DOI: 10.1002/ejic.200900052

Cyclometallated [C,N,O] Complexes as Metalloligands: Synthesis and Structural Characterisation of New Di-, Tri-, Tetra- and Pentanuclear Heterometallic Complexes

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Keywords: Palladium / Metallation / Phosphanes / Polynuclear complexes / Carbonyl complexes / Metalloligands

Reaction of the Schiff-base ligands 4-(4-NC_5H_4)C_6H_4C(H)=N(C_6H_3OH-2-*t*Bu-5) (**a**) and (4-NC_5H_4)C(H)=N(C_6H_3-OH-2-*t*Bu-5) (**b**) with palladium(II) acetate in toluene at 60 °C gave the tetranuclear orthometallated palladium complexes **1a** and **1b**, respectively, as air-stable solids. Treatment of **1a** and **1b** with triphenylphosphane gave the mononuclear species **2a** and **2b** upon splitting of the polynuclear structure. Reaction of **1a** with the tertiary diphosphanes $Ph_2P(CH_2)_4PPh_2$ (dppb), $Fe(C_5H_4PPh_2)_2$ (dppf), $Ph_2PC(H)=C(H)PPh_2$ (*t*-dppe) and $Ph_2P(CH_2)_6PPh_2$ (dpph), and **1b** with dppb and dppf, in a 1:2 molar ratio gave complexes **3a**–**6a** and **3b** and **4b**, respectively. Reaction of **2a**, **4a** and **6a** with hexacarbonylchromium or -tungsten and **2b** and **3b** with hexacarbonylchromium, -molybdenum or -tungsten in thf under UV activation gave complexes **7a**–**12a** and **5b**–**10b**, respectively, which contain an $M(CO)_5$ fragment coordinated to the pyridine nitrogen atom. Treatment of **2b** with $[RuCl_2(CO)(dmf)(PPh_3)_2]$ in chloroform at room temperature for 2 d afforded **11b**. Treatment of ligands (2-NC_5H_4)C(H)=N(C_6H_4OH-2) (**c**) and (2-NC_5H_4)C(H)=N(C_6H_3OH-2-*t*Bu-5) (**d**) with palladium(II) acetate yielded the mononuclear palladium acetate complexes **1c** and **1d**, respectively. Treatment of **1c** and **1d** with aqueous sodium chloride, or, alternatively, treatment of **c** and **d** with $K_2[PdCl_4]$, gave chloropalladium complexes **2c** and **2d**, respectively. Treatment of **2c** and **2d** with silver perchlorate and triphenylphosphane in acetone gave the mononuclear phosphane complexes **3c** and **3d**, respectively.

Introduction

The field of cyclometallation chemistry is an area of growing importance.[1] Metallacycles exhibit interesting luminescent and electronic properties[2] and are used as metallomesogens[3] in medicine and biology[4] and in catalytic and synthetic processes.[5] Furthermore, they possess potential applications as chiral auxiliaries[6] and are widely used as building blocks in supramolecular species.[7]

We have been interested in the study of cyclometallated complexes derived from terdentate [C,N,O] ligands such as Schiff bases with phenolate oxygen atoms,[8–12] which form tetranuclear structures with eight-membered Pd_4O_4 cores. We have also shown that the related tetranuclear species derived from terdentate [C,N,S] thiosemicarbazones react with bis(diphenylphosphanyl)methane to give new mononuclear complexes containing a monodentate phosphane, thus giving rise to a new class of bidentate [P,S] chelating metalloligands capable of coordinating a second metal centre and therefore with possible uses as building blocks in the construction of polynuclear structures.[13]

In our quest for new types of metalloligands bearing cyclometallated units, we have recently studied metallacycles containing pyridine and pyrimidine rings. Although the latter have been extensively studied as building blocks in the construction of supramolecular assemblies,[14–22] few examples in which the heterocyclic ring is part of a cyclometallated ligand have been reported.[23–25]

Herein we describe the synthesis of new terdentate [C,N,O] palladacycles bearing uncoordinated pyridine rings, a new type of metalloligand which is capable of forming di-, tri-, tetra- or pentanuclear complexes with up to three different metal centres.

Results and Discussion

For the convenience of the reader, the compounds and reactions discussed herein are shown in Schemes 1, 2 and 3. All compounds described in this paper were characterised by elemental analysis (C, H, N), IR and ^1H and $^{31}P\{^1H\}$

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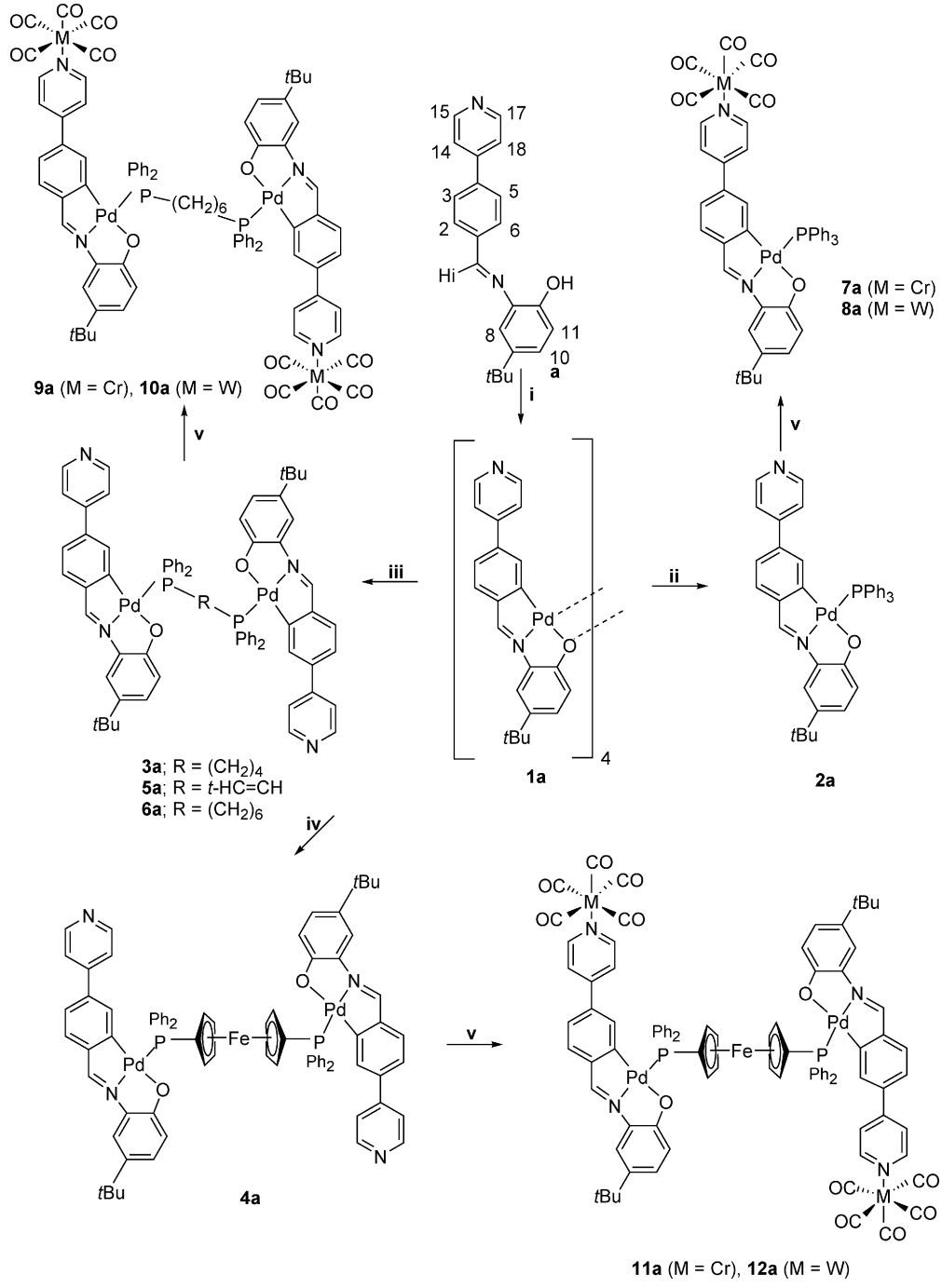
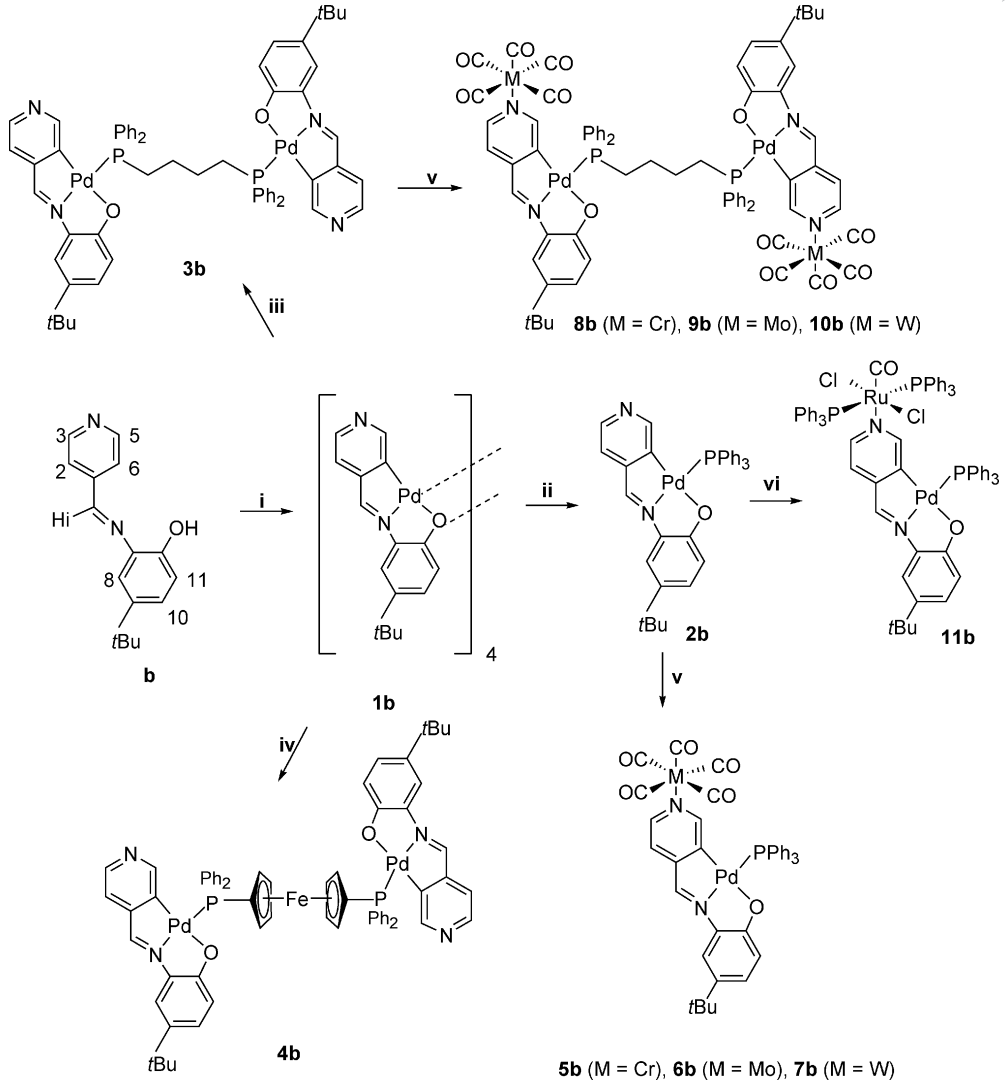
NMR spectroscopy and, in part, FAB and ESI mass spectrometry and X-ray single-crystal diffraction (data in the Experimental Section).

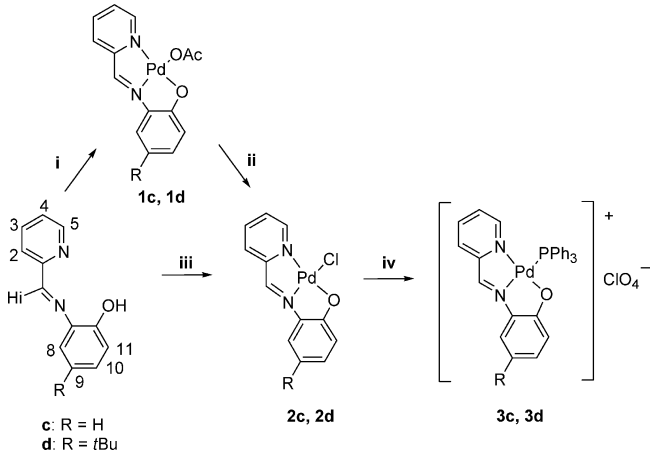
Treatment of the Schiff-base ligands **a** and **b** with palladium(II) acetate in toluene at 60 °C gives the tetranuclear *ortho*-metallated palladium complexes **1a** and **1b**, respectively, as air-stable solids. The absence of ν(COO) bands in the IR spectra precluded formation of the dinuclear species with bridging acetate ligands typically obtained when using palladium(II) acetate as the metal salt; the absence of an ν(O–H) stretch also indicates loss of the OH proton. The ν(C=N) band is shifted to lower wavenumber with respect to that of the free ligand due to *N*-coordination of the imine.[26,27] In the ^{1}H NMR spectra, absence of the H6 and OH resonances is in agreement with metallation of the ligand and OH deprotonation, respectively. All resonances were found to be highfield-shifted with respect to those of the uncoordinated ligand, with the most noticeable shifts corresponding to the H5 and HC=N signals. The low δ values for these signals arise from the tetrameric structure of



Scheme 1. (i) $Pd(OAc)_2$, toluene, 60 °C; (ii) PPh_3, acetone (1:4); (iii) Ph_2PRPPh_2, chloroform or acetone (1:2); (iv) $Fe(C_5H_4PPh_2)_2$, dichloromethane (1:2); (v) $M(CO)_6$, UV (365 nm), thf.



Scheme 2. (i) $Pd(OAc)_2$, toluene, 60 °C; (ii) PPh_3, dichloromethane (1:4); (iii) $Ph_2P(CH_2)_4PPh_2$, dichloromethane (1:2); (iv) $Fe(C_5H_4PPh_2)_2$, dichloromethane (1:2); (v) $M(CO)_6$, UV (365 nm), thf; (vi) $[RuCl_2(CO)(dmf)(PPh_3)_2]$, chloroform.



Scheme 3. (i) $Pd(OAc)_2$, toluene, 60 °C; (ii) NaCl, water/methanol; (iii) $K_2[PdCl_4]$, water/ethanol (complex **2c**); (iv) $AgClO_4$, PPh_3, acetone (1:1).

the complexes, which places these protons in the proximity of the shielding zone of the phenyl rings of a neighbouring metallated unit; a similar behaviour has been described by us previously.[8,10,11]

In the absence of an X-ray structural analysis for **1a** and **1b**, we tentatively assign a tetranuclear formulation on the basis of the mass spectrometric data and of our previous findings in related compounds. Thus, the FAB mass spectra display a cluster of peaks with the characteristic isotopic pattern corresponding to the tetranuclear structure (*m*/*z* = 1740 and 1434 for **1a** and **1b**, respectively). The mass spectrum of **1a** also shows peaks assigned to fragments corresponding to two thirds and one half of the molecular mass.

Treatment of **1a** and **1b** with triphenylphosphane gave the mononuclear species **2a** and **2b**, respectively, due to splitting of the polynuclear structure by Pd–$O_{bridging}$ bond cleavage. The ^1H NMR spectra of **2a** and **2b** show the H5 and *H*C=N proton resonances coupled to the ^{31}P nucleus [$^4J_{P,H}$ = 1.8 (**2a**) and 3.8 Hz (**2b**) for H5 and ca. 10 Hz for

*H*C=N]. In the $^{31}P\{^{1}H\}$ spectra, the unique phosphorus resonance is a singlet at $\delta \approx 34.5$ ppm for **2a** and $\delta \approx 33.0$ ppm for **2b**; these findings are in agreement with the phosphorus atom being *trans* to the nitrogen atom.[8,10,11] The *H*C=N proton resonances [$\delta = 7.98$ (**2a**) and 7.86 ppm (**2b**)] are lowfield-shifted with respect to those for **1a** and **1b**, whereas the H5 resonances [$\delta = 6.37$ (**2a**) and 7.18 ppm (**2b**)] are shifted to high field due to shielding of the phosphane phenyl rings.[8,10,11] The FAB mass spectra show the peaks assigned to the molecular ions ($m/z = 693$ and 630 for **2a** and **2b**, respectively).

Reaction of **1a** with the tertiary diphosphanes $Ph_2P(CH_2)_4PPh_2$ (dppb), $Fe(C_5H_4PPh_2)_2$ (dppf), $Ph_2PC(H)=C(H)PPh_2$ (*t*-dppe) and $Ph_2P(CH_2)_6PPh_2$ (dpph) and of **1b** with dppb and dppf, in a 1:2 molar ratio gave complexes **3a**–**6a** and **3b** and **4b**, respectively. The IR and NMR spectra of these complexes were found to be similar to those of the mononuclear triphenylphosphane complexes **2a** and **2b**. Thus, the ^{1}H NMR spectra show coupling of the H5 and *H*C=N resonances to the ^{31}P nuclei. Only one singlet is observed in the $^{31}P\{^{1}H\}$ NMR spectra for the two equivalent ^{31}P nuclei, in accordance with the symmetric nature of the dinuclear complexes. The FAB mass spectra of these complexes show a set of peaks assigned to the molecular ions, with the corresponding isotopic patterns. The crystal structure of **4a** was determined by single-crystal X-ray diffraction, thereby confirming the proposed structure.

Crystal Structure of 4a

Suitable crystals were grown by slowly concentrating a 1,2-dichloroethane/dichloromethane/*n*-hexane solution of the complex. The molecular structure is illustrated in Figure 1. Crystal data are given in the Experimental Section, and selected bond lengths and angles with estimated standard deviations are listed in Table 1.

The asymmetric unit comprises one half molecule of **4a** with an inversion centre located on the Fe atom of the dppf ligand. The structure consists of discrete trinuclear molecules in which two cyclometallated moieties are bridged by a dppf ligand. The palladium atoms are coordinated to the Schiff-base ligand through the C(6) carbon atom of the

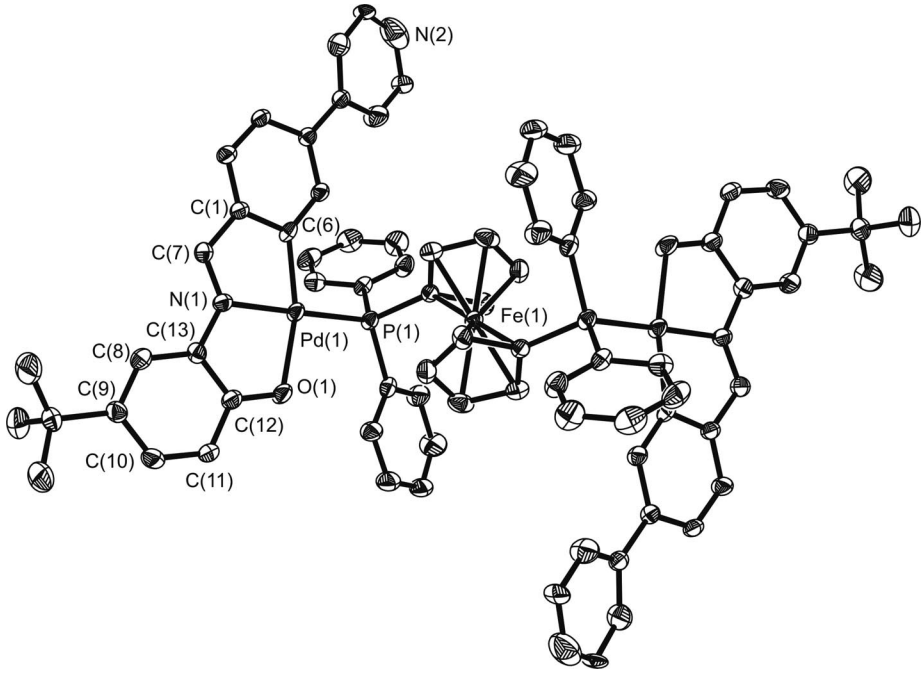


Figure 1. Molecular structure of **4a** with labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2c**, **3c** and **4a**.

2c		**3c**		**4a**	
Pd(1)–N(1)	2.018(4)	Pd(1)–N(1)	2.069(3)	Pd(1)–C(6)	1.982(7)
Pd(1)–N(2)	1.945(4)	Pd(1)–N(2)	1.989(3)	Pd(1)–N(1)	2.022(5)
Pd(1)–O(1)	2.012(3)	Pd(1)–O(1)	2.016(2)	Pd(1)–O(1)	2.101(5)
Pd(1)–Cl(1)	2.295(2)	Pd(1)–P(1)	2.300(1)	Pd(1)–P(1)	2.275(2)
N(1)–Pd(1)–N(2)	81.0(2)	N(1)–Pd(1)–N(2)	79.7(1)	C(6)–Pd(1)–N(1)	81.7(2)
N(2)–Pd(1)–O(1)	84.2(2)	N(2)–Pd(1)–O(1)	83.4(1)	N(1)–Pd(1)–O(1)	79.4(2)
O(1)–Pd(1)–Cl(1)	92.3(1)	O(1)–Pd(1)–P(1)	92.61(7)	O(1)–Pd(1)–P(1)	102.7(1)
N(1)–Pd(1)–Cl(1)	98.6(1)	N(1)–Pd(1)–P(1)	104.40(8)	C(6)–Pd(1)–P(1)	96.5(2)
N(1)–Pd(1)–O(1)	165.2(2)	N(1)–Pd(1)–O(1)	162.6(1)	C(6)–Pd(1)–O(1)	160.7(2)
N(2)–Pd(1)–Cl(1)	176.3(1)	N(2)–Pd(1)–P(1)	175.62(9)	N(1)–Pd(1)–P(1)	174.8(2)

phenyl ring, the N(1) atom, the phenolate O(1) oxygen atom, and the P(1) phosphorus atom of the coordinated dppf in a slightly distorted square-planar geometry. The angles between adjacent atoms in the coordination sphere of the palladium atom are close to the expected value of 90°, with the most noticeable distortions corresponding to N(1)–Pd(1)–O(1) [79.4(2)°] and O(1)–Pd(1)–P(1) [102.7(1)°]. The sum of the angles around the palladium atom is ca. 360°.

The Pd(1)–N(1) [2.022(5) Å] and Pd(1)–O(1) [2.101(5) Å] bond lengths are similar to others reported for related compounds;[8,28–30] the Pd(1)–O(1) bond length shows the strong *trans* influence of the C(6) carbon atom.

The geometry around the palladium atom [Pd(1), C(6), N(1), O(1), P(1)] is planar (r.m.s. = 0.060, plane1). The metallated ring [Pd(1), C(1), C(6), C(7), N(1), plane 2] and the coordination ring [Pd(1), N(1), C(8), C(13), O(1), plane 3] are also planar (r.m.s. = 0.016 and 0.048, respectively). Planes 1, 2, 3, the metallated phenyl ring and the phenol ring are approximately coplanar.

The reaction of **2a**, **4a** and **6a** with hexacarbonylchromium or -tungsten, and of **2b** and **3b** with hexacarbonylchromium, -molybdenum or -tungsten, in thf under UV activation gave **7a**–**12a** and **5b**–**10b** (see Schemes 1 and 2), which contain an $M(CO)_5$ fragment coordinated to the pyridine nitrogen atom.

The IR spectra of the complexes show three bands in the carbonyl region characteristic of $[M(CO)_5L]$ complexes with pseudo C_{4v} symmetry.[31–33] The ^{1}H NMR spectra are similar to those of the parent complexes **2a**, **4a**, **6a**, **2b** and **3b**, with only minor shifts in all resonances. The most notable difference corresponds to the protons adjacent to the pyridine nitrogen atom, where the H15/H17 resonances are shifted upfield in the spectra of complexes with the pyridine ring coordinated to the $Cr(CO)_5$ fragment and to low field in those coordinated to $W(CO)_5$. In the spectra of the **b** derivatives, the H3 and H5 resonances are lowfield-shifted [δ(H3,H5): $Cr(CO)_5$ complex < $Mo(CO)_5$ complex < $W(CO)_5$ complex]. The mass spectra of all complexes show a set of peaks assignable to the molecular ions (see Experimental Section).

The complexes are all air-stable as solids, although in solution they decompose to give, in some cases, intractable mixtures. The derivatives of ligand **b** are considerably more stable than those of **a**, and complexes prepared with the carbonylmolybdenum reagent are less stable than their chromium or tungsten analogues. This is probably the reason why we were unable to prepare the carbonylmolybdenum complexes from ligand **a** or, in cases where only small amounts of complexes were obtained, they could not be isolated. We have also observed that decomposition occurs much faster in acetone, acetonitrile or alcohols than in chloroform, dichloromethane or thf. In fact, the **b** derivatives are stable in solution for long periods without noticeable decomposition. Furthermore, we studied the decomposition of **7a** in dichloromethane, which is complete after two months, in detail and found that it leads to the tetranuclear complex **1a** and $[M(CO)_5(PPh_3)]$. The low yields obtained in some cases are possibly due to the aforementioned instability.

The reaction of **2b** with $[RuCl_2(CO)(dmf)(PPh_3)_2]$ in chloroform at room temperature for 2 d afforded **11b**. The IR spectrum of this complex shows a strong band at 1943 cm^{-1} assigned to the ν(CO) stretch. Its ^{1}H NMR spectrum is similar to that of the parent complex **2b**, although the H3 resonance is shifted considerably upfield to δ = 5.43 ppm due to the presence of the ruthenium fragment coordinated to the adjacent nitrogen atom. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets assigned to the ^{31}P nuclei of the triphenylphosphane ligands bonded to the palladium atom [δ = 31.3 ppm (1 P)] and ruthenium [δ = 22.5 ppm (2 P)] atoms. The ESI mass spectrum shows a cluster of peaks centred at *m*/*z* = 1311 for the molecular ion.

The reaction of **c** and **d** with palladium(II) acetate yielded the mononuclear acetate complexes **1c** and **1d**, respectively, rather than the expected tetranuclear compounds (see above). The ν(C=N) stretch in the IR spectra of these complexes [1572 (**1c**) and 1566 cm^{-1} (**1d**)] is shifted to lower wavenumbers with respect to those of the free ligands due to *N*-coordination of the ligands.[26,27] The differences between the strong bands assigned to the symmetric and asymmetric ν(COO) vibrations in the IR spectra [237 (**1c**) and 216 cm^{-1} (**1d**)] are in agreement with terminal acetate ligands[34] (see Experimental Section). Loss of the OH proton was confirmed by the absence of the ν(O–H) band and the OH signal in the IR and ^{1}H NMR spectra, respectively, and the presence of the H2 proton resonance in the ^{1}H NMR spectra precluded metallation of the pyridine ring. However, the H5 resonance was found to be shifted by around 0.8 ppm to high field due to coordination through the pyridine nitrogen atom. The HC=N resonance was also shifted by ca. +0.3 ppm, thereby indicating coordination through the imine nitrogen atom. This shift is smaller than that observed in the tetrameric complexes **1a** and **1b**. The FAB mass spectra show peaks centred at *m*/*z* = 303 (**1c**) and 359 (**1d**) assigned to loss of the acetate ligand.

Treatment of **1c** and **1d** with aqueous sodium chloride, or, alternatively, treatment of **c** and **d** with $K_2[PdCl_4]$, gave complexes **2c** and **2d**, respectively, after acetate/chlorine exchange. Complex **2c** has been prepared previously by treatment of the ligand with $Li_2[PdCl_4]$.[35] The ^{1}H NMR and IR spectra show absence of the O_2CMe resonance and of the ν(COO) bands, respectively. The molecular structure of complex **2c** was determined by X-ray single-crystal diffraction.

Crystal Structure of 2c

Suitable crystals were grown by slowly concentrating a chloroform/*n*-hexane solution of the complex. The molecular structure is illustrated in Figure 2. Crystal data are given in the Experimental Section, and selected bond lengths and angles with estimated standard deviations are listed in Table 1.

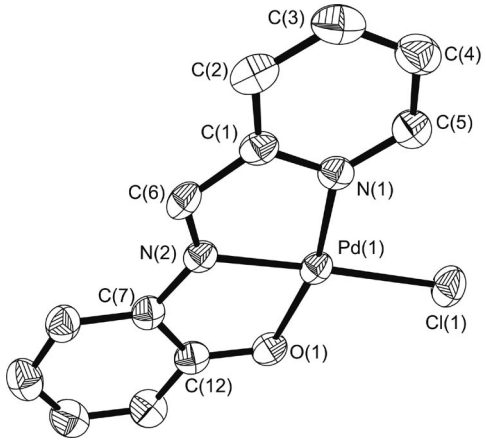


Figure 2. Molecular structure of **2c** with labelling scheme. Hydrogen atoms have been omitted for clarity.

The structure consists of discrete molecules separated by van der Waals distances in which the palladium atom is bonded in a slightly distorted square-planar geometry to the ligand through the N(1) nitrogen atom of the pyridine ring, the imine N(2) atom, the O(1) phenolate oxygen atom, and the Cl(1) chlorine atom. The angles between adjacent atoms in the coordination sphere of the palladium atom are close to the expected value of 90°, with the most noticeable distortions corresponding to N(1)–Pd(1)–N(2) [81.0(2)°] and N(1)–Pd(1)–Cl(1) [98.6(1)°]. The sum of the angles about the palladium atom is ca. 360°. The Pd(1)–N(1) [2.018(4) Å] and Pd(1)–N(2) [1.945(4) Å] bond lengths are similar to those reported for related compounds.[36–40] The Pd(1)–O(1) bond [2.012(3) Å] is somewhat shorter than the value predicted from the covalent radii of these two atoms[41] but similar to values found earlier.[28–32]

The geometry around the palladium atom [Pd(1), N(1), N(2), O(1), Cl(1)] is planar (r.m.s. = 0.035, plane1). The coordination rings [Pd(1), C(1), C(6), N(1), N(2), plane 2] and [Pd(1), N(2), C(7), C(12), O(1), plane 3] are also planar (r.m.s. = 0.010 and 0.015, respectively). Planes 1, 2 and 3, the phenol ring and the pyridine ring are nearly coplanar (largest angle 3.9° between plane 2 and the phenol ring).

The presence of an aromatic system constituted by the fusion of heterocyclic and phenyl rings, plus two five-membered metallacycles, indicates that π–π interactions are likely to play an important role in controlling the crystal packing in this type of structure. Thus, π–π interactions were observed between the pyridine ring (plane 1) and coordination plane 3 on the one hand, and between the two coordination planes 2 of two symmetrically related molecules [distance between ring centres: 3.387(2) (py–plane 3) and 3.375(2) Å (plane 2–plane 2)] on the other (Figure 3 and Table 2). In fact, within the packing dimer, the pyridine and coordination rings are not stacked in a roughly "face-to-face" fashion but rather show a so-called "slipped stacking".[42] Similar interactions have been described previously[43–45] and strongly suggest an active electronic delocalisation within the metal chelate rings with some degree of "metalloaromaticity". The metal chelate rings (planes 2) are also parallel and within the distance expected for a π–π "slipped stacking". Whether this disposition is a consequence of an attractive interaction between the "metalloaromatic" rings or is a requirement of the pyridine–plane 3 interaction has not yet been established.

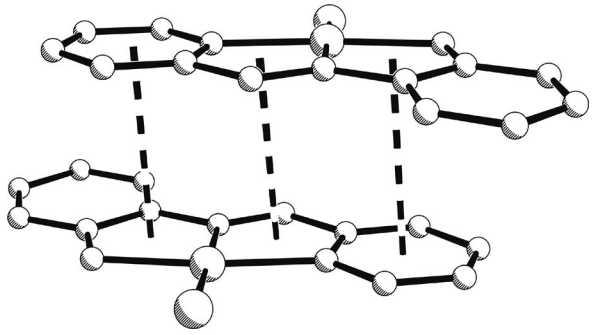


Figure 3. Intermolecular π–π stacking interactions in **2c**. Dashed lines link the centres of the rings involved in each interaction.

Table 2. Intermolecular π–π stacking parameters in the crystal of **2c** identified by using PLATON;[52] c1 and c2 are the centroids of the corresponding planes.

Parameter	Plane 3/pyridine	Plane 2/plane 2
d(c1–c2) [Å]/α [°]	3.387(3)/1.14	3.375(2)/0.02
d[⊥c1–P(2)] [Å]/β [°]	3.36–5.79	3.34–7.95
d[⊥c2–P(1)] [Å]/γ [°]	3.37–6.60	3.34–7.95

Treatment of **2c** and **2d** with silver perchlorate and triphenylphosphane in acetone gave the mononuclear complexes **3c** and **3d**, respectively, where the phosphane ligand occupies the coordination position left vacant after AgCl removal. The ^{1}H NMR spectra of these complexes show coupling of the HC=N proton to the ^{31}P nucleus ($J_{P,H} \approx$ 13 Hz). The H5 resonance does not show coupling to the phosphorus nuclei, although it is upfield-shifted due to shielding by the phosphane phenyl rings.[8,46,47] The FAB mass spectra show peaks corresponding to [(L-H)Pd(PPh$_3$)]$^+$ fragments with loss of the perchlorate counterion, and the conductivity measurements carried out in dry acetonitrile are in agreement with 1:1 electrolyte complexes.

Crystal Structure of 3c

Suitable crystals were grown by slowly concentrating an acetone solution of complex **3c**. The molecular structure is illustrated in Figure 4. Crystal data are given in the Experimental Section, and selected bond lengths and angles with estimated standard deviations are listed in Table 1.

The crystal structure comprises one [Pd{2-(NC$_5$H$_4$)C(H)=N[2′-(O)C$_6$H$_4$]}(PPh$_3$)]$^+$ cation and one ClO$_4^-$ anion per asymmetric unit. The palladium atom is bonded in a slightly distorted square-planar geometry to the N(2) nitrogen atom of the pyridine ring, the imine N(1) atom and O(1) phenolate oxygen atom of the ligand, and the phosphorus P(1) atom of the triphenylphosphane. The angles between adjacent atoms in the coordination sphere of the palladium atom are close to the expected value of 90°, with

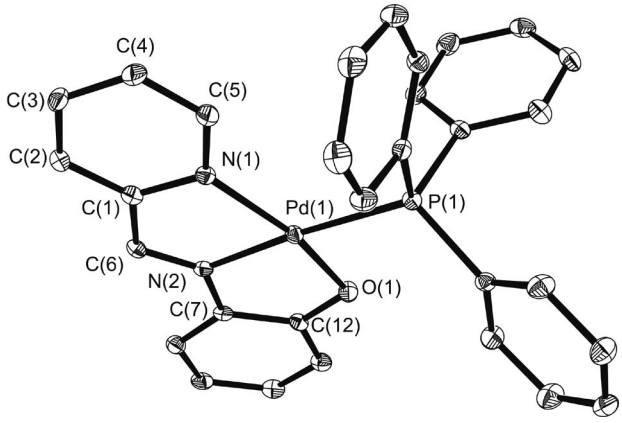


Figure 4. Structure of the cation of **3c** with labelling scheme. Hydrogen atoms have been omitted for clarity.

the most noticeable distortions corresponding to N(2)–Pd(1)–N(1) [79.7(1)°] and N(1)–Pd(1)–P(1) [104.4(1)°]. The sum of the angles about palladium is ca. 360°. The Pd–O(1) [2.016(2)], Pd–P(1) [2.300(1)], Pd–N(1) [2.069(3)] and Pd–N(2) [1.989(3)] bond lengths are close to expected values.[31,48]

The coordination sphere around the palladium atom [Pd(1), O(1), N(2), N(1), P(1), plane 1] is planar (r.m.s. = 0.029). The [Pd(1), C(1), C(6), N(1), N(2), plane 2] and [Pd(1), N(2), C(7), C(12), O(1), pane 3] rings are also planar (r.m.s. = 0.021 and 0.016, respectively) and coplanar with the pyridine and the phenol rings; consequently, the cation is planar with the exception of the phosphane phenyl groups. In the crystal, the cations are arranged in dimers with π–π stacking interactions between the metal chelate ring [Pd(1), N(2), C(7), C(12), O(1), plane 3] and the phenol ring [distance between ring centres: 3.474(2) Å; Figure 5 and Table 3].

Table 3. Intermolecular π–π stacking parameters in the crystal of **3c** identified by using PLATON;[52] c1 is the centroid of plane 3, and c2 is the centroid of the phenol ring.

Parameter	Plane 3/phenol ring
d(c1–c2) [Å]/*α* deg	3.474(2)/1.19
d[⊥c1–P(2)] [Å]/*β* [°]	3.41–10.06
d[⊥c2–P(1)] [Å]/*γ* [°]	3.42–11.04

Conclusions

We have shown that it is possible to obtain cyclometallated compounds with donor atoms that are able to bind further to additional metal atoms. Thus, compounds derived from Schiff-base ligands bearing pyridine rings may behave as metalloligands by coordination to a second metal atom through the non-coordinated nitrogen atom of the heterocycle (ligands **a** and **b**). This is hindered in the case of the *ortho*-substituted pyridines, where the palladium atom binds to the nitrogen atom itself in the absence of a Pd–C σ-bond (ligands **c** and **d**). Hence, the palladacycles described herein yield heteromultinuclear complexes upon reaction with carbonyl transition metal complexes, which in the case of the dinuclear compound with bridging dppf as starting material yields a unique pentanuclear complex bearing three different metal atoms (**11a**, **12a**). The derivatives of ligand **b**, where the heterocycle supports a Pd–C σ-bond, have been shown to be considerably more stable than

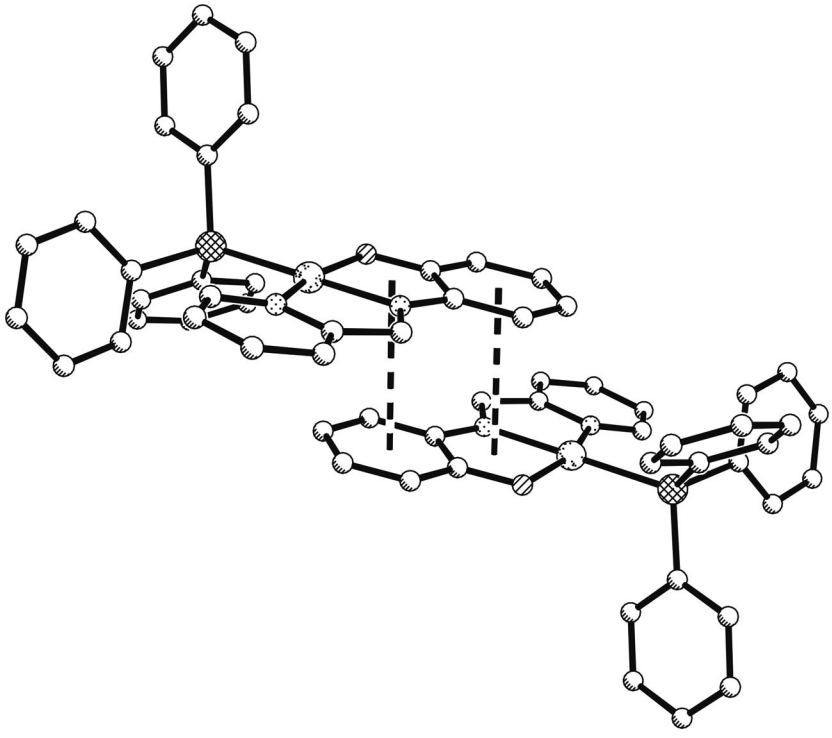


Figure 5. Intermolecular π–π stacking interactions in **3c**. Dashed lines link the centres of the rings involved in each stacking interaction.

those of **a**, where the heterocycle is a substituent of the metallated ring. Similarly, complexes prepared with the carbonylmolybdenum reagent are less stable than their chromium or tungsten analogues, and only in the case of **b** compounds could the three group-6 metal complexes be obtained.

Experimental Section

General Procedures: Solvents were purified by standard methods.[49] Chemicals were reagent grade. The phosphanes PPh_3, *t*-$Ph_2PC(H)=(H)CPPh_2$ (*t*-dppe), $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2P(CH_2)_6PPh_2$ (dpph) and $Fe(C_5H_4PPh_2)_2$ (dppf) were purchased from Aldrich-Chemie. $[RuCl_2(CO)(dmf)(PPh_3)_2]$ (dmf = *N*,*N*′-dimethylformamide) was prepared according to literature methods.[50] Microanalyses were carried out by using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded with a Bruker VECTOR 22 spectrometer. NMR spectra were obtained for $CDCl_3$ and CD_3SOCD_3 solutions and referenced to $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$) with Bruker AV-300F or AC-500F spectrometers. All chemical shifts are reported downfield from these standards. The FAB mass spectra were recorded by using a Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix. The ESI mass spectra were recorded with a QSTAR Elite mass spectrometer by using dichloromethane/acetonitrile or dichloromethane/ethanol as solvents. Conductivity measurements were performed with a CRISON GLP 32 conductivimeter for 10^{-3} M solutions in dry acetonitrile.

Syntheses of the Ligands

Preparation of 4-(4-NC_5H_4)$C_6H_4C(H)=N(C_6H_3OH$-2-*t*Bu-5) (a): 4-(4-NC_5H_4)C_6H_4CHO (0.202 g, 1.10 mmol) was added to a solution of 2-amino-4-*tert*-butylphenol (0.181 g, 1.10 mmol) in dry chloroform (50 mL) and the solution heated under reflux in a Dean–Stark apparatus. After cooling to room temperature, the chloroform was removed to give a yellow solid. Yield: 0.249 g (81%). $C_{22}H_{22}N_2O$ (330.42): calcd. C 80.0, H 6.7, N 8.5; found C 79.5, H 6.5, N 8.2. IR: $\tilde{\nu}$ = 1601 (s) ν(C=N), 3432 (w) ν(OH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.77 (s, 1 H, Hi), 8.71 (d, $^3J_{H14,H15}$ = 5.9 Hz, 2 H, H15, H17), 8.06 (d, $^3J_{H2,H3}$ = 8.3 Hz, 2 H, H2, H6 or H3, H5), 7.77 (d, $^3J_{H2,H3}$ = 8.3 Hz, 2 H, H2, H6 or H3, H5), 7.83 (br., 1 H, OH; signal from a spectrum recorded in $[D_6]$DMSO), 7.57 (d, $^3J_{H14,H15}$ = 5.9 Hz, 2 H, H14, H18), 7.34 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.28 (dd, $^3J_{H10,H11}$ = 8.7, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H10), 6.98 (d, $^3J_{H10,H11}$ = 8.7 Hz, 1 H, H11), 1.36 (s, 9 H, *t*Bu) ppm.

Schiff bases **b**, **c** and **d** were prepared in a similar manner and isolated as yellow (**b**), orange (**c**) or pale-green (**d**) solids.

(4-NC_5H_4)C(H)=N(C_6H_3OH-2-*t*Bu-5) (b): Yield: 0.252 g (90%). $C_{16}H_{18}N_2O$ (254.14): calcd. C 75.6, H 7.1, N 11.0; found C 76.1, H 7.1, N 11.1. IR: $\tilde{\nu}$ = 1602 (s) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.02 (s, 1 H, OH; signal from a spectrum recorded in $[D_6]$DMSO), 8.79 (d, $^3J_{H2,H3}$ = 4.5 Hz, 2 H, H3, H5), 8.71 (s, 1 H, Hi), 7.77 (d, $^3J_{H2,H3}$ = 4.5 Hz, 2 H, H2, H6), 7.31 (d, $^3J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.10 (dd, $^3J_{H8,H10}$ = 2.2, $^3J_{H10,H11}$ = 8.8 Hz, 1 H, H10), 6.98 (d, $^3J_{H10,H11}$ = 8.8 Hz, 1 H, H11), 1.35 (s, 9 H, *t*Bu) ppm.

(2-NC_5H_4)C(H)=N(C_6H_4OH-2) (c): Yield: 0.205 g (94%). $C_{12}H_{10}N_2O$ (198.22): calcd. C 72.7, H 5.1, N 14.1; found C 72.4, H 5.3, N 14.0. IR: $\tilde{\nu}$ = 1627 (s) ν(C=N), 3373 (s) ν(OH) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 9.98 (br., 1 H, OH), 8.70 (m, 2 H, Hi, H5), 8.37 (d, $^3J_{H2,H3}$ = 7.5 Hz, 1 H, H2), 7.84 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.5, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H3), 7.50 (m, $^3J_{H3,H4}$ = 7.5, $^3J_{H4,H5}$ = 4.8, $^4J_{H2,H4}$ = 1.2 Hz, 1 H, H4), 7.27 (dd, $^3J_{H8,H9}$ = 7.7, $^4J_{H8,H10}$ = 1.5 Hz, 1 H, H8), 7.12 (m, 1 H, H10), 6.91 (dd, $^3J_{H10,H11}$ = 7.7, $^4J_{H9,H11}$ = 1.5 Hz, 1 H, H11), 6.84 (td, $^3J_{H8,H9}$ = $^3J_{H9,H10}$ = 7.7, $^3J_{H9,H11}$ = 1.5 Hz, 1 H, H9) ppm.

(2-NC_5H_4)C(H)=N(C_6H_3OH-2-*t*Bu-5) (d): Yield: 0.254 g (91%). $C_{16}H_{18}N_2O$ (254.14): calcd. C 75.6, H 7.1, N 11.0; found C 75.5, H 7.3, N 10.7. IR: $\tilde{\nu}$ = 1588 (s) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 8.22 (br., 1 H, OH), 8.73 (s, 1 H, Hi), 8.68 (d, $^3J_{H4,H5}$ = 4.7 Hz, 1 H, H5), 8.34 (d, $^3J_{H2,H3}$ = 7.7 Hz, 1 H, H2), 7.93 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.7, $^4J_{H3,H5}$ = 1.4 Hz, 1 H, H3), 7.49 (m, $^3J_{H3,H4}$ = 7.4, $^3J_{H4,H5}$ = 4.8, $^4J_{H2,H4}$ = 1.1 Hz, 1 H, H4), 7.22 (d, $^4J_{H8,H10}$ = 2.4 Hz, 1 H, H8), 7.14 (dd, $^3J_{H10,H11}$ = 8.4 Hz, $J_{H8,H10}$ = 2.4 Hz, 1 H, H10), 6.83 (d, $^3J_{H10,H11}$ = 8.4 Hz, 1 H, H11), 1.27 (s, 9 H, *t*Bu) ppm.

Synthesis of the Complexes

Preparation of 1a: A 50-mL Schlenk pressure tube containing ligand **a** (0.100 g, 0.304 mmol), palladium acetate (0.069 g, 0.306 mmol) and dry toluene (20 mL) was sealed under argon and the resulting mixture heated at 60 °C for 24 h. After cooling to room temperature, the resulting violet solid was filtered off and dried under vacuum. Yield: 0.025 g (19%). $C_{88}H_{80}N_8O_4Pd_4$ (1739.31): calcd. C 60.7, H 4.6, N 6.4; found C 60.6, H 4.7, N 6.1. IR: $\tilde{\nu}$ = 1578 (m sh) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.77 (d, $^3J_{H14,H15}$ = 6.5 Hz, 2 H, H15, H17), 7.84 (s, 1 H, Hi), 7.53 (d, $^3J_{H14,H15}$ = 6.5 Hz, 2 H, H14, H18), 7.26 (d, $^3J_{H2,H3}$ = 6.0 Hz, 1 H, H2), 7.14–7.06 (m, 3 H, H3, H5, H10), 6.89 (d, $^4J_{H8,H10}$ = 1.4 Hz, 1 H, H8), 6.61 (d, $^3J_{H10,H11}$ = 8.8 Hz, 1 H, H11), 1.29 (s, 9 H, *t*Bu) ppm. FAB MS: *m*/*z* 869.2 $[\{(L\text{-}H_2)Pd\}_2H]^+$, 1304 $[\{(L\text{-}H_2)Pd\}_3H]^+$, 1740 $[\{(L\text{-}H_2)Pd\}_4H_2]^+$.

Complexes **1b**, **1c** and **1d** were prepared in a similar manner and isolated as violet solids.

1b: Yield: 0.023 g (23%). $C_{64}H_{64}N_8O_4Pd_4$ (1458.95): calcd. C 53.6, H 4.5, N 7.1; found C 53.7, H 4.7, N 7.3. IR: $\tilde{\nu}$ = 1567 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.38 (d, $^3J_{H2,H3}$ = 5.4 Hz, 1 H, H3), 7.69 (br., 1 H, Hi or H5), 7.41 (br., 1 H, Hi or H5), 7.10 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 2.0 Hz, 1 H, H10), 6.93 (d, $^3J_{H8,H10}$ = 2.0 Hz, 1 H, H8), 6.90 (d, $^3J_{H2,H3}$ = 5.4 Hz, 1 H, H2), 6.52 (d, $^3J_{H10,H11}$ = 9.0 Hz, 1 H, H11), 1.21 (s, 9 H, *t*Bu) ppm. FAB-MS: *m*/*z* = 1434 $[(L\text{-}H_2)Pd]_4^+$.

1c: Yield: 0.107 g (97%). $C_{14}H_{12}N_2O_3Pd$ (362.68): calcd. C 46.4, H 3.3, N 7.7; found C 46.2, H 3.6, N 7.4. IR: $\tilde{\nu}$ = 1572 (s, sh) ν(C=N), 1556 (s, sh) ν_{as}(COO), 1319 (m) ν_s(COO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H, Hi), 8.15 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.8, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H3), 7.91 (d, $^4J_{H4,H5}$ = 5.4 Hz, H5), 7.76 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.59 (m, 1 H, H4), 7.35 (dd, $^3J_{H8,H9}$ = 8.1, $^4J_{H8,H10}$ = 1.3 Hz, 1 H, H8), 7.04 (m, 1 H, H10), 6.48–6.40 (m, 2 H, H9, H11), 1.82 (s, 3 H, OAc) ppm. FAB MS: *m*/*z* = 303 $[(L\text{-}H)Pd]^+$.

1d: Yield: 0.098 g (77%). $C_{18}H_{20}N_2O_3Pd$ (418.78): calcd. C 51.7, H 4.8, N 6.7; found C 52.2, H 4.3, N 7.0. IR: $\tilde{\nu}$ = 1566 (m, sh) ν(C=N), 1540 (m, sh) ν_{as}(COO), 1324 (m) ν_s(COO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, Hi), 8.13 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.8, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H3), 7.89 (d, $^4J_{H4,H5}$ = 5.6 Hz, H5), 7.72 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.55 (m, 1 H, H4), 7.28 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.14 (dd, $^3J_{H10,H11}$ = 8.9, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H10), 6.39 (d, $^3J_{H10,H11}$ = 8.9 Hz, 1 H, H11), 1.87 (s, 3 H, OAc), 1.21 (s, 9 H, *t*Bu) ppm. FAB MS: *m*/*z* = 359 $[(L\text{-}H)Pd]^+$.

Preparation of Complex 2a: PPh_3 (0.056 g, 0.209 mmol) was added to a suspension of **1a** (0.091 g, 0.052 mmol) in acetone (20 mL). This mixture was stirred for 72 h and the solvent removed to give a violet solid, which was recrystallised from dichloromethane/hexane and dried under vacuum. Yield: 0.016 g (11%). $C_{40}H_{35}N_2OPPd$ (697.11): calcd. C 68.9, H 5.1, N 4.0; found C 68.1, H 5.3, N 3.9. IR: $\tilde{\nu}$ = 1538 (m, sh) ν(C=N) cm^{-1}. ^1H NMR (300 MHz,H_{15} = 5.7 Hz, 2 H, H15,H17), 7.98 (d, $^4J_{P,Hi}$ = 10.2 Hz, 1 H, Hi), 7.21 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.10 (dd, $^3J_{H2,H3}$ = 7.8, $^4J_{H3,H5}$ = 1.7 Hz, 1 H, H3), 7.07 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.04 (dd, $^3J_{H10,H11}$ = 8.7, $^3J_{H8,H10}$ = 2.2 Hz, 1 H, H10), 6.66 (d, $^3J_{H14,H15}$ = 5.7 Hz, 2 H, H14, H18), 6.48 (d, $^3J_{H10,H11}$ = 8.7 Hz, 1 H, H11), 6.37 (dd, $^4J_{P,H5}$ = 3.8, $^4J_{H3,H5}$ = 1.7 Hz, 1 H, H5] ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 34.58 (s) ppm. FAB MS: *m*/*z* = 696 $[(L\text{-}H_2)Pd(PPh_3)]^+$.

Complexes **3a**, **4a**, **5a**, **6a**, **2b**, **3b** and **4b** were prepared as violet solids according to a similar procedure by using dichloromethane (**4a**, **2b**, **3b**, **4b**), chloroform (**3a**, **6a**) or acetone (**5a**) as solvents. Complex **5a** was recrystallised from acetone/hexane instead of dichloromethane/hexane. An excess of the cyclometallated complex **1b** (10%) was used in the synthesis of **2b**.

3a: Yield: 0.113 g (42%). $C_{72}H_{68}N_4O_2P_2Pd_2$ (1296.12): calcd. C 66.7, H 5.3, N 4.3; found C 67.1, H 5.5, N 4.0. IR: $\tilde{\nu}$ = 1535 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, $^3J_{H14,H15}$ = 6.1 Hz, 2 H, H15, H17), 7.91 (d, $^4J_{P,Hi}$ = 8.2 Hz, 1 H, Hi), 7.16 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.09–7.05 (m, 2 H, H3, H8), 7.0 (dd, $^3J_{H10,H11}$ = 8.8, $^4J_{H8,H10}$ = 2.1 Hz, 1 H, H10), 6.69 (d, $^3J_{H14,H15}$ = 6.1 Hz, 2 H, H14, H18), 6.39–6.35 (m, 2 H, H5, H11), 1.28 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 30.22 (s) ppm. FAB MS: *m*/*z* = 1296 $[(L\text{-}H_2)_2Pd_2(dppb)]^+$.

4a: Yield: 0.151 g (51%). $C_{78}H_{68}FeN_4O_2P_2Pd_2$ (1422.22): calcd. C 65.8, H 4.8, N 3.9; found C 66.1, H 5.0, N 3.6. IR: $\tilde{\nu}$ = 1534 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, $^3J_{H14,H15}$ = 5.2 Hz, 2 H, H15, H17), 7.95 (d, $^4J_{P,Hi}$ = 10.5 Hz, 1 H, Hi), 7.20 (d, $^3J_{H2,H3}$ = 7.7 Hz, 1 H, H2), 7.09 (dd, $^3J_{H2,H3}$ = 7.7, $^4J_{H3,H5}$ = 1.4 Hz, 1 H, H3), 7.07 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.03 (dd, $^3J_{H10,H11}$ = 8.7, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H10), 6.62 (d, $^3J_{H14,H15}$ = 5.2 Hz, 2 H, H14, H18), 6.51 (d, $^3J_{H10,H11}$ = 8.7 Hz, 1 H, H11), 6.33 (dd, $^4J_{P,H5}$ = 3.9, $^4J_{H3,H5}$ = 1.4 Hz, 1 H, H5], 5.22–4.28 (br., $CH_{ferrocene}$), 1.28 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 24.91 (s) ppm. FAB MS: *m*/*z* = 1424 $[(L\text{-}H_2)_2Pd_2(dppf)]^+$.

5a: Yield: 0.208 g (79%). $C_{70}H_{62}N_4O_2P_2Pd_2$ (1266.05): calcd. C 66.4, H 4.9, N 4.4; found C 66.0, H 5.2, N 4.2. IR: $\tilde{\nu}$ = 1535 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, $^3J_{H14,H15}$ = 5.3 Hz, 2 H, H15, H17), 7.16 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.09–7.05 (m, 3 H, H3, H8, H10), 6.71 (d, $^3J_{H14,H15}$ = 5.3 Hz, 2 H, H14, H18), 6.43 (d, $^3J_{H10,H11}$ = 9.4 Hz, 1 H, H11), 6.35 (m, 1 H, H5), 1.30 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 30.22 (s), 30.88 (s) ppm. FAB MS: *m*/*z* = 1267 $[\{(L\text{-}H_2)_2Pd_2(t\text{-}dppe)\}H]^+$.

6a: Yield: 0.110 g (40%). $C_{74}H_{72}N_4O_2P_2Pd_2$ (1324.18): calcd. C 67.1, H 5.5, N 4.2; found C 66.7, H 5.6, N 4.1. IR: $\tilde{\nu}$ = 1534 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.38 (d, $^3J_{H14,H15}$ = 5.8 Hz, 2 H, H15, H17), 7.93 (d, $^4J_{P,Hi}$ = 10.2 Hz, 1 H, Hi), 7.16 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.09–7.02 (m, 2 H, H3, H8), 6.70 (dd, $^3J_{H10,H11}$ = 8.8, $^4J_{H8,H10}$ = 2.1 Hz, 1 H, H10), 6.69 (d, $^3J_{H14,H15}$ = 5.8 Hz, 2 H, H14, H18), 6.51 (d, $J_{H10,H11}$ = 8.8 Hz, 1 H, H11), 6.38 (dd, $^4J_{P,H5}$ = 3.9, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H5), 1.27 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 29.98 (s) ppm. FAB MS: *m*/*z* = 1325 $[\{(L\text{-}H_2)_2Pd_2(dpph)\}H]^+$.

2b: Yield: 0.030 g (23%). $C_{34}H_{31}N_2OPPd$ (621.02): calcd. C 65.7, H 5.0, N 4.5; found C 65.4, H 4.7, N 4.3. IR: $\tilde{\nu}$ = 1575 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, $^3J_{H2,H3}$ = 4.8 Hz, 1 H, H3), 7.86 (d, $^4J_{P,Hi}$ = 9.90 Hz, 1 H, Hi), 7.18 (d, $^4J_{H5,P}$ = 1.8 Hz, 1 H, H5), 7.06 (dd, $^3J_{H10,H11}$ = 8.8, $^4J_{H8,H10}$ = 2.3 Hz, 1 H, H10), 7.01 (d, $^4J_{H8,H10}$ = 2.3 Hz, 1 H, H8), 6.91 (d, $^3J_{H2,H3}$ = 4.8 Hz, 1 H, H2), 6.45 (d, $^3J_{H10,H11}$ = 8.8 Hz, H11), 1.25 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 33.02 (s) ppm. FAB MS: *m*/*z* = 620 $[(L\text{-}H_2)Pd(PPh_3)]^+$.

3b: Yield: 0.071 g (30%). $C_{60}H_{60}N_4O_2P_2Pd_2$ (1143.93): calcd. C 63.0, H 5.3, N 4.9; found C 62.8, H 5.5, N 4.7. IR: $\tilde{\nu}$ = 1578 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, $^3J_{H2,H3}$ = 4.7 Hz, 1 H, H3), 7.03 (dd, $^3J_{H10,H11}$ = 8.8, $^4J_{H8,H10}$ = 2.3 Hz, 1 H, H10), 6.98 (d, $^4J_{H8,H10}$ = 2.3 Hz, 1 H, H8), 6.85 (d, $^3J_{H2,H3}$ = 4.7 Hz, 1 H, H2), 6.34 (d, $^3J_{H10,H11}$ = 8.8 Hz, H11), 1.27 (s, 9 H, *t*Bu) ppm; Hi and H5 signals hidden beneath the phenyl proton signals. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 28.46 (s) ppm. FAB MS: *m*/*z* = 892 $[\{(L\text{-}H_2)Pd_2(dppb)\}H]^+$, 1144 $[(L\text{-}H_2)_2Pd_2\text{-}(dppb)]^+$.

4b: Yield: 0.135 g (51%). $C_{66}H_{60}N_4FeO_2P_2Pd_2$ (1271.84): calcd. C 62.3, H 4.7, N 4.4; found C 61.6, H 4.9, N 4.2. IR: $\tilde{\nu}$ = 1576 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, $^3J_{H2,H3}$ = 4.6 Hz, 1 H, H3), 7.83 (d, $^4J_{P,Hi}$ = 10.1 Hz, 1 H, Hi), 7.11 (d, $^3J_{P,H5}$ = 1.9 Hz, 1 H, H5), 7.07 (dd, $^3J_{H10,H11}$ = 8.9, $^4J_{H8,H10}$ = 2.3 Hz, 1 H, H10), 7.03 (d, $^4J_{H8,H10}$ = 2.3 Hz, 1 H, H8), 6.89 (d, $^3J_{H2,H3}$ = 4.6 Hz, 1 H, H2), 6.50 (d, $^3J_{H10,H11}$ = 8.9 Hz, 1 H, H11], 5.14–4.30 (br., $CH_{ferrocene}$), 1.28 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 23.09 (s) ppm. FAB MS: *m*/*z* = 928 $[(L\text{-}H_2)Pd(dppf)]^+$, 1271 $[\{(L\text{-}H_2)_2Pd_2(dppf)\}H]^+$.

Preparation of 7a: A solution of $Cr(CO)_6$ (14.4 mg, 0.065 mmol) in dry and deoxygenated tetrahydrofuran (6 mL) was prepared in a 25-mL Schlenk flask under argon and irradiated with UV light (365 nm) for 45 min. The resulting yellow solution was transferred dropwise by cannula to a deoxygenated solution of **2a** (43.2 mg, 0.062 mmol) in thf (8 mL). During the addition, the violet solution of **2a** changed colour to dark blue. This solution was stirred for 24 h and the solvent removed under vacuum to give a blue solid, which was chromatographed on a column packed with alumina. Elution with dichloromethane afforded an oil, which was treated with light petroleum (60–80 °C) and the blue solid obtained filtered off and dried in vacuo. Yield: 7.2 mg (13%). $C_{45}H_{35}CrN_2O_6PPd$ (889.16): calcd. C 60.8, H 4.0, N 3.1; found C 61.1, H 4.3, N 2.9. IR: $\tilde{\nu}$ = 1606 (m) ν(C=N), 2065 (w), 1980 (w, sh), 1924 (s) ν(CO) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, $^3J_{H14,H15}$ = 6.5 Hz, 2 H, H15, H17), 8.02 (m, 1 H, Hi), 7.25 (d, $^3J_{H2,H3}$ = 6.5 Hz, 1 H, H2), 7.08–7.12 (m, 3 H, H3, H8, H10), 6.57 (d, $^3J_{H14,H15}$ = 4.5 Hz, 2 H, H14, H18), 6.53 (br., 1 H, H11), 6.38 (br., 1 H, H5), 1.27 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 34.50 (s) ppm. ESI-MS: *m*/*z* = 889 $[(L\text{-}H_2)Pd(PPh_3)\{Cr(CO)_5\}H]^+$.

Complexes **8a**–**12a** and **5b**–**10b** were obtained as blue (**8a**–**12a**) or green (**5b**–**10b**) solids by using the appropriate hexacarbonyl complex and applying a procedure similar to that described for **7a**.

8a: Yield: 21.5 mg (34%). $C_{45}H_{35}N_2O_6PPdW$ (1021.00): calcd. C 52.9, H 3.4, N 2.7; found C 52.5, H 4.3, N 2.5. IR: $\tilde{\nu}$ = 1608 (m) ν(C=N), 2069 (w), 1977 (w sh), 1919 (s) ν(CO) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.52 (d, $^3J_{H14,H15}$ = 6.5 Hz, 2 H, H15,H17), 7.98 (d, $^4J_{P,Hi}$ = 10.0 Hz, 1 H, Hi), 7.24 (d, $^3J_{H2,H3}$ = 8.0 Hz, 1 H, H2), 7.10 (dd, $^3J_{H2,H3}$ = 8.0, $^4J_{H3,H5}$ = 1.75 Hz, 1 H, H3), 7.08–7.05 (m, 2 H, H8, H10), 6.59 (d, $^3J_{H14,H15}$ = 6.5 Hz, 2 H, H14, H18), 6.49 (d, $^3J_{H10,H11}$ = 9.5 Hz, 1 H, H11), 6.35 (dd, $^4J_{P,H5}$ = 3.8, $^4J_{H3,H5}$ = 1.75 Hz, 1 H, H5), 1.29 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR

(121.49 MHz, $CDCl_3$): δ = 34.51 (s) ppm. ESI-MS: *m*/*z* = 1020 [(L-H_2)Pd(PPh_3){$W(CO)_5$}H_2]$^+$.

9a: Yield: 15.9 mg (15%). $C_{84}H_{72}Cr_2N_4O_{12}P_2Pd_2$ (1708.27): calcd. C 59.1, H 4.2, N 3.3; found C 58.4, H 4.3, N 3.0. IR: $\tilde{\nu}$ = 1606 (m) ν(C=N), 2067 (w), 1978 (w, sh), 1900 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, $^3J_{H14,H15}$ = 6.6 Hz, 2 H, H15, H17), 7.96 (d, $^4J_{P,Hi}$ = 10.2 Hz, 1 H, Hi), 7.21 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.07–7.04 (m, 3 H, H3, H8, H10), 6.53 (d, $^3J_{H14,H15}$ = 6.6 Hz, 2 H, H14, H18), 6.47 (d, $^3J_{H10,H11}$ = 9.3 Hz, 1 H, H11), 6.30 (dd, $^4J_{P,H5}$ = 3.6, $^4J_{H3,H5}$ = 1.8 Hz, 1 H, H5), 1.27 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 34.53 (s) ppm. ESI-MS: *m*/*z* = 1324 [{(L-H_2)$_2$$Pd_2$(dpph)}H]$^+$, 1516 [{($LH_2$)$_2$-$Pd_2$(dpph)}{$Cr(CO)_5$}H]$^+$, 1709.16 [{(L-$H_2$)$_2$$Pd_2$(dpph)}{Cr-$(CO)_5$}$_2$H]$^+$.

10a: Yield: 89.2 mg (73%). $C_{84}H_{72}N_4O_{12}P_2Pd_2W_2$ (1971.96): calcd. C 51.2, H 3.7, N 2.8; found C 50.8, H 3.7, N 3.1. IR: $\tilde{\nu}$ = 1607 (m) ν(C=N), 2069 (w), 1975 (w, sh), 1887 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, $^3J_{H14,H15}$ = 6.7 Hz, 2 H, H15, H17), 7.93 (d, $^4J_{P,Hi}$ = 10.2 Hz, 1 H, Hi), 7.18 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.06–7.03 (m, 3 H, H3, H8, H10), 6.59 (d, $^3J_{H14,H15}$ = 6.7 Hz, 2 H, H14, H18), 6.49 (d, $^3J_{H10,H11}$ = 9.6 Hz, 1 H, H11), 6.32 (dd, $^4J_{P,H5}$ = 3.6, $^4J_{H3,H5}$ = 1.8 Hz, 1 H, H5), 1.27 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 30.30 (s) ppm. FAB MS: *m*/*z* = 1969 [{(L-H_2)$_2$$Pd_2$(dpph)}{$W(CO)_5$}$_2$]$^+$.

11a: Yield: 35.9 mg (32%). $C_{88}H_{68}Cr_2FeN_4O_{12}P_2Pd_2$ (1808.13): calcd. C 58.4, H 3.8, N 3.1; found C 58.0, H 4.0, N 2.9. IR: $\tilde{\nu}$ = 1605 (m) ν(C=N), 2065 (w), 1980 (w, sh), 1916 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, $^3J_{H14,H15}$ = 6.6 Hz, 2 H, H15, H17), 7.92 (d, $^4J_{P,Hi}$ = 10.2 Hz, 1 H, Hi), 7.19 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.06–7.01 (m, 3 H, H3, H8, H10), 6.52–6.47 (m, 3 H, H11, H14, H18), 6.25 (dd, $^4J_{P,H5}$ = 4.1, $^4J_{H3,H5}$ = 1.7 Hz, 1 H, H5), 5.20–4.31 (m, $CH_{ferrocene}$), 1.27 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 24.68 (s) ppm. FAB MS: *m*/*z* = 1809 [{(L-H_2)$_2$$Pd_2$(dppf)}{$Cr(CO)_5$}$_2$$H_2$]$^+$.

12a: Yield: 87.3 mg (68%). $C_{88}H_{68}FeN_4O_{12}P_2Pd_2W_2$ (2071.81): calcd. C 51.0, H 3.3, N 2.7; found C 50.8, H 3.5, N 2.5. IR: $\tilde{\nu}$ = 1607 (m) ν(C=N), 2069 (w), 1974 (w, sh), 1883 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, $^3J_{H14,H15}$ = 6.6 Hz, 2 H, H15, H17), 7.92 (d, $^4J_{P,Hi}$ = 10.5 Hz, 1 H, Hi), 7.21 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.09–7.01 (m, 3 H, H3, H8, H10), 6.53–6.48 (m, 3 H, H11, H14, H18), 6.28 (dd, $^4J_{P,H5}$ = 3.9, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H5), 5.22–4.31 (m, $CH_{ferrocenes}$), 1.27 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 24.67 (s) ppm. FAB MS: *m*/*z* = 2072 [{(L-H_2)$_2$$Pd_2$(dppf)}{$W(CO)_5$}$_2$]$^+$.

5b: Yield: 10.1 mg (6%). $C_{39}H_{31}CrN_2O_6PPd$ (813.06): calcd. C 57.6, H 3.8, N 3.4; found C 57.0, H 4.0, N 3.2. IR: $\tilde{\nu}$ = 1522 (m, sh), ν(C=N), 2061 (w), 1949 (w, sh), 1894 (s) ν(CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, $^3J_{H2,H3}$ = 5.5 Hz, 1 H, H3), 7.83 (d, $^4J_{P,Hi}$ = 10.0 Hz, 1 H, Hi), 7.23 (d, $^4J_{P,H5}$ = 2.0 Hz, 1 H, H5), 7.11 (dd, $^3J_{H10,H11}$ = 5.4, $^4J_{H8,H10}$ = 1.5 Hz, 1 H, H10), 7.01 (d, $^4J_{H8,H10}$ = 1.5 Hz, 1 H, H8), 6.82 (d, $^3J_{H2,H3}$ = 5.5 Hz, 1 H, H2), 6.41 (d, $^3J_{H10,H11}$ = 5.4 Hz, 1 H, H11), 1.29 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 33.57 (s) ppm. FAB MS: *m*/*z* = 813 [(L-H_2)Pd(PPh_3){$Cr(CO)_5$}H]$^+$.

6b: Yield: 6.9 mg (12%). $C_{39}H_{31}MoN_2O_6PPd$ (857.01): calcd. C 54.6, H 3.6, N 3.3; found C 54.1, H 3.9, N 3.2. IR: $\tilde{\nu}$ = 1519 (m, sh) ν(C=N), 2069 (w), 1981 (w, sh), 1902 (s) ν(CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, $^3J_{H2,H3}$ = 5.5 Hz, 1 H, H3), 7.85 (d, $^4J_{P,Hi}$ = 10.00 Hz, 1 H, Hi), 7.27 (d, $^4J_{P,H5}$ = 2.0 Hz, 1 H, H5), 7.11 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 2.0 Hz, 1 H, H10), 7.01 (d, $^4J_{H8,H10}$ = 2.0 Hz, 1 H, H8), 6.83 (d, $^4J_{H2,H3}$ = 5.5 Hz, 1 H, H2), 6.42 (d, $^3J_{H10,H11}$ = 9 Hz, 1 H, H11), 1.24 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 33.56 (s) ppm. FAB MS: *m*/*z* = 858 [(L-H_2)Pd(PPh_3){$Mo(CO)_5$}]$^+$.

7b: Yield: 28.1 mg (48%). $C_{39}H_{31}N_2O_6PPdW$ (944.91): calcd. C 49.6, H 3.3, N 3.0; found C 49.0, H 3.5, N 3.1. IR: $\tilde{\nu}$ = 2079 (w), 1984 (w, sh), 1910 (s) ν(CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, $^3J_{H2,H3}$ = 5.7 Hz, 1 H, H3), 7.79 (d, $^4J_{P,Hi}$ = 9.90 Hz, 1 H, Hi), 7.38 (d, $^4J_{P,H5}$ = 2.1 Hz, 1 H, H5), 7.07 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 1.5 Hz, 1 H, H10), 7.01 (d, $^4J_{H8,H10}$ = 1.5 Hz, 1 H, H8), 6.82 (d, $^3J_{H2,H3}$ = 5.7 Hz, 1 H, H2), 6.41 (d, $^3J_{H10,H11}$ = 9.0 Hz, 1 H, H11), 1.24 (s, 9 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 33.46 (s) ppm. FAB MS: *m*/*z* = 945 [(L-H_2)Pd(PPh_3){$W(CO)_5$}]$^+$.

8b: Yield: 10.4 mg (11%). $C_{70}H_{60}Cr_2N_4O_{12}P_2Pd_2$ (1528.02): calcd. C 55.0, H 3.9, N 3.7; found C 54.8, H 4.1, N 3.7. IR: $\tilde{\nu}$ = 1519 (m, sh) ν(C=N), 2063 (w), 1978 (w, sh), 1925 cm^{-1} (s) ν(CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, $^3J_{H2,H3}$ = 5.7 Hz, 1 H, H3), 7.03 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 2.4 Hz, 1 H, H10), 6.94 (d, $^4J_{H8,H10}$ = 2.4 Hz, H8), 6.67 (d, $^3J_{H2,H3}$ = 5.7 Hz, 1 H, H2), 6.30 (d, $^3J_{H10,H11}$ = 9.0 Hz, 1 H, H11 d), 1.26 (s, 9 H, *t*Bu) ppm; Hi and H5 signals hidden by the phenyl proton signals. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 28.46 (s) ppm. ESI-MS: *m*/*z* = 1336 [(L-H_2)$_2$$Pd_2$(dppb){$Cr(CO)_5$}H]$^+$, 1527 [(L-$H_2$)$_2$$Pd_2$(dppb){Cr-$(CO)_5$}$_2$]$^+$.

9b: Yield: 4.0 mg (4%). $C_{70}H_{60}Mo_2N_4O_{12}P_2Pd_2$ (1615.91): calcd. C 52.0, H 3.7, N 3.5; found C 52.4, H 4.0, N 3.6. IR: $\tilde{\nu}$ = 1517 (m, sh) ν(C=N), 2069 (w), 1982 (w, sh), 1902 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, $^3J_{H2,H3}$ = 5.4 Hz, 1 H, H3), 7.04 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 2.1 Hz, 1 H, H10), 6.95 (d, $^4J_{H8,H10}$ = 2.1 Hz, H8), 6.73 (d, $^3J_{H2,H3}$ = 5.4 Hz, 1 H, H2), 6.33 (d, $^3J_{H10,H11}$ = 9.0 Hz, 1 H, H11 d), 1.26 (s, 9 H, *t*Bu) ppm; Hi and H5 signals hidden by the phenyl proton signals. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 28.59 (s) ppm. ESI-MS: *m*/*z* = 1144.24 [(L-H_2)$_2$$Pd_2$(dppb)H]$^+$, 1380 [(L-$H_2$)$_2$$Pd_2$(dppb){$Mo(CO)_5$}H]$^+$, 1616 [(L-$H_2$)$_2$$Pd_2$(dppb){$Mo(CO)_5$}$_2$]$^+$.

10b: Yield: 17.0 mg (19%). $C_{70}H_{60}Mo_2N_4O_2P_2Pd_2$ (1455.92): calcd. C 46.9, H 3.4, N 3.1; found C 46.7, H 3.5, N 3.3. IR: $\tilde{\nu}$ = 1517 (m, sh) ν(C=N), 2067 (w), 1971 (w, sh), 1890 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, $^3J_{H2,H3}$ = 5.7 Hz, 1 H, H3), 7.04 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 2.4 Hz, 1 H, H10), 6.95 (d, $^4J_{H8,H10}$ = 2.4 Hz, H8), 6.71 (d, $^3J_{H2,H3}$ = 5.7 Hz, 1 H, H2), 6.31 (d, $^3J_{H10,H11}$ = 9.0 Hz, 1 H, H11 d), 1.26 (s, 9 H, *t*Bu) ppm; Hi and H5 signals hidden by the phenyl proton signals. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ = 28.41 (s) ppm. ESI-MS: *m*/*z* = 1791 [(L-H_2)$_2$$Pd_2$(dppb){$W(CO)_5$}$_2$H]$^+$.

Preparation of 11b: A solution of complex **2b** (0.0202 g, 0.0325 mmol) in dry and deoxygenated chloroform (15 mL) was prepared in a 50-mL Schlenk flask under argon. A solution of [$RuCl_2$(CO)(dmf)(PPh_3)$_2$] (0.0260 g, 0.0326 mmol) in dry and deoxygenated chloroform (10 mL) was added dropwise, with magnetic stirring, to the resulting violet solution, upon which the colour of the solution changed to deep blue. The solution was stirred at room temperature for 2 d and the solvent removed in vacuo to give a solid, which was chromatographed on a column packed with alumina. Elution with dichloromethane/methanol (2%) afforded the desired product as a green oil, which was dried in vacuo. Yield: 10.0 mg (23%). $C_{71}H_{61}N_2O_2P_3Cl_2RuPd$ (1345.57): calcd. C 63.7, H 4.6, N 2.1; found C 62.5, H 4.0, N 2.6. IR: $\tilde{\nu}$ = 1587 (s), ν(C=N), 1943 (s) ν(CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, $^3J_{H2,H3}$ = 6.1 Hz, 1 H, H2), 6.95 (d, $^4J_{H8,H10}$ = 2.1 Hz, 1 H, H8), 6.31 (d, $^3J_{H10,H11}$ = 9.0 Hz, H11), 5.47 (d, $^3J_{H2,H3}$ = 6.1 Hz, 1 H, H3), 1.26 (s, 9 H, *t*Bu) ppm; Hi and H5 signals hidden by the

phenyl proton signals. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 31.31 (s), 22.49 (s) ppm. ESI-MS: *m*/*z* = 1311 $[(L\text{-}H_2)Pd(PPh_3)\text{-}\{RuCl(PPh_3)_2Cl(CO)\}]^+$.

Preparation of 2c. Method 1: A saturated aqueous solution of NaCl (25 mL) was added dropwise to a solution of **1c** (0.101 g, 0.279 mmol) in acetone (25 mL) and the resulting mixture stirred for 24 h. The red precipitate formed was filtered off, washed with water and dried under vacuum to give complex **2c** as a red solid. Yield: 0.097 g (90%). $C_{14}H_9ClN_2OPd$ (363.11): calcd. C 46.3, H 2.5, N 7.7; found C 46.2, H 2.8, N 7.4. IR: $\tilde{\nu}$ = 1577 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 8.44 (s, 1 H, Hi), 8.35 (d, $^3J_{H4,H5}$ = 5.4 Hz, 1 H, H5), 8.14 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.8, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H3), 7.76 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.60 (m, 1 H, H4), 7.38 (dd, $^3J_{H8,H9}$ = 8.2, $^4J_{H8,H10}$ = 1.2 Hz, 1 H, H8), 7.04 (m, 1 H, H10), 6.49–6.43 (m, 2 H, H9, H11) ppm. FAB MS: *m*/*z* = 339 $[(L\text{-}H)Pd]^+$. **Method 2:** Ethanol (10 mL) was added to a stirred solution of potassium tetrachloropalladate (0.318 g, 0.974 mmol) in water (2 mL). The fine yellow suspension of potassium tetrachloropalladate obtained was treated with ligand **c** (0.200 g, 1.010 mmol, 15% excess) and the resulting mixture stirred for 72 h. The red precipitate formed was filtered off and dried under vacuum. Yield: 0.230 g (65%).

Preparation of 2d: Complex **2d** was prepared as a red solid according to Method 1. Yield: 0.094 g (85%). $C_{16}H_{17}ClN_2OPd$ (395.19): calcd. C 48.6, H 4.3, N 7.1; found C 48.0, H 3.8, N 6.9. IR: $\tilde{\nu}$ = 1602 (m) ν(C=N) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H, Hi), 8.32 (dd, $^3J_{H4,H5}$ = 5.5, $^4J_{H3,H5}$ = 1.2 Hz, 1 H, H5), 8.12 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.8, $^4J_{H3,H5}$ = 1.5 Hz, 1 H, H3), 7.72 (d, $^3J_{H2,H3}$ = 7.8 Hz, 1 H, H2), 7.57 (m, 1 H, H4), 7.32 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.13 (dd, $^3J_{H10,H11}$ = 8.9, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H10), 6.40 (m, 1 H, H11) ppm. FAB MS: *m*/*z* = 360.1 $[(L\text{-}H)PdH]^+$.

Preparation of 3c: Silver perchlorate (53 mg, 0.255 mmol) was added to a solution of **2c** (87 mg, 0.257 mmol) in acetone (15 mL). The resulting mixture was then stirred for 5 h and PPh_3 (67 mg, 0.255 mmol) added. The mixture was stirred for a further 24 h and filtered through Celite to remove the AgCl precipitate formed and the solvent removed to give a violet solid, which was recrystallised from chloroform/hexane. Yield: 0.127 g (75%). $C_{30}H_{24}ClN_2O_5PPd$ (77.59): calcd. C 54.1, H 3.6, N 4.2; found C 53.8, H 3.7, N 3.9. IR: $\tilde{\nu}$ = 1595 (m) ν(C=N), 1133 (s) ν(ClO_4) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.77 (d, $^4J_{P,Hi}$ = 12.9 Hz, 1 H, Hi), 8.12 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.8, $^4J_{H3,H5}$ = 1.4 Hz, 1 H, H3), 7.89 (dd, $^3J_{H2,H3}$ = 7.8, $^4J_{H2,H4}$ = 1.4 Hz, 1 H, H2), 7.49 (dd, $^3J_{H8,H9}$ = 8.2, $^4J_{H8,H10}$ = 1.3 Hz, 1 H, H8), 7.22 (m, 1 H, H4), 7.08 (m, 1 H, H10), 6.76 (d, $^3J_{H4,H5}$ = 5.6 Hz, 1 H, H5), 6.59 (m, 1 H, H9), 6.40 (d, $^3J_{H10,H11}$ = 7.0 Hz, 1 H, H11) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 25.71 (s) ppm. FAB MS: *m*/*z* = 565 $[(L\text{-}H)Pd(PPh_3)]^+$. Specific molar conductivity (in acetonitrile): Λ_m = 81.4 $S\,cm^2\,mol^{-1}$.

Preparation of 3d: This complex was prepared in a similar manner to **3c**. Yield: 0.119 g (65%). $C_{34}H_{32}ClN_2O_5PPd$ (721.48): calcd. C 56.6, H 4.5, N 3.9; found C 56.4, H 4.5, N 3.7. IR: $\tilde{\nu}$ = 1596 (m) ν(C=N), 1034 (s) ν(ClO_4) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.59 (d, $^4J_{P,Hi}$ = 13.0 Hz, 1 H, Hi), 8.15 (dd, $^3J_{H2,H3}$ = 7.8, $^4J_{H2,H4}$ = 1.4 Hz, 1 H, H2), 7.91 (td, $^3J_{H2,H3}$ = $^3J_{H3,H4}$ = 7.8, $^4J_{H3,H5}$ = 1.4 Hz, 1 H, H3), 7.40 (d, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H8), 7.11 (dd, $^3J_{H10,H11}$ = 9.0, $^4J_{H8,H10}$ = 2.2 Hz, 1 H, H10), 6.91 (m, 1 H, H4), 6.60 (m, 1 H, H5), 6.38 (d, $^3J_{H10,H11}$ = 9.0 Hz, 1 H, H11), 1.27 (s, 9 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 25.27 (s) ppm. FAB MS: *m*/*z* = 621 $[(L\text{-}H)Pd(PPh_3)]^+$. Specific molar conductivity (in acetonitrile): Λ_m = 101.8 $S\,cm^2\,mol^{-1}$.

X-ray Crystallographic Study: Three-dimensional, room temperature X-ray data were collected with a Bruker Smart 1k CCD diffractometer by using graphite-monochromated Mo-K_α radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. The Cl(1), Cl(2) and Cl(3) chlorine atoms of the chloroform solvent molecule in the crystal of **2c** were disordered and, consequently, refined in two complementary positions with occupancies of 50%. Refinement converged upon allowing for the thermal anisotropy of all non-hydrogen atoms.

Table 4. Crystal and structure refinement data for **2c**, **3c** and **4a**.

	2c	**3c**	**4a**
Empirical formula	$C_{13}H_{10}Cl_4N_2OPd$	$C_{30}H_{24}ClN_2O_5PPd$	$C_{80}H_{72}Cl_2N_4O_2P_2FePd_2$
M_r	458.43	665.33	1522.91
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.026(1)	9.053(1)	11.012(2)
b [Å]	7.093(1)	10.113(1)	11.213(2)
c [Å]	17.324(1)	16.302(2)	13.935(2)
α [°]		84.840(2)	97.622(3)
β [°]	90.179(2)	79.405(2)	94.350(3)
γ [°]		66.158(2)	95.215(3)
V [Å^3]	1600.7(2)	1341.6(3)	1691.7(5)
Z	4	2	1
μ [mm^{-1}]	1.824	0.896	0.916
Crystal size [mm]	$0.80\times0.14\times0.10$	$0.14\times0.13\times0.05$	$0.24\times0.19\times0.04$
$2\theta_{max}$ [°]	56.6	56.6	50.4
Reflections collected	11382	17848	17828
Unique reflections	3989 (R_{int} = 0.08)	6612 (R_{int} = 0.05)	5955 (R_{int} = 0.10)
Transmissions	0.83, 0.32	0.95, 0.88	0.96, 0.81
R [F, $I > 2\sigma(I)$]	0.0496	0.0402	0.0534
wR [F^2, all data]	0.0867	0.1030	0.1376
ρ_{max} [e Å^3]	0.418	0.843	0.607

Structure solution and refinement were carried out by using the program package SHELX-97.[51] Further details can be found in Table 4. CCDC-259264 (**2c**), -259265 (**3c**), and -259266 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Ministerio de Educación y Ciencia (CTQ2006-15621-C02-02/BQU), the Xunta de Galicia and the Universidad de La Coruña for financial support.

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Received: January 15, 2009
Published Online: April 6, 2009

