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A facile method for the synthesis of heterobimetallic chloro-bridged complexes containing $(R_3P)_2MCl$ (M = Pt or Pd) fragments

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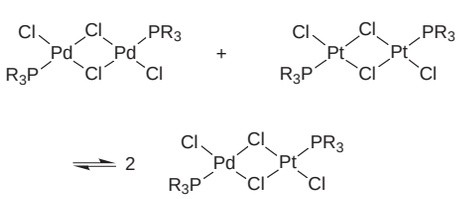
A convenient synthesis of cationic, heterobimetallic complexes of general formulae $[(R_3P)_2M^1(\mu\text{-}Cl)_2M^2(chel)]BF_4$, $[(R_3P)_2M^1(\mu\text{-}Cl)_2Rh(cod)]BF_4$ and $[(R_3P)_2M^1(\mu\text{-}Cl)_2M^3(chel)]BF_4$ (M^1, M^2 = Pd^{II} or Pt^{II}; M^3 = Rh^{III} or Ir^{III}, chel = anion of 2-phenylpyridine, benzo[*h*]quinoline, $C_6H_5CHRNMe_2$ or η^3-allyl) has been elaborated. These complexes were formed in quantitative yields by metathesis reactions of the dicationic complexes $[\{(R_3P)_2M^1(\mu\text{-}Cl)\}_2][BF_4]_2$ with the corresponding neutral, homodimeric compounds $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ and $[\{(chel)M^3(\mu\text{-}Cl)\}_2]$. Reactions with half-sandwich complexes such as $[\{(p\text{-cym})RuCl(\mu\text{-}Cl)\}_2]$, (cym = cymene), on the other hand, were shown to result in chloride transfer. The structures of $[(Bu_3P)_2Pt(\mu\text{-}Cl)_2Pd(\eta^3\text{-}C_3H_5)]BF_4$ and $[(Bu_3P)_2Pt(\mu\text{-}Cl)_2Rh(bzq)_2]BF_4$ (bzq = benzo[*h*]quinoline anion) were determined by X-ray diffraction analyses.

Introduction

The formation of heterobimetallic palladium(II) and platinum(II) phosphine complexes by means of chloro-bridge metathesis was first described by Masters *et al.*[1] Based on ^{31}P NMR spectroscopic studies they were able to show that the heterodinuclear complexes $[(R_3P)ClPd(\mu\text{-}Cl)_2PtCl(PR_3)]$ are produced in solutions containing equal amounts of $[\{(R_3P)ClPd(\mu\text{-}Cl)\}_2]$ and $[\{(R_3P)ClPt(\mu\text{-}Cl)\}_2]$, with homo- and hetero-bimetallic complexes being in a dynamic equilibrium and no significant preference for either of them (Scheme 1).



Scheme 1

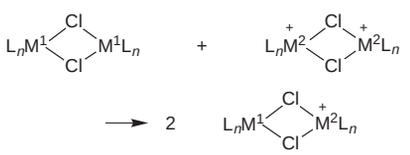
Subsequent work by Clark *et al.* has confirmed this observation[2] but a drawback for further reactions was the fact that heterobimetallic complexes were only produced in statistical amounts.[3]

In recent years a few other examples of chloro-bridged complexes in which $(R_3P)MCl_2$ or $(R_3P)_2MCl$ fragments (M = Pd or Pt) are asymmetrically joined with different transition metal complexes have been described[4–11] but a general methodology for the synthesis of such compounds is still missing. The development of useful synthetic routes seems therefore of interest, especially since these complexes are attractive starting materials for the synthesis of specific heterobimetallic complexes and potentially advantageous as catalysts for organic reactions.[12]

Here we report that heterobimetallic complexes containing $(R_3P)_2MCl$ (M = Pd or Pt) fragments together with late transition metals such as Pd^{II}, Pt^{II}, Rh^{I}, Rh^{III}, and Ir^{III} are easily accessible through metathesis reactions of dicationic phosphine complexes with various chloro-bridged complexes. Contrary to reactions with neutral phosphine complexes the yields are virtually quantitative, except for some half-sandwich complexes for which chloride transfer was observed.

Results and discussion

In view of the fact that chloro-bridged, heterobimetallic complexes of palladium(II) and platinum(II) tend to form dynamic equilibria with the respective homodimeric complexes[1–5] we thought of ways selectively to stabilize the heterodimeric form. The utilization of dicationic complexes in metathesis reactions seemed appropriate since the heterobimetallic products should be thermodynamically favored due to reduced electrostatic repulsions between the charged metal centers (Scheme 2).



Scheme 2

In accordance with the general idea outlined above the Pd–Pt complexes **1**–**3**, **5**, and **6** were obtained in quantitative yields when a solution (R = Et or Bu) or a suspension (R = Ph) of $[\{(R_3P)_2Pt(\mu\text{-}Cl)\}_2][BF_4]_2$ in dichloromethane was stirred with equivalent amounts of the orthometallated, homodimeric complexes $[\{(C_6H_4CHRNMe_2)Pd(\mu\text{-}Cl)\}_2]$ (R = H or Me) or of the allyl complex $[\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2]$. For the PEt_3 and PBu_3 complexes the reactions were complete within seconds; for the less soluble PPh_3 complexes the reactions were complete as soon as the starting material was dissolved. Isolation of the products was then achieved by evaporation of the solvent. Similarly the asymmetrically joined, binuclear palladium complexes **4** and **7** were obtained using $[\{Et_3P)_2Pd(\mu\text{-}Cl)\}_2][BF_4]_2$.

The ^{31}P NMR spectra (CH_2Cl_2) are characteristic of the new species formed: the heterodimeric products show a pronounced difference in chemical shifts as compared to the homodimeric starting materials. Furthermore the reduced symmetry of **1**–**4** results in a different spin system (AB as compared to A_4 for $[\{(R_3P)_2M(\mu\text{-}Cl)\}_2][BF_4]_2$). Accordingly two doublets are observed with a coupling constant of 16 Hz (for **1**–**3** flanked by the corresponding ^{195}Pt satellites). In order to obtain well resolved spectra of **1**–**4** they have to be recorded at temperatures below 220 K. At room temperature coalescence effects

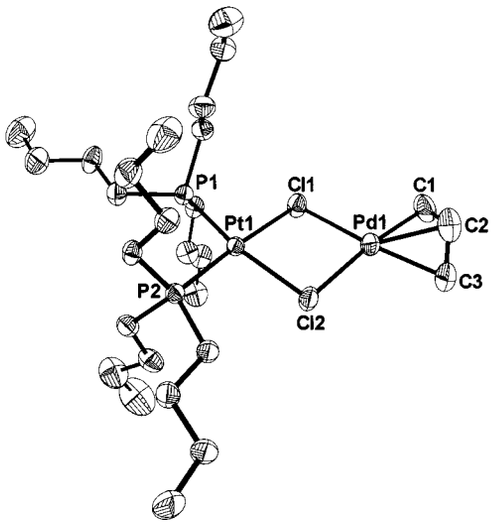
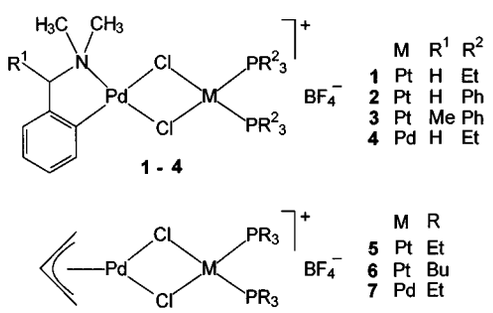
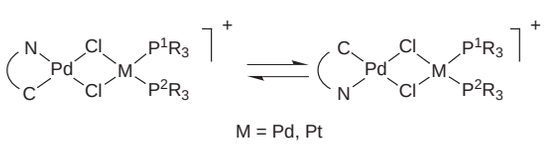


Fig. 1 Molecular structure of the cation in crystals of complex **6**. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (°): Pt1–P1 2.260(3), Pt1–P2 2.243(2), Pt1–Cl2 2.384(3), Pt1–Cl1 2.407(3), Pd1–Cl1 2.396(3), Pd1–Cl2 2.397(3) and Pd1 · · · Pt1 3.570(3); P2–Pt1–P1 98.80(9), Cl2–Pt1–Cl1 82.98(10) and Cl1–Pd1–Cl2 82.97(10).



result in significant line broadening. This dynamic process most likely consists of a "*cis-trans*" isomerization, a behavior which has been previously observed for other chloro-bridged complexes (Scheme 3).[4,13] From the coalescence temperature T_c, the coupling constant J_{PP}, and the difference in chemical shift $\Delta\nu$ of the ^{31}P NMR signals a $\Delta G^{\ddagger}$ value of 58 (±1) kJ mol^{-1} was calculated for **3**.[14]

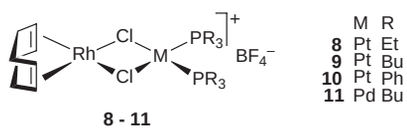


Scheme 3

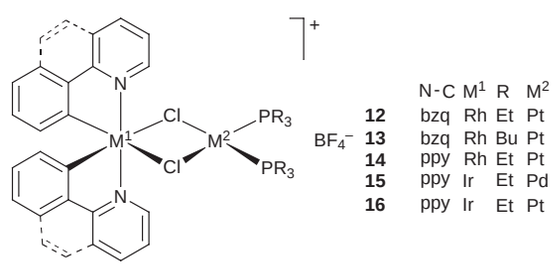
As a result of coupling to two magnetically non-equivalent phosphorus atoms (AXX′ spin system) the carbon atoms attached to the phosphorus atom of complex **5** and **6** appear as multiplets (^{13}C NMR). Similar complex signals are observed for the PR_3 groups of the other platinum complexes discussed below. The PR_3 carbon atoms of the palladium complexes (*e.g.* **7**), on the other hand, appear as simple doublets indicating that the $^3J_{PC}$ and $^4J_{PC}$ coupling *via* Pd–P bonds is less efficient.

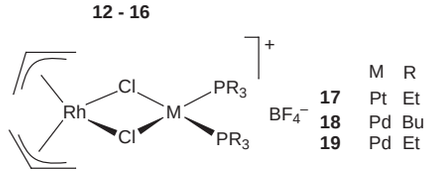
The structural assignments are supported by a single crystal X-ray analysis of complex **6** (Fig. 1). Suitable crystals can be obtained by slow diffusion of diethyl ether in a solution of **6** in dichloromethane. The square-planar configuration around the platinum atom in the cation of **6** is distorted with angle P1–Pt–P2 of 98.8° and Cl1–Pt–Cl2 of 83.0°. This distortion can be explained in terms of steric hindrance of the two bulky phosphine groups and similar values are found for the related $[\{(Ph_3P)_2Pd(\mu\text{-}Cl)\}_2][BF_4]_2$[15] and $[PtCl_4(PEt_3)_2]$.[16] The bond lengths of the two metal atoms to the surrounding ligand atoms are within the expected range. The dimeric cation has a slightly bent chloride bridge, the dihedral angle between Cl1–Pt–Cl2 and Cl1–Pd–Cl2 being 167.9°. Bent structures are occasionally found for homodimeric allylpalladium complexes[17] but not for $[\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2]$[18] and are also a feature found for some heterodimeric chloro-bridged complexes (see below).[4,5] It is interesting that upon slow crystallization for some complexes the starting materials could be isolated (*e.g.* **2** and **3**). This indicates that even with charged complexes metathesis reactions are reversible, which is in agreement with previous studies on heterobimetallic chloro-bridged complexes.

Similar to **1**–**7**, the rhodium(I) complexes **8**–**11** were obtained by reactions of $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ (cod = η^4-cycloocta-1,5-diene) with the respective palladium or platinum phosphine complex. Upon co-ordination of the (cod)RhCl fragment to the $(R_3P)_2MCl$ fragment the ^{1}H signals of the vinylic protons of the cod ligand are shifted towards higher fields. Aside from this the NMR data of the organic ligands are very similar to those observed for the starting materials except for the ^{31}P NMR spectra in which the signals of the PR_3 groups are shifted towards higher fields (≈3 ppm).



Metathesis reactions of the kind described here are not restricted to electron-rich d^8 transition metal ions such as Rh^I, Pd^{II} and Pt^{II}. This was shown using the complexes $[\{(ppy)_2M(\mu\text{-}Cl)\}_2]$ (M = Rh^{III} or Ir^{III}, ppy = 2-phenylpyridine anion), $[\{(bzq)_2Rh(\mu\text{-}Cl)\}_2]$ (bzq = benzo[*h*]quinoline anion), and $[\{(\eta^3\text{-}C_3H_5)_2Rh(\mu\text{-}Cl)\}_2]$. Orthometallated rhodium and iridium complexes of the general formula $[\{(N\text{–}C)_2M(\mu\text{-}Cl)\}_2]$ have found considerable attention because of their interesting photophysical and electrochemical properties.[19,20] The complex $[\{(ppy)_2Ir(\mu\text{-}Cl)\}_2]$, for example, is a powerful photoreducing agent.[19f] Recently, we have shown that these complexes have a high tendency to undergo metathesis reaction with other *neutral* chloro-bridged complexes such as $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ to form heterobimetallic or mixed-valence complexes in almost quantitative yields.[4] We now report that analogous reactions are possible with the *dicationic* complexes $[\{(R_3P)_2M(\mu\text{-}Cl)\}_2][BF_4]_2$ (M = Pd or Pt) to afford racemic mixtures of the dinuclear complexes **12**–**16**. Likewise, the rhodium(III) allyl complexes **17**–**19** can be obtained in quantitative yields using $[\{(\eta^3\text{-}C_3H_5)_2Rh(\mu\text{-}Cl)\}_2]$ as the starting material.





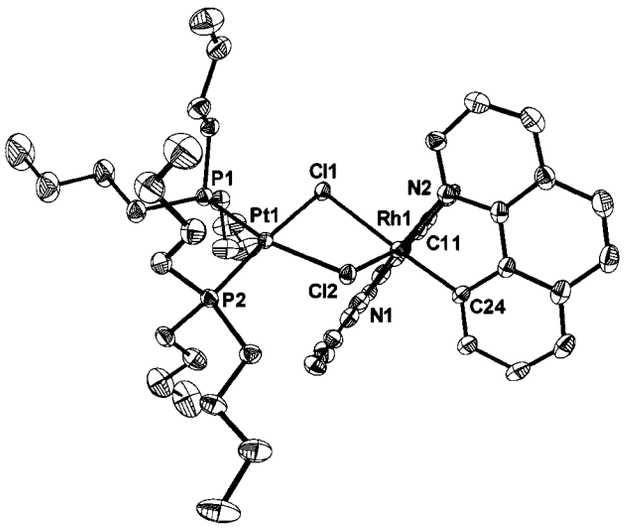


Fig. 2 Molecular structure of the cation in crystals of complex **13**. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (°): Pt1–P1 2.2589(14), Pt1–P2 2.2571(13), Pt1–Cl2 2.3799(12), Pt1–Cl1 2.4002(13), Rh1–C11 1.996(5), Rh1–C24 1.999(5), Rh1–N2 2.047(4), Rh1–N1 2.067(4), Rh1–Cl2 2.5330(13), Rh1–Cl1 2.5356(13) and Rh1 · · · Pt1 3.633(3); P2–Pt1–P1 98.56(5), Cl2–Pt1–Cl1 83.47(4), Cl1–Rh1–Cl2 77.77(4) and N2–Rh1–N1 172.3(2).

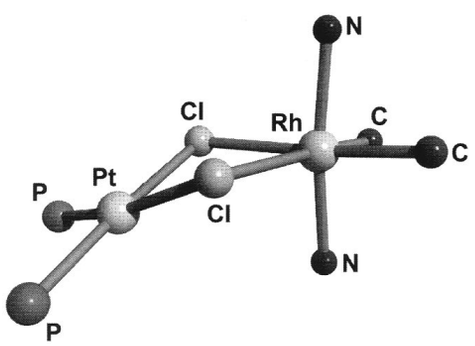
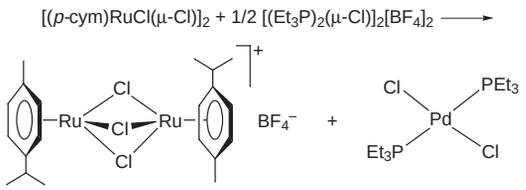


Fig. 3 Co-ordination around the two metal centers of complex **13**. Only the atoms directly bonded to the platinum and rhodium atoms are shown in order to highlight the bent chloro-bridge.

In accordance with the structures depicted, the ^{1}H and ^{13}C NMR spectra of complexes **12**–**16** show only one set of signals for the metallated phenylpyridine or benzoquinoline ligands. Similarly, only one set of signals is found for the two allyl ligands of **17**–**19**. The allyl groups themselves are asymmetrically bound to the rhodium atom with two clearly distinguishable terminal C atoms (^{13}C NMR) and five non-equivalent H atoms (^{1}H NMR). Owing to the high symmetry of **12**–**19**, dynamic processes, as observed for **1**–**4** or for $[(ppy)_2Rh(\mu\text{-}Cl)_2MCl(PR_3)]$ (M = Pd or Pt; R = Et or Bu),[4] could not be detected.

Yellow crystals of complex **13**, suitable for structure determination, were obtained by slow diffusion of diethyl ether into a solution of **13** in dichloromethane (Fig. 2). Again, the configuration around the platinum atom can be described as distorted square planar with angles and bond distances that are very similar to those found for **6**. As expected,[4,19f] the two nitrogen atoms of the metallated benzoquinoline ligands adopt a *trans* configuration. The $Pt(\mu\text{-}Cl)_2Rh$ unit is markedly non-planar with a dihedral angle of 150.6° (Fig. 3). Recently a comprehensive theoretical and structural analysis was performed in order to unravel the factors which determine the degree of bending of square-planar complexes with the general formula $[L_2M(\mu\text{-}Cl)_2ML_2]$.[21] The authors conclude that the driving forces for bending are attractive metal–metal interactions. For the dication of **13**, however, we assume that such interactions are negligible due to a Pt · · · Rh distance of 3.63 Å and that steric interactions are more likely to be the cause for the bent structure of the highly flexible[21] chloro-bridge.

Contrary to the results described so far, reactions with the chloro-bridged half-sandwich complexes $[\{(p\text{-cym})RuCl(\mu\text{-}Cl)\}_2]$, $[\{Cp^*RhCl(\mu\text{-}Cl)\}_2]$, and $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, cym = cymene) did not afford the desired heterobimetallic complexes but a mixture of products. The NMR spectroscopic studies revealed (*cf.* ref. 22) that in these systems chloride transfer occurred resulting in the formation of neutral $[MCl_2(R_3P)_2]$[23] complexes together with cationic, binuclear cymene or Cp* complexes with three chloro-bridges (Scheme 4).[23]



Scheme 4

Conclusion

We have shown that heterobimetallic, chloro-bridged complexes containing $(R_3P)_2MCl$ (M = Pd or Pt) fragments can be obtained in quantitative yields by metathesis reactions of dicationic platinum(II) and palladium(II) phosphine complexes with various dichloro-bridged complexes of the late transition metals. This simple and efficient synthetic method seems to be applicable to a wide range of compounds with the exception of complexes that have additional, labile halide ligands. The heterodinuclear complexes described here are expected to be useful starting materials for other heterobimetallic compounds. Furthermore, the electrophilic character of the cationic $(R_3P)_2MCl$ fragment may enhance the reactivity of ligands co-ordinated to the opposite metal fragment. This is especially important for compounds with (allyl)Pd and (N–C)Pd moieties since such complexes are known to be powerful reagents in organic syntheses.[24]

Experimental

General procedures

All reactions were performed under an atmosphere of dry dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and stored under dinitrogen prior to usage. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL EX 400 or a GSX 270 spectrometer. All spectra were recorded at room temperature; exceptions are indicated. The IR spectra were recorded from 4000 to 600 cm^{-1} with a Nicolet 520 FT-IR instrument.

Materials

The complexes $[\{(R_3P)_2M(\mu\text{-}Cl)\}_2][BF_4]_2$ (M = Pd or Pt; R = Et, *n*-Bu or Ph),[25] $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$,[26] $[\{(C_6H_4CH_2NMe_2)Pd(\mu\text{-}Cl)\}_2]$,[27] $[\{(C_6H_4CHMeNMe_2)Pd(\mu\text{-}Cl)\}_2]$,[28] $[\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2]$,[29] $[\{(ppy)_2M(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir),[30] $[\{(bzq)_2Rh(\mu\text{-}Cl)\}_2]$,[30b] $[\{(\eta^3\text{-}C_3H_5)_2Rh(\mu\text{-}Cl)\}_2]$,[30b] $[\{(p\text{-cym})RuCl(\mu\text{-}Cl)\}_2]$,[31] and $[\{Cp^*MCl(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir)[32] were prepared as described in the literature.

Synthesis of complexes 1–19

Dichloromethane (10 ml) was added to a mixture of 0.1 mmol of $[\{(R_3P)_2M(\mu\text{-}Cl)\}_2][BF_4]_2$ and 0.1 mmol of the respective chloro-bridged complex. After 1 h the solvent was removed *in vacuo*. The products were then stirred for 2 h in 20 ml of hexanes. Yellow powders were obtained in quantitative yield after

evaporation of the solvent under reduced pressure and drying *in vacuo*.

[(C$_6$H$_4$CH$_2$NMe$_2$)Pd(μCl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 1. mp 167–170 °C (decomp.) (Found: C, 31.08; H, 5.23; N, 1.87. $C_{21}H_{42}BCl_2F_4NP_2PdPt$ requires C, 30.40; H, 5.10; N, 1.69%). ^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C): δ 1.13–1.20 (m, 18 H, CH_3, PEt_3), 1.97 (s, br, 12 H, CH_2, PEt_3), 2.72 (s, 6 H, CH_3), 3.93 (s, 2 H, NCH_2) and 6.71–6.98 (m, C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$, 50 °C): δ 8.42 (d, ^2J = 3.4, CH_3, PEt_3), 16.74 (d, ^1J = 38.4 Hz, CH_2, PEt_3), 52.88 (NCH_3), 72.04 (CH_2N), 122.25, 125.32, 125.77, 131.37, 141.97 and 146.98 (C_6H_4). ^{31}P NMR (162 MHz, CH_2Cl_2, −50 °C): δ 13.81 (d, $^2J_{PP}$ = 18.4, $^1J_{PtP}$ = 3553) and 14.83 (d, $^2J_{PP}$ = 17.8, $^1J_{PtP}$ = 3585 Hz). IR (KBr): 1060s (BF_4) and 1042s cm^{-1} (BF_4).

[(C$_6$H$_4$CH$_2$NMe$_2$)Pd(μ-Cl)$_2$Pt(PPh$_3$)$_2$]BF$_4$ 2. mp 147–151 °C (decomp.) (Found: C, 44.12; H, 3.79; N, 1.13. $C_{45}H_{42}BCl_2F_4NP_2PdPt\cdot 2CH_2Cl_2$ requires C, 43.83; H, 3.60; N, 1.09%). ^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C): δ 2.60 (s, 6 H, CH_3), 3.93 (s, 2 H, NCH_2), 6.23 (d, ^3J = 7.9, 1H, C_6H_4), 6.69 (t, ^3J = 7.1, 1H, C_6H_4), 6.90 (d, ^3J = 6.3, 1H, C_6H_4), 6.95 (t, ^3J = 7.7 Hz, 1H, C_6H_4) and 7.26–7.52 (m, 30 H, PPh_3). ^{13}C NMR (101 MHz, CD_2Cl_2, −50 °C): δ 52.89 (NCH_3), 72.56 (CH_2N), 122.68, 125.29, 125.71, 126.39, 128.85–128.97, 131.26, 132.41–132.51, 134.32–134.65, 142.87 and 147.63 (PPh_3, C_6H_4). ^{31}P NMR (162 MHz, CH_2Cl_2, −50 °C): δ 12.23 (d, $^2J_{PP}$ = 15.5, $^1J_{PtP}$ = 3814) and 14.07 (d, $^2J_{PP}$ = 16.4, $^1J_{PtP}$ = 3813). IR (KBr): 1094s, (BF_4) and 1058s cm^{-1} (BF_4).

[(C$_6$H$_4$CHMeNMe$_2$)Pd(μ-Cl)$_2$Pt(PPh$_3$)$_2$]BF$_4$ 3. mp 151–155 °C (decomp.) (Found: C, 47.03; H, 3.92; N 1.17. $C_{46}H_{44}BCl_2F_4NP_2PdPt\cdot\frac{2}{3}CH_2Cl_2$ requires C, 47.16; H, 3.84; N, 1.18%). ^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C): δ 1.56 (d, 3 H, CHCH_3), 2.42 (s, 3 H, NCH_3), 2.74 (s, 3 H, NCH_3), 3.96 (q, 1 H, NCH), 6.27 (d, ^3J = 7.9, 1H, C_6H_4), 6.71 (t, ^3J = 7.2, 1H, C_6H_4), 6.82 (d, ^3J = 7.4, 1H, C_6H_4), 6.98 (t, ^3J = 7.6 Hz, 1H, C_6H_4) and 7.29–7.52 (m, 30 H, PPh_3). ^{13}C NMR (68 MHz, CD_2Cl_2,–50 °C): δ 19.42 (CHCH_3), 47.34 (NCH_3), 52.63 (NCH_3), 75.10 (CHN), 123.15, 125.51, 125.83, 126.50, 128.98–129.80, 131.17, 132.68, 134.33–134.84, 143.11 and 152.63 (PPh_3, C_6H_4). ^{31}P NMR (162 MHz, CH_2Cl_2, −60 °C): δ 12.52 (d, $^2J_{PP}$ = 16, $^1J_{PtP}$ = 3794) and 13.92 (d, $^2J_{PP}$ = 16, $^1J_{PtP}$ = 3822 Hz). IR (KBr): 1095s (BF_4) and 1058s cm^{-1} (BF_4).

[(C$_6$H$_4$CH$_2$NMe$_2$)Pd(μ-Cl)$_2$Pd(PEt$_3$)$_2$]BF$_4$ 4. mp 54–55 °C (decomp.) (Found: C, 33.09; H, 5.67; N, 1.78. $C_{21}H_{42}BCl_2F_4NP_2Pd_2\cdot 0.5CH_2Cl_2$ requires C, 32.96; H, 5.53; N, 1.79%). ^{1}H NMR (270 MHz, CD_2Cl_2,–70 °C): δ 1.17–1.26 (m, 18 H, CH_3, PEt_3), 1.93–1.99 (m, 12 H, CH_2, PEt_3), 2.73 (s, 6 H, CH_3), 3.92 (s, 2 H, NCH_2) and 6.82–6.96 (m, 4 H, C_6H_4). ^{13}C NMR (68 MHz, CD_2Cl_2, −70 °C): δ 8.76 (CH_3, PEt_3), 17.06 (d, ^1J = 31.6, CH_2, PEt_3), 17.20 (d, ^1J = 31.0 Hz, CH_2, PEt_3), 52.98 (NCH_3), 72.73 (CH_2N), 122.60, 125.28, 125.46, 131.89, 143.37 and 147.67 (C_6H_4). ^{31}P NMR (109 MHz, CD_2Cl_2, −70 °C): δ 42.98 (d, $^2J_{PP}$ = 3.6) and 44.64 (d, $^2J_{PP}$ = 3.5 Hz). IR (KBr): 1059s (BF_4) and 1033s cm^{-1} (BF_4).

[(η^3-C$_3$H$_5$)Pd(μ-Cl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 5. mp 135–138 °C (decomp.) (Found: C, 24.49; H, 4.70. $C_{15}H_{35}BCl_2F_4P_2PdPt$ requires C, 24.46; H, 4.79%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.20 (dt, $^3J_{HH}$ = 8.5, $^3J_{PH}$ = 18.1, 18 H, CH_3, PEt_3), 1.91–2.09 (m, 12 H, CH_2, PEt_3), 3.17 (d, ^3J = 12.1, 2 H, CH_2, allyl), 4.26 (d, ^3J = 6.7, 2 H, CH_2, allyl) and 5.59 (tt, ^3J = 12.3, $^3J'$ = 6.6 Hz, 1 H, CH, allyl). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 8.02–8.42 (m, CH_3, PEt_3), 16.92–17.21 (m, CH_2, PEt_3), 64.96 (CH_2, allyl) and 113.05 (CH, allyl). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 14.13 ($^1J_{PtP}$ = 3590 Hz). IR (KBr): 1094s (BF_4) and 1056s cm^{-1} (BF_4).

[(η^3-C$_3$H$_5$)Pd(μ-Cl)$_2$Pt(PBu$_3$)$_2$]BF$_4$ 6. mp 115–118 °C (decomp.) (Found: C, 35.85; H, 6.71. $C_{27}H_{59}BCl_2F_4P_2PdPt$ requires C, 35.84; H, 6.57%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 0.96 (t, ^3J = 6.9, 18 H, CH_3, PBu_3), 1.42–1.93 (m, 36 H, CH_2, PBu_3), 3.18 (d, ^3J = 12.1, 2 H, CH_2, allyl), 4.28 (d, ^3J = 6.6, 2 H, CH_2, allyl) and 5.59 (tt, ^3J = 12.1, $^3J'$ = 7.0 Hz, 1 H, CH, allyl). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 13.44 (CH_3, PBu_3), 23.53–24.27 (m, CH_2, PCH_2, PCH_2CH_2), 26.49 (PCH_2CH_2-CH_2), 65.04 (CH_2, allyl) and 113.05 (CH, allyl). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 5.75 ($^1J_{PtP}$ = 3598 Hz). IR (KBr): 1085s (BF_4) and 1063s cm^{-1} (BF_4).

[(η^3-C$_3$H$_5$)Pd(μ-Cl)$_2$Pd(PEt$_3$)$_2$]BF$_4$ 7. mp 121–124 °C (decomp.) (Found: C, 27.84; H, 5.52. $C_{15}H_{35}BCl_2F_4P_2Pd_2$ requires C, 27.81; H, 5.44%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.27 (dt, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 19.1, 18 H, CH_3, PEt_3), 1.95–2.07 (m, 12 H, CH_2, PEt_3), 3.10 (d, ^3J = 12.1, 2 H, CH_2, allyl), 4.18 (d, ^3J = 7.0, 2 H, CH_2, allyl) and 5.54 (tt, ^3J = 12.1, $^3J'$ = 7.0, 1 H, CH, allyl). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 8.54 (d, ^2J = 3.1, CH_3, PEt_3), 17.59 (d, ^2J = 30.5 Hz, CH_2, PEt_3), 64.15 (CH_2, allyl) and 112.53 (CH, allyl). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 44.09. IR (KBr): 1055s (BF_4) and 1039s cm^{-1} (BF_4).

[(cod)Rh(μ-Cl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 8. mp 179–184 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.26 (dt, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 18.4 Hz, 18 H, CH_3, PEt_3), 1.79–1.83 (m, 4 H, CH_2, cod), 1.98–2.06 (m, 12 H, CH_2, PEt_3), 2.45–2.48 (m, 4 H, CH_2, cod) and 4.32 (s, br, 4 H, CH, cod). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 8.27 (CH_3, PEt_3), 16.68–17.19 (m, CH_2, PEt_3), 30.69 (CH_2, cod) and 80.61 (d, $^1J_{RhC}$ = 13.8 Hz, CH, cod). ^{31}P NMR (162 MHz, CH_2Cl_2, 50 °C): δ 15.51 ($^1J_{PtP}$ = 3628 Hz). IR (KBr): 1053s (BF_4) and 1040s cm^{-1} (BF_4). (Found: C, 30.38; H, 5.35. Calc. for $C_{20}H_{42}$-$BCl_2F_4P_2PtRh$: C, 30.02; H, 5.29%).

[(cod)Rh(μ-Cl)$_2$Pt(PBu$_3$)$_2$]BF$_4$ 9. mp 86–90 °C (decomp.) (Found: C, 39.02; H, 6.46. $C_{32}H_{66}BCl_2F_4P_2PtRh\cdot\frac{1}{3}CH_2Cl_2$ requires C, 38.96; H, 6.74%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.99 (t, ^3J = 7.0 Hz, 18 H, CH_3, PBu_3), 1.46–1.94 (m, 40 H, CH_2, PBu_3, cod), 2.43–2.47 (m, 4 H, CH_2, cod) and 4.32 (s, br, 4 H, CH, cod). ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.48 (CH_3, PBu_3), 23.82–24.61 (m, CH_2, PCH_2, PCH_2CH_2), 26.61 (PCH_2-CH_2CH_2), 30.73 (CH_2, cod) and 80.52 (d, $^1J_{RhC}$ = 13.7 Hz, CH, cod). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 7.11 ($^1J_{PtP}$ = 3634 Hz). IR (KBr): 1089s (BF_4) and 1052s cm^{-1} (BF_4).

[(cod)Rh(μ-Cl)$_2$Pt(PPh$_3$)$_2$]BF$_4$ 10. mp 147–150 °C (decomp.) (Found: C, 47.68; H, 3.89. $C_{44}H_{42}BCl_2F_4P_2PtRh\cdot\frac{1}{3}CH_2Cl_2$ requires C, 47.68; H, 3.85%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.77–1.83 (m, 4 H, CH_2, cod), 2.47–2.51 (m, 4 H, CH_2, cod), 4.06 (s, br, 4 H, CH, cod) and 7.24–7.53 (m, 30 H, PPh_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ 30.72 (CH_2, cod), 80.60 (d, $^1J_{RhC}$ = 13.8 Hz, CH, cod), 125.82–126.89, 128.79–129.12, 132.48–132.52 and 134.38–134.54 (m, PPh_3). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 11.47 ($^1J_{PtP}$ = 3860 Hz). IR (KBr): 1084s (BF_4) and 1058s cm^{-1} (BF_4).

[(cod)Rh(μ-Cl)$_2$Pd(PBu$_3$)$_2$]BF$_4$ 11. mp 100–114 °C (decomp.) (Found: C, 42.39; H, 7.66. $C_{32}H_{66}BCl_2F_4P_2PdRh\cdot 0.5CH_2Cl_2$ requires C, 42.32; H, 7.32%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 0.99 (t, ^3J = 7.3 Hz, 18 H, CH_3, PBu_3), 1.44–1.97 (m, 40 H, CH_2, PBu_3, cod), 2.42–2.46 (m, 4 H, CH_2, cod) and 4.25 (s, br, 4 H, CH, cod). ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.47 (CH_3, PBu_3), 24.18 (d, $^2J_{PC}$ = 15.1, PCH_2CH_2), 25.25 (d, $^1J_{PC}$ = 29.9 Hz, PCH_2), 26.92 (d, $^3J_{PC}$ = 2.4 Hz, $PCH_2CH_2CH_2$), 30.78 (CH_2, cod) and 80.30 (d, $^1J_{RhC}$ = 14.0 Hz, CH, cod). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 36.45. IR (KBr): 1088s (BF_4) and 1054 cm^{-1} (BF_4).

[(bzq)$_2$Rh(μ-Cl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 12. mp 180–183 °C (decomp.) (Found: C, 42.92; H, 4.33; N, 2.59. $C_{38}H_{46}BCl_2F_4N_2P_2PtRh$ requires C, 43.53; H, 4.42; N, 2.67%). ^{1}H NMR (400 MHz,

Table 1 Crystal data for complexes **6** and **13**

	6	**13**
Empirical formula	$C_{27}H_{59}BCl_2F_4P_2PdPt$	$C_{51}H_{72}BCl_4F_4N_2P_2PtRh$
M	904.88	1301.66
Crystal size/mm	0.27 × 0.37 × 0.53	0.53 × 0.33 × 0.27
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	13.675(2)	13.072(2)
b/Å	14.791(3)	15.041(2)
c/Å	19.541(4)	15.622(3)
α/°		103.631(13)
β/°	104.75(2)	93.33(2)
γ/°		103.126(13)
V/Å^3	3804.7(12)	2886.7(8)
Z	4	2
D_c/g cm^{-3}	1.580	1.498
μ/mm^{-1}	4.405	2.993
θ range/°	2.51 to 23.99	2.41 to 23.97
hkl Index ranges	−15 to 15, −16 to 0, −22 to 0	−14 to 14, −17 to 0, −17 to 17
Reflections collected	6153	9416
Independent reflections	5961 (R_{int} = 0.0938)	9025 (R_{int} = 0.0099)
Absorption correction	Semiempirical	Semiempirical
Maximum and minimum transmission	0.9975 and 0.6635	0.9998 and 0.9120
Data/restraints/parameters	5961/82/389	9025/148/688
Goodness of fit on F^2	1.162	1.101
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0520, 0.1241	0.0304, 0.0805
(all data)	0.0750, 0.1426	0.0365, 0.0859
Largest difference peak, hole/e Å^{-3}	1.305, −1.527	0.851, −0.579

CD_2Cl_2): δ 1.12 (dt, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 17.9, 18 H, CH_3, PEt_3), 1.90–1.99 (m, 12 H, CH_2, PEt_3), 6.14 (d, ^3J = 7.4, 2 H, CH, bzq), 7.01 (t, ^3J = 7.3, 2 H, CH, bzq), 7.43 (d, ^3J = 7.8, 2 H, CH, bzq), 7.78–7.88 (m, 6 H, CH, bzq), 8.56 (d, ^3J = 7.4, 2 H, CH, bzq) and 9.76 (d, ^3J = 4.8 Hz, 2 H, NCH, bzq). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 8.14 (CH_3, PEt_3), 16.07–16.57 (m, CH_2, PEt_3), 121.56, 122.22, 123.83, 127.28, 128.79, 129.37, 130.12, 133.81, 137.08, 139.60, 149.79, 154.10 (CH, bzq) and 159.53 (d, $^1J_{RhC}$ = 38.6 Hz, RhC). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 13.29 ($^1J_{PtP}$ = 3528 Hz). IR (KBr): 1059s cm^{-1} (BF_4).

[(bzq)$_2$Rh(μ-Cl)$_2$Pt(PBu$_3$)$_2$]BF$_4$ 13. mp 123–125 °C (decomp.) (Found: C, 49.15; H, 5.21; N, 2.29. $C_{50}H_{70}BCl_2F_4N_2P_2PtRh$ requires C, 49.36; H, 5.80; N, 2.30%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.91 (t, ^3J = 7.2, 18 H, CH_3, PBu_3), 1.38–1.88 (m, 36 H, CH_2, PBu_3), 6.14 (d, ^3J = 7.5, 2 H, CH, bzq), 7.02 (t, ^3J = 7.6, 2 H, CH, bzq), 7.44 (d, ^3J = 8.0, ^5J = 1.3, 2 H, CH, bzq), 7.80–7.87 (m, 6 H, CH, bzq), 8.59 (d, ^3J = 8.3, 2 H, CH, bzq) and 9.74 (d, ^3J = 5.2 Hz, 2 H, NCH, bzq). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 13.46 (CH_3, PBu_3), 23.28–23.96 (m, PCH_2, PCH_2CH_2), 26.48 ($PCH_2CH_2CH_2$), 121.60, 121.97, 123.79, 127.34, 128.85, 129.47, 130.11, 133.85, 137.10, 139.55, 149.54, 154.17 (CH, bzq) and 159.59 (d, $^1J_{RhC}$ = 38.4 Hz, RhC). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 5.27 ($^1J_{PtP}$ = 3534 Hz). IR (KBr): 1089s (BF_4) and 1056s cm^{-1} (BF_4).

[(ppy)$_2$Rh(μ-Cl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 14. mp 181–183 °C (decomp.) (Found: C, 39.21; H, 4.45; N, 2.58. $C_{34}H_{46}BCl_2F_4N_2P_2PtRh\cdot\frac{2}{3}CH_2Cl_2$ requires C, 39.39; H, 4.51; N, 2.65%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.15 (dt, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 18.4, 18 H, CH_3, PEt_3), 1.92–2.00 (m, 12 H, CH_2, PEt_3), 6.12 (d, ^3J = 7.8, 2 H, CH, ppy), 6.80 (t, ^3J = 7.4, 2 H, CH, ppy), 6.99 (t, ^3J = 7.2, 2 H, CH, ppy), 7.46 (d, ^3J = 7.0, 2 H, CH, ppy), 7.62 (d, ^3J = 7.8, 2 H, CH, ppy), 7.96 (d, ^3J = 8.2, 2 H, CH, ppy), 8.04 (t, ^3J = 7.5, 2 H, CH, ppy) and 9.46 (d, ^3J = 5.6 Hz, 2 H, NCH, ppy). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 8.14 (CH_3, PEt_3), 16.09–16.60 (m, CH_2, PEt_3), 119.60, 123.00, 123.54, 124.31, 129.70, 132.66, 138.49, 143.77, 150.69, 164.17 (CH, ppy) and 163.10 (d, $^1J_{RhC}$ = 37.9 Hz, RhC). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 13.25 ($^1J_{PtP}$ = 3530 Hz). IR (KBr): 1060s (BF_4) and 1040s cm^{-1} (BF_4).

[(ppy)$_2$Ir(μ-Cl)$_2$Pd(PEt$_3$)$_2$]BF$_4$ 15. mp 180–184 °C (decomp.) (Found: C, 39.05; H, 4.72; N, 2.54. $C_{34}H_{46}BCl_2F_4IrN_2P_2Pd\cdot CH_2Cl_2$ requires C, 38.71; H, 4.46; N, 2.58%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.19 (dt, $^3J_{HH}$ = 7.7, $^3J_{PH}$ = 18.7, 18 H, CH_3, PEt_3), 1.88–1.96 (m, 12 H, CH_2, PEt_3), 6.11 (d, ^3J = 7.7, 2 H, CH, ppy), 6.69 (t, ^3J = 6.7, 2 H, CH, ppy), 6.86 (t, ^3J = 7.4, 2 H, CH, ppy), 7.43–7.46 (m, 2 H, CH, ppy), 7.56 (d, ^3J = 7.5, 2 H, CH, ppy), 7.94–7.96 (m, 4 H, CH, ppy) and 9.63 (d, ^3J = 5.9 Hz, 2 H, NCH, ppy). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 8.42 (d, ^2J = 2.8, CH_3, PEt_3), 17.20 (d, ^2J = 31.2 Hz, CH_2, PEt_3), 119.23, 122.32, 122.89, 124.18, 129.52, 131.57, 138.22, 142.21, 144.03, 150.44 and 167.57 (CH, ppy). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 43.81. IR (KBr): 1057s (BF_4) and 1031s cm^{-1} (BF_4).

[(ppy)$_2$Ir(μ-Cl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 16. mp 194–197 °C (decomp.) (Found: C, 36.94; H, 4.28; N, 2.46. $C_{34}H_{46}BCl_2F_4IrN_2P_2Pt$ requires C, 37.48; H, 4.25; N, 2.57%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.13 (dt, $^3J_{HH}$ = 7.7, $^3J_{PH}$ = 18.2 Hz, 18 H, CH_3, PEt_3), 1.86–1.98 (m, 12 H, CH_2, PEt_3), 6.10 (d, ^3J = 7.7, 2 H, CH, ppy), 6.69 (t, ^3J = 7.4, 2 H, CH, ppy), 6.88 (t, ^3J = 7.6, 2 H, CH, ppy), 7.41–7.47 (m, 2 H, CH, ppy), 7.55 (d, ^3J = 7.8, 2 H, CH, ppy), 7.94–7.96 (m, 4 H, CH, ppy) and 9.55 (d, ^3J = 6.0 Hz, 2 H, NCH, ppy). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 8.10 (CH_3, PEt_3), 15.81–16.57 (m, CH_2, PEt_3), 119.27, 122.53, 122.97, 124.24, 129.60, 131.53, 138.41, 142.71, 143.95, 150.41 and 167.35 (CH, ppy). ^{31}P NMR (109 MHz, CD_2Cl_2): δ 15.21 ($^1J_{PtP}$ = 3521 Hz). IR (KBr): 1063s (BF_4) and 1032s cm^{-1} (BF_4).

[(η^3-C$_3$H$_5$)$_2$Rh(μ-Cl)$_2$Pt(PEt$_3$)$_2$]BF$_4$ 17. mp 125–128 °C (decomp.) (Found: C, 27.19; H, 5.24. $C_{18}H_{40}BCl_2F_4P_2PtRh\cdot 0.5CH_2Cl_2$ requires C, 27.21; H, 5.06%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.22 (dt, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 18.1, 18 H, CH_3, PEt_3), 1.83 (d, ^3J = 10.6, 2 H, CH_2, allyl), 1.97–2.04 (m, 4 H, CH_2, PEt_3), 2.86 (d, ^3J = 5.9, 2 H, CH_2, allyl), 3.76 (d, ^3J = 12.3, 2 H, CH_2, allyl), 4.93–4.95 (m, 2 H, CH, allyl) and 5.12 (dd, ^3J = 6.3 Hz, 2 H, CH_2, allyl). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 8.01–8.42 (m, CH_3, PEt_3), 15.70–17.09 (m, CH_2, PEt_3), 45.52 (d, $^1J_{RhC}$ = 12.9, CH_2, allyl), 77.91 (d, $^1J_{RhC}$ = 4.8, CH_2, allyl) and 95.05 (d, $^1J_{RhC}$ = 6.1 Hz, CH, allyl). ^{31}P NMR (109 MHz, CH_2Cl_2): δ 12.84 ($^1J_{PtP}$ = 3540 Hz). IR (KBr): 1097s (BF_4), 1060s (BF_4) and 1036s cm^{-1} (BF_4).

$[(\eta^3\text{-}C_3H_5)_2Rh(\mu\text{-}Cl)_2Pd(PBu_3)_2]BF_4$ 18. mp 110–111 °C (decomp.) (Found: C, 41.40; H, 7.57. $C_{30}H_{64}BCl_2F_4P_2PdRh\cdot\frac{1}{3}CH_2Cl_2$ requires C, 41.30; H, 7.39%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 0.99 (t, ^3J = 7.1, 18 H, CH_3, PBu_3), 1.44–1.97 (m, 38 H, CH_2, allyl, PBu_3), 2.77 (d, ^3J = 6.3, 2 H, CH_2, allyl), 3.74 (d, ^3J = 12.2, 2 H, CH_2, allyl), 4.82–4.98 (m, 2 H, CH, allyl) and 5.09 (d, ^3J = 6.1 Hz, 2 H, CH_2, allyl). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 13.46 (CH_3, PBu_3), 24.17 (d, $^2J_{PC}$ = 14.3, PCH_2CH_2), 24.74 (d, $^1J_{PC}$ = 29.9, PCH_2), 26.85 ($PCH_2CH_2CH_2$), 45.10 (d, $^1J_{RhC}$ = 13.5, CH_2, allyl), 76.95 (d, $^1J_{RhC}$ = 3.3, CH_2, allyl) and 94.01 (d, $^1J_{RhC}$ = 4.6 Hz, CH, allyl). ^{31}P NMR (162 MHz, CH_2Cl_2): δ 33.10. IR (KBr): 1089s (BF_4) and 1054s cm^{-1} (BF_4).

$[(\eta^3\text{-}C_3H_5)_2Rh(\mu\text{-}Cl)_2Pd(PEt_3)_2]BF_4$ 19. mp 137–138 °C (decomp.) (Found: C, 30.94; H, 5.89. $C_{18}H_{40}BCl_2F_4P_2PdRh$ requires C, 31.54; H, 5.88%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.28 (dt, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 18.8, 18 H, CH_3, PEt_3), 1.79 (d, ^3J = 10.7 Hz, 2 H, CH_2, allyl), 1.94–2.06 (m, 4 H, CH_2, PEt_3), 2.77 (d, ^3J = 6.2, 2 H, CH_2, allyl), 3.74 (d, ^3J = 12.1, 2 H, CH_2, allyl), 4.81–4.96 (m, 2 H, CH, allyl) and 5.10 (dd, ^3J = 7.1, $^3J'$ = 1.1 Hz, 2 H, CH_2, allyl). ^{13}C NMR (68 MHz, CD_2Cl_2): δ 8.50 (d, $^2J_{PC}$ = 2.6, CH_3, PEt_3), 17.38 (d, $^1J_{PC}$ = 31.2, CH_2, PEt_3), 44.95 (d, $^1J_{RhC}$ = 12.5, CH_2, allyl), 77.22 (d, $^1J_{RhC}$ = 5.8, CH_2, allyl) and 94.91 (d, $^1J_{RhC}$ = 5.9 Hz, CH, allyl). ^{31}P NMR (162 MHz, CH_2Cl_2): δ 41.84. IR (KBr): 1084s (BF_4), 1061s (BF_4) and 1039s cm^{-1} (BF_4).

X-Ray crystallographic investigations

An Enraf-Nonius CAD 4 diffractometer was employed for data collection using Mo-Kα radiation (T = 295 K). The structures were solved by direct methods (SHELXS 86) and refined by means of full-matrix least squares procedures using SHELXL 93 (Table 1).[33] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. The BF_4 anion of complex **6** is disordered and restraints were employed. Complex **13** crystallizes with one molecule of dichloromethane. The BF_4 anion, the solvent molecule and parts of the *n*-butyl groups are disordered; restraints were used for all of them.

CCDC reference number 186/1306.

See http://www.rsc.org/suppdata/dt/1999/759/ for crystallographic files in .cif format.

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