# Weak M–H···H–C and M–Cl···H–C Interactions in Orthometalated Iridium and Rhodium Complexes[**]

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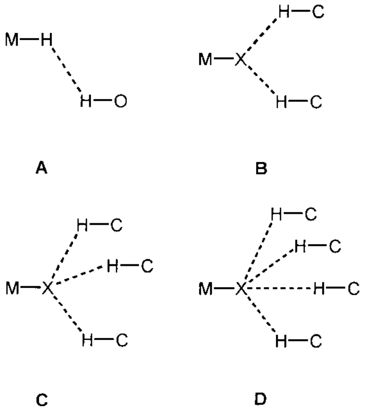
**Abstract:** Four different types of intramolecular MX···HC interactions have been observed in a series of five, structurally very similar, orthometalated iridium(III) and rhodium(III) complexes. For X = H and M = Ir or Rh, two-center or three-center interactions with MH···HC distances of 1.80–1.83 (M = Ir) or 2.00–2.20 Å (M = Rh) were observed. For X = Cl the MCl···HC distances of the three-center arrangement (M = Ir) were in the range of 2.38–2.60 Å, while values of 2.41–2.89 Å were found for the four-center geometry (M = Rh). These weak interactions open new perspectives for the mechanism of cyclometalations.

**Keywords:** azo compounds · hydrogen bonds · iridium · metalations · rhodium

## Introduction

A detailed knowledge of the nature of weak intra- and intermolecular interactions may facilitate the rational design of physical and chemical properties in artificial and biological systems. A typical example is the outstanding and well-documented role of hydrogen bonding in organic systems,[1, 2] although only a few cases have been reported in the field of organometallic chemistry. These are intermolecular H···H bonds (3–7 kcal mol$^{-1}$) between a metal hydride fragment as the donor and a NH or OH ligand group as the acceptor (Scheme 1, type A), as observed, for example, in hexacoordinated Ir$^{III}$(H)$_2$ complexes with amino or hydroxypyridine ligands ($\widehat{\mathrm{LN}}$H, $\widehat{\mathrm{LO}}$H). The presence of hydrogen bonding was deduced from the IrH···HN and IrH···HO distances which lie in the range of 1.7–2.2 Å and are therefore significantly less than twice the van der Waals radius of H (2.40 Å).[3, 4] Further evidence of their existence stems from the shortening of the hydride $T_1$ relaxation time and H–H coupling with the HN or HO groups, as has been observed in a few cases.[3, 4] The reactivity-controlling properties of these weak H···H bonds were demonstrated by H$_2$ elimination, which proceeds by intramolecular protonation of Ir–H by the H–$\widehat{\mathrm{OL}}$ ligand.[4] In addition, a few intermolecular versions of these MH···HX (X = N,O) interactions are known.[5]



Scheme 1. Four different types of intramolecular MX···HC interactions.

Contrary to these results on structurally different compounds, we report in the following on five, structurally very similar complexes which exhibit numerous weak intramolecular interactions between M–H or M–Cl and ligand CH groups as well as an intermolecular CH···O interaction. These hexacoordinate Ir$^{III}$ and Rh$^{III}$ compounds contain an orthometalated azobenzene or arylimine ring and two phosphane ligands in *trans* position, and were isolated during our work on the mechanism of the rhodium-catalyzed synthesis of indoles from 1,2-diaryldiazenes and alkynes.[6] The recently published survey of the Cambridge Crystallographic Database revealed that several complexes contain unfurcated MH···HC bonds with distances of 1.5–2.2 Å (Scheme 1, type A,).[7a] In two cases a bifurcated arrangement of the type (sp$^3$)CH···MH···HC(sp$^3$) was observed which exhibits

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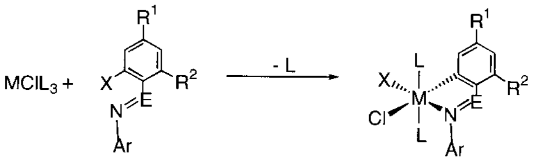
H$\cdots$H distances of 2.40 Å (M = Rh[7b]) and 2.00 Å (Ir[7c]) (Scheme 1, type B, X = H). And during preparation of this manuscript it was reported that a tetrafurcated system $[(sp^3)CH]_2\cdots IrH\cdots[HC(sp^3)]_2$ exists in $[IrCl_2(NH_3)(H)(PCy_3)_2]$ (Scheme 1, type D, X = H).[7d] In contrast, there is much less information in the literature about weak MCl$\cdots$HC bonds. A unique example is $[Ir(H)_2Cl(PtBu_2Ph)_2]$, which also contains a bifurcated system $(sp^3)CH\cdots IrCl\cdots HC(sp^3)$ with short Cl$\cdots$H contacts of 2.52 and 2.55 Å (Scheme 1, type B, X = Cl).[7c] The corresponding Cl$\cdots$HC distances in organic compounds are in the range between 2.57 and 2.94 Å (note that the sum of the van der Waals radii is 2.95 Å).[8]

## Results

The orthometalated compounds **1–3** and **4b** were synthesized according to Scheme 2 ($R^1$ = H). The preparation and molecular structure of **4a** was published recently.[9] The results of the single-crystal X-ray structural determinations are summarized in Figure 1 and Tables 1 and 2.



Scheme 2. Synthesis of the complexes **1–4b**.

| | M | L | X | $R^1$ | $R^2$ | Ar | E |
|---|---|---|---|---|---|---|---|
| **1** | Ir | $PPh_3$ | H | MeO | H | p-$MeOC_6H_4$ | N |
| **2** | Ir | $PPh_3$ | H | H | Cl | Ph | N |
| **3** | Rh | $PCy_3$ | H | H | H | Ph | N |
| **4a** | Rh | $PPh_3$ | Cl | Cl | H | Ph | N |
| **4b** | Rh | $PPh_3$ | Cl | H | Cl | Ph | CH |

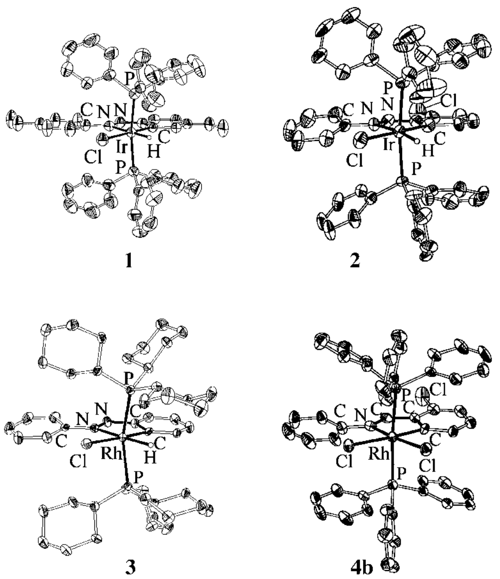


Figure 1. Molecular structures of **1**, **2**, **3**, and **4b**.

Table 1. Selected bond lengths [Å] of **1–4b**.[a]

| Compounds | **1** | **2**[b] | **3** | **4a** | **4b** |
|---|---|---|---|---|---|
| M–X[c] | 1.65[d] | 1.65 | 1.65[d] | 2.359(1) | 2.354(2) |
| M–Cl3 | 2.506(2) | 2.498(3) | 2.497(1) | 2.494(1) | 2.483(2) |
| M–N1 | 2.215(4) | 2.194(8) | 2.245(4) | 2.079(3) | 2.084(4) |
| N1=N2 | 1.280(6) | 1.289(10) | 1.278(5) | 1.279(5) | 1.303(5)[e] |
| N2–C1 | 1.367(7) | 1.392(13) | 1.400(5) | 1.366(5) | 1.435(6)[e] |
| C1–C6 | 1.381(7) | 1.376(14) | 1.416(5) | 1.413(6) | 1.429(9) |
| C6–M | 1.989(5) | 2.035(9) | 1.988(4) | 1.991(4) | 2.014(4) |
| M–P1 | 2.327(1) | 2.335(3) | 2.368(1) | 2.392(1) | 2.394(2) |
| M–P2 | 2.327(1) | 2.337(3) | 2.374(1) | 2.386(1) | 2.378(2) |

[a] Atom numbering scheme according to Scheme 3, which is different to the crystal structure data deposited. [b] One of the two crystallographically independent molecules. [c] X = H1 or Cl2. [d] The bond length before normalization was 1.66 (**1**) and 1.54 (**3**). [e] C7≡N2.

Table 2. Selected bond angles [°] of **1–4b**.[a]

| | **1** | **2** [b] | **3** | **4a** | **4b** |
|---|---|---|---|---|---|
| Cl3-M-X[c] | 76 | 71 | 92 | 92.76(4) | 92.43(4) |
| Cl3-M-N1 | 104.8(1) | 103.3(2) | 102.0(1) | 98.4(1) | 96.7(1) |
| C6-M-X | 102 | 109 | 89 | 90.4(1) | 90.0(2) |
| C6-M-N1 | 76.2(2) | 76.0(4) | 77.4(1) | 78.4(2) | 80.9(2) |
| M-N1-N2 | 113.9(3) | 116.5(6) | 113.8(3) | 116.7(3) | 113.5(3)[d] |
| M-C6-C1 | 114.8(4) | 113.4(8) | 113.3(3) | 111.9(3) | 111.9(3) |
| N2-C1-C6 | 120.3(5) | 121.9(1) | 121.3(4) | 118.8(4) | 115.6(4) |
| P1-M-X | 84 | 79 | 76 | 88.54(4) | 87.23(6) |
| P2-M-X | 84 | 89 | 84 | 86.55(4) | 87.82(6) |
| P1-M-Cl3 | 88.6(2) | 87.8(1) | 90.57(4) | 87.44(4) | 91.13(4) |
| P2-M-Cl3 | 88.6(2) | 89.4(1) | 87.59(4) | 91.67(4) | 90.36(4) |
| P1-M-P2 | 167.0(1) | 167.4(1) | 158.84(4) | 174.96(4) | 174.89(4) |

[a] See legend to Table 1. [b] One of the two crystallographically independent molecules. [c] X = H1 or Cl2. [d] C7≡N2.

In the case of **1** and **3** the solvent dichloromethane was included in the crystal; however, the distances to any metal atom were larger than 3.00 Å and therefore it is omitted in Figure 1. Each of the complexes **1–4b** consists of a five-membered, planar metallacycle containing the hexacoordinate metal ion. The latter is further ligated by two *trans* phosphane ligands, one chloro ligand *trans* to the σ-aryl group, and a hydride (**1–3**) or second chloride (**4a**, **4b**) in the remaining coordination site.

In the $^1H$ NMR spectra, the hydride signals of **1**, **2,** and **3** appear at $\delta = -14$ to $-18$. For **1** and **3**, the hydrido ligands could be localized from a difference Fourier synthesis.

**Abstract in German:** *Vier verschiedene Typen intramolekularer MX$\cdots$HC-Wechselwirkungen lassen sich in einer Reihe von fünf strukturell verwandten, orthometallierten $M^{III}$-Komplexen nachweisen. Für X = H und M = Ir bzw. Rh wurden zwei- bzw. dreizentrige Anordnungen mit MH$\cdots$HC-Abständen von 1.80–1.83 (M = Ir) bzw. 2.00–2.20 Å (M = Rh) gefunden. Für X = Cl liegen die MCl$\cdots$HC-Abstände der dreizentrigen Anordnungen (M = Ir) bei 2.38–2.60 Å, der vierzentrigen bei 2.41–2.89 Å. Diese schwachen Wechselwirkungen eröffnen für den Mechanismus von Cyclometallierungsreaktionen neue Perspektiven.*

Interatomic distances were calculated[8] by means of normalized C–H (1.09 Å) and M–H (1.65 Å) bond lengths, as described in the literature.[2b, 4, 7a, 10] The results of these calculations are summarized in Figures 2 and 3 and Tables 3 and 4.

## Discussion

Bond lengths between the metal and the phosphorus ligands and within the metallacycles are as expected and do not exhibit any unusual features. The strong *trans* influence of the σ-aryl group[4, 11] in all compounds results in elongated M–Cl3 bond lengths of 2.48–2.50 Å, compared to the M–Cl2 distances of 2.36 and 2.35 Å observed for **4a** and **4b,** respectively. These values are in accordance with the values of 2.51 and 2.36 Å reported for $Ir^{III}$–Cl bonds with a *trans* hydrido and chloro ligand, respectively.[12] From this agreement one can assume that the *trans* influences of aryl and diazene are the same as for hydride and chloride, respectively. This is further corroborated by the Rh–Cl bond length of a *trans*-Cl-Rh-Cl moiety of an octahedral $Rh^{III}$ complex which is also 2.36 Å.[12] Based on these comparisons, the Ir–H bond length in **1** is expectd to be about 1.57 Å, as reported for a *trans* Cl-Ir-H group;[12] however, a longer value of 1.66 Å is observed**.** A similar conclusion is not possible for the Rh–H bond (1.54 Å) of **3** because comparable data are not available. However, since a Rh–H bond length of 1.31 Å was reported for $[RhH(PPh_3)_4]$,[13] the same trend appears likely. The unmetalated phenyl ring lies in the plane of the metallacycle in **1**, while it is rotated out of the plane by 15, 10, 40, and 50° in the case of **2**, **3**, **4a**, and **4b**, respectively.

It is evident from the calculated distances that both hydrido and chloro ligands are involved in multicenter interactions with the C–H bonds of neighboring ligands. As a criterion, only MX···HC distances shorter than 2.20 (X = H) and 2.95 Å (X = Cl) were considered, although this is an arbitrary limit since the influence of electrostatic forces may reach much further.[2a] Agostic interactions are absent, as indicated by the fact that all M···HC distances are longer than 3.00 Å.

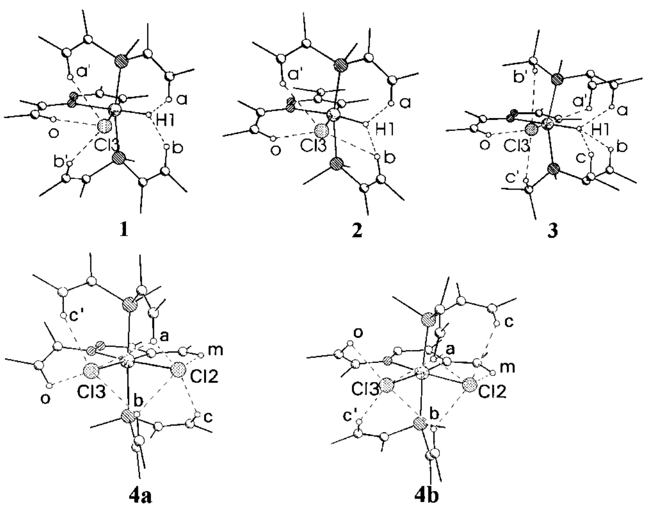


Figure 2. Short intramolecular contacts in **1**–**4b**.

Table 4. Calculated MH···HC and MCl···HC distances [Å].

| | | X···$H_a$ | X···$H_b$ | X···$H_c$ | X···$H_o$ | X···$H_m$ |
|---|---|---|---|---|---|---|
| **1** | (X = H) | 1.80 | 1.80 | – | – | – |
| | (X = Cl3) | 2.56 | 2.56 | – | 2.39 | – |
| **2** | (X = H) | 1.81 | 1.83 | – | – | – |
| | (X = Cl3) | 2.63 | 2.65 | – | 2.38 | – |
| **3** | (X = H) | 2.00 | 2.06 | 2.20 | – | – |
| | (X = Cl3) | 2.89 | 2.81 | 2.60 | 2.41 | – |
| **4a** | (X = Cl2) | 2.43 | 2.71 | 2.61 | – | 2.60 |
| | (X = Cl3) | 2.83 | 2.46 | 2.50 | 2.59 | – |
| **4b** | (X = Cl2) | 2.72 | 2.58 | 2.82 | – | 2.53 |
| | (X = Cl3) | 2.48 | 2.63 | 2.51 | 2.64 | – |

In the two triphenylphosphane complexes **1** and **2**, a bifurcated interaction with an average IrH···HC($sp^2$) distance of 1.81 ± 0.01 Å and average Ir-H-H and H-H-C angles of 131 ± 1 and 133 ± 1° are observed (Figure 2, Scheme 1, type B). These values are in agreement with the average H···H distance of 1.99 Å and M-H-H and H-H-C angles of 130 and 142°, respectively, reported for type A arrangements.[7] The tricyclohexylphosphane complex **3** contains a trifurcated interaction system (Scheme 1, type C, X = H). It has two short RhH···HC($sp^3$) distances of 2.03 ± 0.03 Å and a longer one of 2.20 Å, with corresponding Rh-H-H angles of 140, 136, and 120°, respectively. In all cases, the weak H···H bonding gives rise to the formation of a six-membered ring.

In addition to the slightly elongated M–H bonds, the presence of a weak H···H interaction is also corroborated by the fact that the two phosphane ligands of **1** and **3** are bent towards the hydride, as indicated by the P1-M-H and P2-M-H angles of 84 and 84 (**1**) and 76 and 83° (**3**), respectively. This results in P1-M-P2 angles of 167 (**1**), 167 (**2**), and 159° (**3**).

$^1H$ NMR investigations indicate that weak C–H···H–Ir interactions are also present in $CDCl_3$ solution (Scheme 3). In

Table 3. Angles [°] of the intramolecular MH···HC and MCl···HC interactions, see Figure 2.

| | | $MXH_a$ | $MXH_b$ | $MXH_c$ | $MXH_o$ | $MXH_m$ | $XH_aC$ | $XH_bC$ | $XH_cC$ | $XH_oC$ | $XH_mC$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | (X = H1) | 131 | 131 | – | – | 136 | 136 | – | – | – | – |
| | (X = Cl3) | 82 | 82 | – | 80 | – | 152 | 152 | – | 163 | – |
| **2** | (X = H1) | 132 | 130 | – | – | – | 123 | 136 | – | – | – |
| | (X = Cl3) | 78 | 76 | – | 79 | – | 146 | 127 | – | 150 | – |
| **3** | (X = H1) | 140 | 136 | 120 | – | – | 120 | 129 | 118 | – | – |
| | (X = Cl3) | 78 | 88 | 84 | 81 | – | 118 | 115 | 133 | 154 | – |
| **4a** | (X = Cl2) | 87 | 96 | 79 | – | 84 | 129 | 116 | 139 | – | 114 |
| | (X = Cl3) | 82 | 89 | 77 | 82 | – | 118 | 133 | 152 | 116 | – |
| **4b** | (X = Cl2) | 83 | 97 | 79 | – | 84 | 115 | 119 | 123 | – | 116 |
| | (X = Cl3) | 82 | 79 | 87 | 82 | – | 134 | 129 | 153 | 111 | – |

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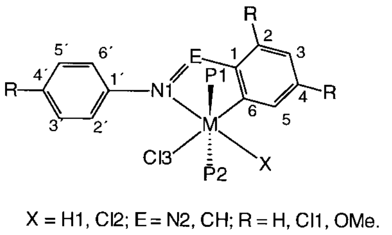

Scheme 3. Atom-numbering scheme of complexes **1**–**4b** used for NMR spectra.

a NOE experiment, selective saturation of the hydride resonance of **1** at $\delta = -16.7$ led to an enhancement of the signal from the *ortho* protons of the phosphane phenyl and from the *meta* proton of the orthometalated phenyl ring of the azo ligand ($H_m$, as in Figure 2) by 5% and 8%, respectively; the *meta* and *para* protons were not influenced. Complementary irradiation of the *ortho* proton resonance increased the intensity of the hydrido signal by 27%, while irradiation of $H_m$ led only to an enhancement of 5%. The hydride **1** has a short minimum $T_1$ relaxation time of 0.36 s at 400 Mhz and 240 K in $CD_2Cl_2$ that is caused by the C–H···H–Ir interaction. A H···H distance between the hydride and the closest H–C group is calculated to be 1.8 ± 1 Å, assuming that the rate of dipole–dipole relaxation of the hydride depends on the contribution of one *ortho* proton.[14] This value is the same as that found in the X-ray structural analysis. When the contributions of two *ortho* protons are considered,[7d] a distance of 2.0 ± 0.1 Å is obtained, which still can be attributed to a short contact.

The MCl···HC interaction is of types C and D (Scheme 1, X = Cl). In all the complexes, in addition to the phosphane hydrogen atoms, the *ortho* proton ($H_o$) of the unmetalated phenyl ring also becomes involved in the interaction, and in **4a** and **4b** additionally the *meta* proton $H_m$. In **1** and **2** the average IrCl···$H_{a,b}C(sp^2)$ length is 2.60 ± 0.05 Å, and the distance from $H_o$ to the neighboring chloro ligand increases from 2.38 (**1**, **2**) over 2.41 (**3**) and 2.59 (**4a**) to 2.64 Å (**4b**). This elongation corresponds to the increasing twist angle of the unmetalated phenyl ring relative to the planar metallacycle (vide supra). In complex **3** the unconventional hydrogen bonding can be represented by type D with one short RhCl···$H_oC(sp^2)$ distance of 2.41 Å and three longer RhCl···$HC(sp^3)$ distances of 2.89, 2.81, and 2.60 Å, in agreement with the greater acceptor properties of $HC(sp^2)$ compared to those of $HC(sp^3)$.[15] In contrast to the triphenylphosphane complexes, the weak tetrafurcated RhCl···HC interaction with the tricyclohexylphosphane ligand gives rise to the formation of a five- instead of a six-membered ring. A type D interaction is also present in **4a** and **4b**, which results in RhCl2···$HC(sp^2)$ distances of 2.43 and 2.66 ± 0.05 Å (**4a**), and 2.58 and 2.77 ± 0.05 Å (**4b**). The short contact (RhCl2···$H_m$: 2.60 (**4a**), 2.53 Å (**4b**)) of Cl2 with the *meta* proton $H_m$ of the orthometalated phenyl ring gives rise to a five-membered ring. An analogous interaction between IrH and $H_m$ is absent in **1** and **2** since the corresponding distances are larger than 2.85 Å, which is far greater than the sum of the van der Waals radii (2.40 Å). This may be due to the much smaller size of the hydride with regard to the chloride ligand. Contrary to the situation for Cl2, the weak bonding of the Cl3 ligand gives rise to two short and two long distances (**4a**: 2.48 ± 0.02 and 2.71 ± 0.12 Å; **4b**: 2.50 ± 0.02 and 2.63 ± 0.05 Å).

In the solid state structure of **1** there are two short intermolecular C–H···O interactions with H···O contacts of 2.54 Å and a C-H-O angle of 149° between the methoxy group of the unmetalated phenyl ring and neighboring triphenylphosphane C–H bonds (Figure 3). Similar values were also observed for carbonic acid dimers.[2, 16, 17]

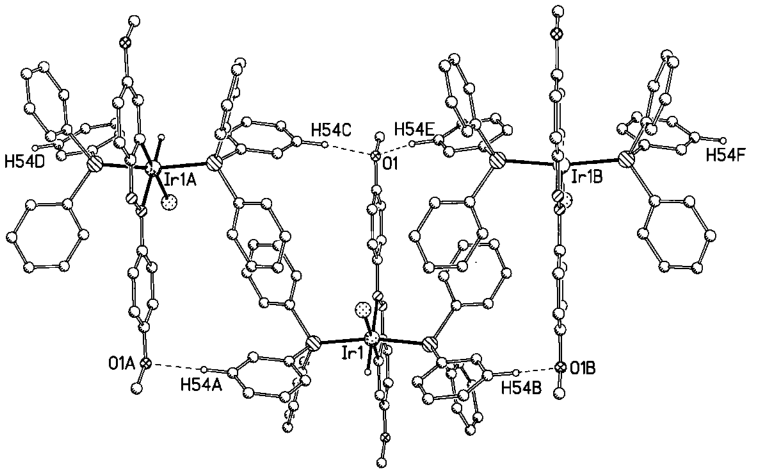

Figure 3. Short intermolecular contacts in **1**.

## Conclusions

The MH···HC interactions observed within this series of five, structurally very similar complexes give rise to bifurcated (M = Ir) and trifurcated (M = Rh) systems, while tri- and tetrafurcated arrangements are observed for MCl···HC interactions in the cases of Ir and Rh, respectively. This weak and unconventional bonding mode may have model character for the initial interactions in orthometalations as it could induce M–C bond formation and $H_2$/HX elimination without a preceding oxidative C–H addition.[7a, 18]

## Experimental Section

Unless otherwise stated, all operations were performed under an atmosphere of dry and oxygen-free nitrogen using standard Schlenk techniques. All solvents were degassed and saturated with nitrogen before use. Rhodium and iridium trichloride were obtained from Degussa AG. Commercially available triphenylphosphane (Aldrich) was used after recrystallization from ethanol. $[RhCl(PPh_3)_3]$,[19] $[IrCl(PPh_3)_3]$,[20] and $[RhCl(C_8H_{14})]_n$[21] were prepared according to literature procedures. The following instruments were used: NMR: Jeol FT-JNM-EX270; IR: Perkin–Elmer 983 and FT-IR 1600; Jeol Mstation 700 and Varian MAT212; elemental analysis: Carlo Erba 1106 and 1108 (CHN).

**Complexes 1 and 2**: $[IrCl(PPh_3)_3]$ (200 mg, 0.2 mmol) in toluene (5 mL) was added to the stirred solution of the azobenzene derivative [azoanisole (72.9 mg) or 2-chloroazobenzene (86.7 mg, 0.4 mmol)] in toluene (10 mL). After the mixture had been heated for 2 h at 100 °C, the solvent was removed and the residue was washed with petroleum ether (5 mL) and methanol ($2 \times 5$ mL), and then dried in vacuo. The compounds were recrystallized from $CH_2Cl_2$/MeOH. Yields: **1:** 100 mg (49 %), **2**: 131 mg (66 %).

**1**: Orange-brown microcrystalline powder; m.p. 236–240 °C (decomp); IR (KBr): $\tilde{\nu} = 2139$ (vw) and 2127 (w) (Ir–H) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$): $\delta = 7.58$ (d, 2H; H2′ and H6′), 7.57 (d, 1H; H2), 7.33 (dd, 12H; *ortho* H of $PPh_3$), 7.16 (t, 6H; *para* H of $PPh_3$), 7.07 (t, 12H; *meta* H of $PPh_3$), 6.57 (d, 2H; H3′ and H5′), 6.22 (dd, 1H; H3), 5.72 (s, 1H; H5), 3.79 (s, 3H; OMe of C4′), 3.07 (s, 3H; OMe of C4), −16.7 (t, 1H, $J$(P,H) = 17.2 Hz, Ir–H); anal. calcd for the solvent-free compound, which was obtained by boiling in MeOH, filtering off, and drying in vacuo; $C_{50}H_{44}ClIrN_2O_2P_2$ (994.52): C 60.39, H 4.46; N 2.82; found: C 59.64, H 4.47, N 2.77. **2**: Dark red microcrystalline powder; m.p. 227–230 °C (decomp); IR (KBr): $\tilde{\nu} = 2196$ (vw), 2160 (w), 2140, (vw) 2109 (w) (Ir–H) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$): $\delta = 7.75$ (d, 2H; H2′ and H6′), 7.33 (dd, 12H; *ortho* H of $PPh_3$), 7.23 (d, 2H; H3′ and H5′), 7.18 (t, 6H; *para* H of $PPh_3$), 7.09 (t, 12H; *meta* H of $PPh_3$), 6.61 (d, 1H; H5), 6.56 (d, 1H; H3), 5.87 (t, 1H; H4), −16.7 (t, 1H; Ir–H, $J$(P,H) = 17.2 Hz); anal. calcd for $C_{48}H_{39}Cl_2IrN_2P_2$ (968.91): C 59.50, H 4.06, N 2.89; found: C 59.10, H 4.27, N 2.91.

**Complex 3** was synthesized in an analogous manner to that described in ref. [22] from $[RhCl(C_8H_{14})_2]$ (71.6 mg, 0.2 mmol), azobenzene (72.3 mg, 0.4 mmol), and tricyclohexyl phosphane (98.2 mg, 0,66 mmol) in toluene (10 mL). Orange-brown microcrystals were obtained after three recrystallizations from $CH_2Cl_2$/MeOH. Yield: 19.8 mg (10 %); m.p. 230–235 °C (decomp); IR (KBr): $\tilde{\nu} = 2214$ (vw) and 2150 (w) (Rh–H) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$): $\delta = 8.85$ (d, 2H; H2′ and H6′), 8.11 (d, 1H; H2), 7.70 (d, 1H; H5), 7.45 (t, 2H; H3′and H5′), 7.36 (m, 1H; H4′), 7.12 (t, 1H; H3), 7.04 (t, 1H; H4), 0.73–2.10 (m, 66H of $2PCy_3$), −14.4 (dt, 1H; $J$(Rh,H) = 32.7 Hz, $J$(P,H) = 15.6 Hz, Rh–H); anal. calcd for a sample dried for 5 h in vacuo; $C_{48}H_{76}ClN_2P_2Rh \cdot CH_2Cl_2$ (966.39): C 60.90, H 8.14, N 2.90; found: C 60.16, H 8.30, N 2.82.

**Complex 4a**: Synthesized according to ref. [6].

**Complex 4b**: The mixture of $[RhCl(PPh_3)_3]$ (46.3 mg, 0.05 mmol) and 2,6-dichlorobenzylideneaniline (125 mg 0.5 mmol) in BuOH (2 mL) was heated for 5 min. After filtration the yellow residue was washed with petroleum ether ($3 \times 5$ mL) and then dried in vacuo. A light yellow powder was obtained after recrystallization from $CH_2Cl_2$. Yield: 49.4 mg (99 %); $^1H$ NMR (270 MHz, $CDCl_3$): $\delta = 8.16$ (s, 1H; H7), 7.67–6.98 (m, 31H), 6.98 (t, 1H; H4′), 6.73 (t, 2H; H3′ and H5′), 6.38 (d, 2H; H2′ and H6′), 6.10 ( t, 1H; H4); anal. calcd. for $C_{49}H_{39}Cl_3NP_2Rh \cdot CH_2Cl_2$ (998.01): C 60.17, H 4.14, N 1.40; found: C 59.90, H 4.09, N 1.40.

***$T_1$* measurements**: The spin-lattice relaxation times were measured by the inversion-recovery method (90° pulse) on a Jeol Lamda 400 spectrometer in $CDCl_2$. $T_1$ values of 0.50, 0.45, 0.42, 0.41, 0.38, 0.35, 0.39, 0.43, and 0.54 s were observed at 20, 5, 0, −5, −20, −30, −40, −50, and −65 °C, respectively. The accuracy in temperature measurement was ± 0.1 °C.

**X-ray structure determinations**: The measurements were carried out on an automated four-circle diffractometer (Siemens P4) with graphite-monochromated $Mo_{K\alpha}$ radiation, ($\lambda = 0.71073$ Å). The $\omega$ scan technique was applied with variable scan speeds (3.0–30° $min^{-1}$.). Structures were solved by direct methods SHELXTL-PLUS or SHELXTL-5.03.[23, 24] Structure refinement was carried out by full-matrix least-square methods on $F^2$ (SHELXTL-5.03) and all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms could be localized in a difference Fourier map, except the hydride ligand of **2**. However, for the present investigation all hydrogen atoms were calculated for ideal geometries by using normalized values ($d$(C–H) = 1.09 Å, $d$(Ir–H) = $d$(Rh–H) = 1.65 Å). The hydrogen atoms were allowed to ride on their corresponding preceding atoms, their isotropic thermal parameters were tied to those of adjacent atoms by a factor of 1.5. Table 5 contains the relevant crystal data.

Single crystals of **1** and **3** were obtained from $CH_2Cl_2/CH_3OH$, **2** from $CH_2Cl_2$/pentane and **4a, 4b** directly from $CH_2Cl_2$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100704. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

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Table 5. Crystal data, data collection, and refinement parameters.

| Compounds | **1** | **2** | **3** | **4b** |
|---|---|---|---|---|
| formula | $C_{50}H_{44}ClIrN_2O_2P_2 \cdot CH_2Cl_2$ | $C_{48}H_{39}Cl_2IrN_2P_2$ | $C_{48}H_{76}ClN_2P_2Rh \cdot 1.5\,CH_2Cl_2$ | $C_{49}H_{39}Cl_3NP_2Rh \cdot CH_2Cl_2$ |
| molecular weight | 1079.4 | 968.9 | 1008.8 | 997.9 |
| crystal size [mm] | $0.6 \times 0.6 \times 0.4$ | $0.5 \times 0.4 \times 0.4$ | $0.4 \times 0.4 \times 0.3$ | $0.6 \times 0.5 \times 0.4$ |
| crystal system | orthorhombic | monoclinic | monoclinic | orthorhombic |
| space group | *Pnma* | $P2_1/c$ | $P2_1/n$ | *Pbca* |
| $a$ [Å] | 19.336(2) | 9.761(5) | 13.982(2) | 18.83(1) |
| $b$ [Å] | 15.212(2) | 39.75(3) | 21.106(3) | 21.30(1) |
| $c$ [Å] | 15.778(5) | 21.52(1) | 17.484 (1) | 22.30(2) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 90 | 95.75(4) | 105.28(1) | 90 |
| $\gamma$ [°] | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 4641(2) | 8308(8) | 4977(1) | 8944(9) |
| $Z$ | 4 | 8 | 4 | 8 |
| $\mu$(Mo, $K_\alpha$) [$mm^{-1}$] | 3.161 | 3.456 | 0.657 | 0.789 |
| $\rho_{calcd}$ [$g\,cm^{-3}$] | 1.545 | 1.549 | 1.346 | 1.482 |
| $T$ (K) | 293 | 293 | 200 | 200 |
| $F$(000) | 2160 | 3856 | 2132 | 4064 |
| no. of reflns colld | 6807 | 21613 | 11309 | 12997 |
| no. of unique reflns | 5281 | 17735 | 10867 | 9816 |
| $R_{int}$ | 0.0211 | 0.0673 | 0.0527 | 0.0557 |
| no. of obs. reflns | 3945 | 7624 | 5264 | 5707 |
| obs. criterion | $F_o > 4\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ |
| $\theta$ range [°] | 3.3–54.3 | 3.6–54.1 | 4.3–54.1 | 3.4–54.2 |
| no. of refin. parameters | 318 | 997 | 536 | 532 |
| $R_1$ (obsd data) | 0.0302 | 0.0492 | 0.0448 | 0.0473 |
| $wR_2$ (all data) | 0.0739 | 0.1709 | 0.0945 | 0.0864 |
| $\Delta\rho_{max/min}$ [e Å$^{-3}$] | 0.947/−0.639 | 2.300/−1.822 | 0.914/−0.829 | 0.906/−0.709 |
| $S$ (all data) | 0.926 | 0.758 | 0.747 | 1.297 |

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