), 1.34−1.72 (m, 18 H, CH_2, PBu_3), 6.08 (d, ^3J = 7.3 Hz, 1 H, CH, ppy), 6.11 (d, ^3J = 8.0 Hz, 1 H, CH, ppy), 6.63 (t, ^3J = 7.2 Hz, 1 H, CH, ppy), 6.66 (t, ^3J = 7.5 Hz, 1 H, CH, ppy), 6.78 (t, ^3J = 7.3 Hz, 1 H, CH, ppy), 6.81 (t, ^3J = 7.5 Hz, 1 H, CH, ppy), 7.31 (t, ^3J = 6.4 Hz, 1 H, CH, ppy), 7.41 (t, ^3J = 5.5 Hz, 1 H, CH, ppy), 7.45 (d, ^3J = 8.2 Hz, 1 H, CH, ppy), 7.49 (d, ^3J = 7.5 Hz, 1 H, CH, ppy), 7.78−7.87 (m, 4 H, CH, ppy), 9.63 (d, ^3J = 5.5 Hz, 1 H, NCH, ppy), 10.05 (d, ^3J = 5.6 Hz, 1 H, NCH, ppy). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.84 (CH_3, PBu_3), 21.43 (d, $^1J_{PC}$ = 39.3 Hz, PCH_2), 24.03 (d, $^2J_{PC}$ = 14.6 Hz, PCH_2CH_2), 25.68 (d, $^3J_{PC}$ = 3.1 Hz, $PCH_2CH_2CH_2$), 118.41, 118.75, 121.89, 122.29, 122.44, 123.85, 129.42, 129.53, 131.34, 131.74, 137.43, 137.47, 143.12, 143.68, 143.95, 144.22, 150.61, 151.77, 167.65, 167.78 (CH, ppy). − ^{31}P NMR (109 MHz, CH_2Cl_2): δ = −1.49 ($^1J_{PtP}$ = 3602 Hz). − $C_{34}H_{43}Cl_3N_2PPtIr$ (1004.37): calcd. C 40.66, H 4.32, N 2.79; found C 40.95, H 4.09, N 2.85.

[(ppy)$_2$Ir(μ-Cl)$_2$Pt(PEt$_3$)Cl] (**8**): Yellow powder, m.p. 275−277°C (dec.). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.10 (dt, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 17.5 Hz, 9 H, CH_3, PEt_3), 1.64−1.80 (m, 6 H, CH_2, PEt_3), 6.09 (pt, ^3J = 5.7 Hz, 2 H, CH, ppy), 6.63 (pq, ^3J = 6.9 Hz, 2 H, CH, ppy), 6.78 (pq, ^3J = 6.2 Hz, 2 H, CH, ppy), 7.29−7.49 (m, 4 H, CH, ppy), 7.84 (m, 4 H, CH, ppy), 9.62 (d, ^3J = 5.7 Hz, 1 H, CH, ppy), 10.02 (d, ^3J = 5.2 Hz, 1 H, CH, ppy). − ^{31}P NMR (109 MHz, $CDCl_3$): δ = 5.98 ($^1J_{PtP}$ = 3722 Hz). − $C_{28}H_{31}Cl_3N_2PPtIr$ (920.20): calcd. C 36.55, H 3.40, N 3.04; found C 36.50, H 3.24, N 2.97.

[(bzq)$_2$Rh(μ-Cl)$_2$Pd(PBu$_3$)Cl] (**9**): Orange powder; m.p. 250−253°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 35°C): δ = 0.87 (t, ^3J = 7.2 Hz, 9 H, CH_3, PBu_3), 1.34−1.77 (m, 18 H, CH_2, PBu_3), 6.11 (d, ^3J = 7.4 Hz, 2 H, CH, bzq), 6.95 (t, ^3J = 7.8 Hz, 2 H, CH, bzq), 7.30 (d, ^3J = 7.7 Hz, 2 H, CH, bzq), 7.66−7.79 (m, 6 H, CH, bzq), 8.41 (d, ^3J = 6.7 Hz, 2 H, CH, bzq), 10.10 (d, br, 2 H, NCH, bzq). − ^{13}C NMR (101 MHz, $CDCl_3$, 35°C): δ = 13.68 (CH_3, PBu_3), 23.33 (d, $^1J_{PC}$ = 31.9 Hz, PCH_2), 24.09 (d, $^2J_{PC}$ = 14.4 Hz, PCH_2CH_2), 26.02 (d, $^3J_{PC}$ = 2.5 Hz, $PCH_2CH_2CH_2$), 120.77, 121.62, 123.18, 126.85, 128.64, 129.30, 129.48, 133.55, 135.94, 140.07, 151.12, 154.77 (CH, bzq), RhC: not observed. −

Table 1. Crystal data for complexes **1** and **5**

	1	**5**
Empirical formula	$C_{67}H_{69}Cl_{13}N_4Rh_4$	$C_{34.5}H_{44}Cl_4N_2PPtRh$
Molecular mass [g mol^{-1}]	1818.75	957.49
Crystal size	0.53 × 0.47 × 0.27	0.47 × 0.37 × 0.27
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	*P*-1
a [A]	23.100(9)	11.950(2)
b [A]	12.161(5)	17.517(3)
c [A]	26.498(9)	20.294(3)
α [°]	90.00(3)	66.40(2)
β [°]	104.81(3)	86.53(2)
γ [°] °	90.00(3)	75.318(14)
Volume [A^3]	7197(5)	3761.8(11)
Z	4	4
Density [g cm^{-3}]	1.679	1.691
Absorption coefficient [mm^{-1}]	1.428	4.506
Θ range [°]	2.33 to 23.98	2.56 to 23.97
Index ranges	−26 → 0, −13 → 0, −29 → 30	−13 → 13, −20 → 0, −23 → 21
Reflections collected	5772	12203
Independent reflections	5620 (R_{int} = 0.0166)	11763 (R_{int} = 0.0202)
Absorption correction	semi-empirical	semi-empirical
Max. and min. transmission	0.9999 and 0.6810	0.9999 and 0.6848
Weights	$w = 1/(\sigma^2(F_0^2)+(0.0319\ P)^2 +23.5103P]$; $P = (F_0^2+2F_c^2)/3$	$w = 1/(\sigma^2(F_0^2)+(0.0376\ P)^2 +9.7166P]$; $P = (F_0^2+2F_c^2)/3$
Data / restraints / parameters	5620 / 12 / 418	11763 / 20 / 791
Goodness-of-fit on F^2	1.079	1.110
Final *R* indices [$I>2\sigma(I)$]	$R1$ = 0.0316, $wR2$ = 0.0726	$R1$ = 0.0463, $wR2$ = 0.0896
R indices (all data) °	$R1$ = 0.0403, $wR2$ = 0.0786	$R1$ = 0.0787, $wR2$ = 0.1043
Largest diff. peak/hole [eA^{-3}]	0.643/−0.720	1.064/−0.906

^{31}P NMR (162 MHz, CH_2Cl_2): δ = 32.34. − $C_{38}H_{43}Cl_3N_2PPdRh{\cdot}1/4\ CH_2Cl_2$ (895.67): calcd. C 51.31, H 4.90, N 3.13; found C 51.45, H 5.05, N 3.07.

[(bzq)$_2$Rh(μ-Cl)$_2$Pt(PBu$_3$)Cl] (**10**): Yellow powder; m.p. 280−283°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 8.0 Hz, 9 H, CH_3, PBu_3), 1.35−1.73 (m, 18 H, CH_2, PBu_3), 6.10 (d, ^3J = 7.4 Hz, 2 H, CH, bzq), 6.95 (t, ^3J = 8.1 Hz, 2 H, CH, bzq), 7.33 (d, ^3J = 7.3 Hz, ^5J = 1.3 Hz, 2 H, CH, bzq), 7.67−7.80 (m, 6 H, CH, bzq), 8.42 (d, ^3J = 6.7 Hz, 2 H, CH, bzq), 10.05 (d, br, 2 H, NCH, bzq). − ^{13}C NMR (68 MHz, $CDCl_3$, 35°C): δ = 13.70 (CH_3, PBu_3), 21.54 (d, $^1J_{PC}$ = 39.0 Hz, PCH_2), 23.94 (d, $^2J_{PC}$ = 14.7 Hz, PCH_2CH_2), 25.67 (d, $^3J_{PC}$ = 2.2 Hz, $PCH_2CH_2CH_2$), 120.88, 121.67, 123.23, 126.83, 128.65, 129.23, 130.06, 133.55, 136.02, 139.94, 150.56, 154.56 (CH, bzq), 160.93 (d, $^1J_{RhC}$ = 37.5 Hz, RhC). − ^{31}P NMR (109 MHz, CH_2Cl_2): δ = −2.64 ($^1J_{PtP}$ = 3704 Hz). − $C_{38}H_{43}Cl_3N_2PPtRh$ (963.10): calcd. C 47.39, H 4.50, N 2.91; found C 46.89, H 4.49, N 2.84.

X-ray Crystallographic Investigations: An Enraf Nonius CAD 4 diffractometer was employed for data collection using Mo-K_α radiation (T = 295 K). The structures were solved by direct methods (SHELXS86) and were refined by means of the full-matrix least squares procedures using SHELXL93 (Table 1). All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. **1** crystallizes with 1.5 molecules of chloroform and 0.5 molecules of diethyl ether, all of which are disordered (restraints were used for $CHCl_3$). **5** crystallizes with 0.5 molecules of dichloromethane. The *n*-butyl groups as well as the solvent molecule are disordered (restraints were used for CH_2Cl_2).[21]

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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[22] Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen. Any request for this material should quote the full literature citation and the reference numbers CSD-408186 for **1** and -408187 for **5**.

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