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New functionalized bis(pyrazol-1-yl)methane ligands. Synthesis, spectroscopic characterization of early and late transition metal complexes containing a functionalized N,N or P,P-chelate bis(5-diphenylphosphinopyrazol-1-yl)methane ligand

Antonio Antiñolo, Fernando Carrillo-Hermosilla, Enrique Díez-Barra, Juan Fernández-Baeza, Maria Fernández-López, Agustin Lara-Sánchez, Andrés Moreno, Antonio Otero,* Ana Maria Rodriguez and Juan Tejeda

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Campus Universitario, 13071-Cuidad Real, Spain

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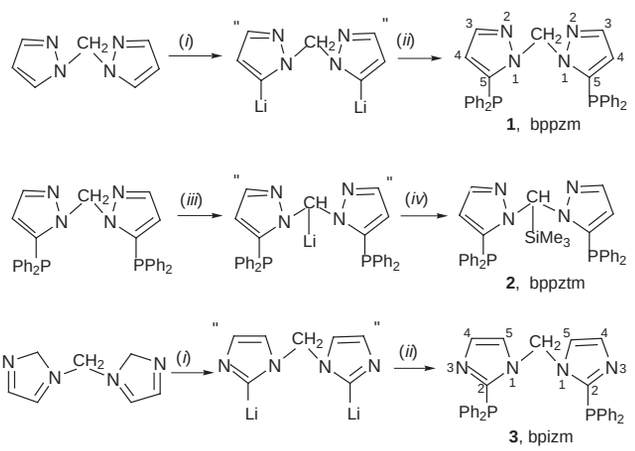
The multistep syntheses of the novel functionalized bis(pyrazol-1-yl)methane ligands, bis(5-diphenylphosphinopyrazol-1-yl)methane (bppzm) **1**, bis(5-diphenylphosphinopyrazol-1-yl)trimethylsilylmethane (bppztm) **2** and bis(2-diphenylphosphinoimidazol-1-yl)methane (bpizm) **3**, have been studied. The coordinative capacity of the bppzm ligand towards a variety of early and late metal fragments was evaluated and seven metallacycles were isolated. The complex $[\{NbCl_3(dme)\}_n]$ (dme = 1,2-dimethoxyethane) reacted with an excess of bppzm to give the binuclear complex $[\{NbCl_3(bppzm)\}_2]$ **4**, and in the same way the reaction of the mononuclear species $[NbCl_3(dme)(RC{\equiv}CR')]$ with **1** gave the appropriate $[NbCl_3(bppzm)(RC{\equiv}CR')]$ complexes (R = R′ = Ph **5**; R = R′ = $SiMe_3$ **6**; R = Ph, R′ = Me **7**; R = Ph, R′ = $SiMe_3$ **8**). In all these niobium complexes, **1** behaves as an N,N chelate ligand. Compound **1** reacts with $[MCl_2(PhCN)_2]$ (M = Pd, Pt) to yield the complexes $[MCl_2(bppzm)]$ (M = Pd **9**, Pt **10**), where a P,P chelate behaviour for **1** was observed. A dynamic conformation of the six- and eight-membered metallacycles formed in the complexes was observed and variable-temperature NMR studies were carried out. Finally, the molecular structure of complex **10** was determined crystallographically and a distorted square-planar geometry was found in which a proton (H_{endo}) of the bridging methylene is in close proximity to the metal centre in the boat–boat conformation of the metallacycle.

Introduction

The use of polyfunctional ligands has increasingly attracted attention in the field of coordination chemistry because it has often been shown that in complexes based on such ligands the functional group(s) may be helpful for controlling or enhancing the reactivity of the metal centre.[1] Several studies on phosphines with functional group substituents have been carried out in the field of transition metal chemistry[2] since bidentate biphosphine compounds in particular are excellent ligands in coordination and organometallic chemistry.[3] Furthermore, the polydentate N-donors poly(pyrazol-1-yl)alkanes[4] are interesting ligands because they are easily modified so as to modulate electronic and steric effects, and they also exhibit interesting conformational and fluxional behaviour that is not possible for planar ligands. With these precedents in mind we have previously explored the preparation of several families of poly(pyrazol-1-yl)methane-containing complexes of early (Nb[5]) and late (Ru[6] and Pd[7]) transition metals. We are now interested in the preparation of new poly(pyrazol-1-yl)methanes containing phosphine groups on the pyrazole rings in order to test their coordinate potential, N,N *versus* P,P coordination modes towards different early and late metal centres. The aim of this report is to present a synthetic route to new functionalized bis(pyrazol-1-yl)methanes as well as the preparation and spectroscopic characterization of complexes of niobium, palladium and platinum with bis(5-diphenylphosphinopyrazol-1-yl)methane.

Results and discussion

The syntheses of the new ligands are outlined in Scheme 1. The different steps involve classic methodologies for the preparation



Scheme 1 Summary of reactions leading to the preparation of compounds **1**–**3**. *Reagents and conditions*: (*i*) 2 Bu^nLi, thf, −70 °C, 30 min; (*ii*) 2 Ph_2PCl, thf, r.t., 12 h; (*iii*) Bu^nLi, thf, −70 °C, 1 h; (*iv*) Me_3SiCl, thf, r.t., 12 h.

of the intermediates leading to the different polyfunctionalized diphosphine ligands. Specific reference to the methods applied, along with a detailed synthetic procedure for each intermediate, is reported in the Experimental section. The compounds were isolated as air-stable colourless solids in good yields (see Experimental section) and were spectroscopically characterized. The ^1H NMR spectra of **1** and **2** show two doublets assigned to H^3 and H^4, with the more shielded signal corresponding to H^4. The signals that correspond to both CH_2 and CH groups in **1** and **2**, respectively, appear as triplets due to coupling with the two phosphorus atoms. Homonuclear NOE

(nuclear Overhauser enhancement) difference spectroscopy was also applied to compound **2** in order to confirm the assignment of the signal for the CH group. Irradiation of the $SiMe_3$ signal produces an enhancement of the signal at δ 7.06 which corresponds to the CH group. The $^{13}C\{^1H\}$ NMR spectra exhibit only one signal each for C^3, C^4 and C^5 as would be expected for the two equivalent pyrazol-1-yl groups in the molecule. The C^5 signal was assigned in the corresponding ^{13}C NMR spectra and the resonances of the C^3 and C^4 carbon atoms by means of two-dimensional heteronuclear chemical shift correlation (HETCOR) experiments. In addition, at higher field values a triplet due to coupling with the two phosphorus atoms was observed for the methylene carbon atoms in **1**. The ^{13}C NMR spectra also confirm the presence of the methinic carbon of compound **2**. The aromatic carbon atoms were assigned on the basis of the values of J_{PC} coupling constants. In compound **2** two resonances were observed due to the aromatic carbons, indicating that the two phenyl rings are non-equivalent. This could be due to the substantial steric hindrance present. The $^{31}P\{^1H\}$ NMR spectra show a singlet for the two phosphorus atoms at δ −31.37 for **1** and δ −37.85 for **2**, indicating that both phosphorus atoms are equivalent. The ^1H NMR spectrum of **3** exhibits two doublets for H^4 and H^5, which were assigned through an NOE experiment, and a triplet is also observed for the CH_2 group due to coupling with the two phosphorus atoms. The $^{13}C\{^1H\}$ NMR spectrum also exhibits one signal each for C^2, C^4 and C^5, which were assigned by both the ^{13}C NMR spectrum and an ^1H–^{13}C heteronuclear correlation (HETCOR) experiment. Finally, the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ −34.51 for both equivalent phosphorus atoms.

Compound **1** was used in the complexation of some metal fragments in order to test its coordinative capacity as a chelating agent. First, we considered its reactivity towards some niobium-containing complexes, namely $[\{NbCl_3(dme)\}_n]$ (dme = 1,2-dimethoxyethane) and $[NbCl_3(dme)(RC{\equiv}CR')]$. Compound **1** reacts at room temperature with a slight excess of a THF suspension of $[\{NbCl_3(dme)\}_n]$ [eqn. (1)] to give,

$$1/n[NbCl_3(dme)]_n + bppzm \longrightarrow \underset{\mathbf{4}}{1/2[NbCl_3(bppzm)]_2} + dme \quad (1)$$

after stirring for 20 h, a suspension from which the complex $[\{NbCl_3(bppzm)\}_2]$ **4** [bppzm = bis(5-diphenylphosphinopyrazol-1-yl)methane] was isolated as a deep brown solid after the appropriate work-up. The different THF solutions of the $[NbCl_3(dme)(RC{\equiv}CR')]$ species also react with **1** at room temperature, in an 1 : 1 molar ratio [eqn. (2)], to afford orange,

$$NbCl_3(dme)(RCCR') + bppzm \longrightarrow NbCl_3(bppzm)(RCCR') + dme \quad (2)$$

R = R′ = Ph **5**
R = R′ = $SiMe_3$ **6**
R = Ph, R′ = Me **7**
R = Ph, R′ = $SiMe_3$ **8**

blue and brown solutions from which air-sensitive solid samples of the complexes $[NbCl_3(bppzm)(RC{\equiv}CR')]$ (R = R′ = Ph **5**; R = R′ = $SiMe_3$ **6**; R = Ph, R′ = Me **7**; R = Ph, R′ = $SiMe_3$ **8**), were isolated after the appropriate work-up (see Experimental section). The different complexes were characterized spectroscopically. The mass spectrum of **4** indicates a binuclear formulation and its IR spectrum shows a strong band at 320 cm^{-1}, which has been assigned to the ν(Nb–Cl) terminal group for a D_{2h} binuclear disposition with the terminal chloride ligands *trans* in an octahedral environment for each niobium atom (see Fig. 1). This is the structural geometry that has been described[5,8] as the most propitious in analogous binuclear

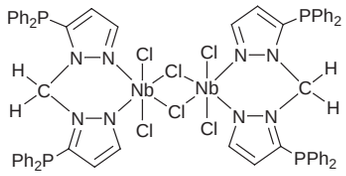


Fig. 1 Proposed structure for complex **4**.

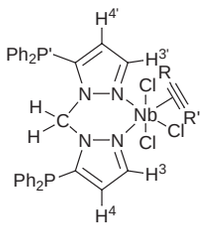
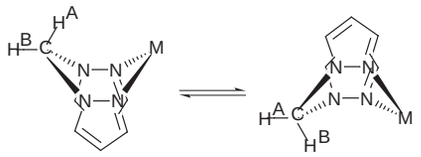


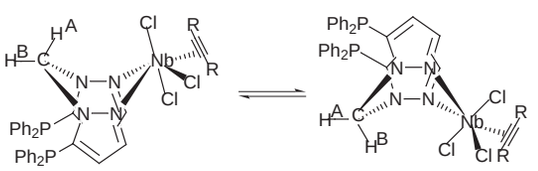
Fig. 2 Proposed structure for complexes **5**–**8**.

complexes with terminal and bridging halide ligands. NMR spectroscopy has proved a useful tool for the characterization of the different bppzm-containing niobium complexes. The ^1H NMR spectrum of **4** shows a set of resonances for H^3, H^4 and CH_2 indicating that both pyrazole rings are equivalent. In the same way, the $^{13}C\{^1H\}$ NMR spectrum exhibits the corresponding signals for C^3, C^4, C^5 and CH_2, and all the resonances are shifted to lower field in comparison with the free ligand (see Experimental section). An especially interesting result concerns the $^{31}P\{^1H\}$ NMR spectrum, where a singlet for the two equivalent phosphorus atoms appears at δ −34.19. This value is close to the value of δ −31.37 found in the free ligand, indicating that a quaternization of both phosphorus atoms by a possible coordination to the niobium centres does not take place and hence that the ligand behaves in this complex as an N,N-donor ligand (Fig. 1). The IR spectra of the alkyne-containing complexes **5**–**8** show a characteristic band located between 1690 and 1710 cm^{-1}, which corresponds to the ν(C≡C) mode of the bound alkynes. The ^1H NMR spectra of these complexes exhibit two resonances for the H^3 and H^4 pyrazole protons, which appear as doublets of doublets indicating that the two pyrazole rings from the bppzm ligand are non-equivalent. The assignment of the H^3 and H^4 signals for each pyrazole ring was carried out by means of the appropriate selective decoupling (INDOR) experiments. These results agree with a proposed octahedral structural disposition where the two pyrazole rings are located in *cis* and *trans* positions with respect to the alkyne ligand (Fig. 2). NOE experiments were carried out in order to confirm this proposed structure. For example, the irradiation in complex **6** of the $SiMe_3$ alkyne group enhances only one of the H^3 signals, clearly that of the *cis* pyrazole ring which has a closer spatial proximity to the alkyne ligand. In addition, the $^{13}C\{^1H\}$ NMR spectra of complexes **5**–**8** exhibit two resonances for the different pyrazole carbon atoms, C^3, C^4, C^5 and their assignments were carried out through the ^1H–^{13}C HMQC correlation experiments. The $^{31}P\{^1H\}$ NMR spectra show two signals, which correspond to an AB spin system for the two non-equivalent phosphorus atoms, with J_{AB} values between 33.6 and 35.7 Hz (see Experimental section), in accordance with the proposed structural geometry (Fig. 2). The chemical shifts are close to the values for the free ligand, indicating that, as was the case for complex **4**, a quaternization of both phosphorus atoms by coordination on the metal centre does not take place. ^1H–^{31}P HMQC correlation experiments have allowed the assignment of the phosphorus resonances that correspond to each pyrazole ring. In the ^1H and $^1H\{^{31}P\}$ NMR spectra of **5**–**8** recorded at room temperature, the CH_2 resonance appears as a triplet or singlet respectively, indicating that a dynamic behaviour in solution takes place involving a boat-to-boat inversion in the six-membered



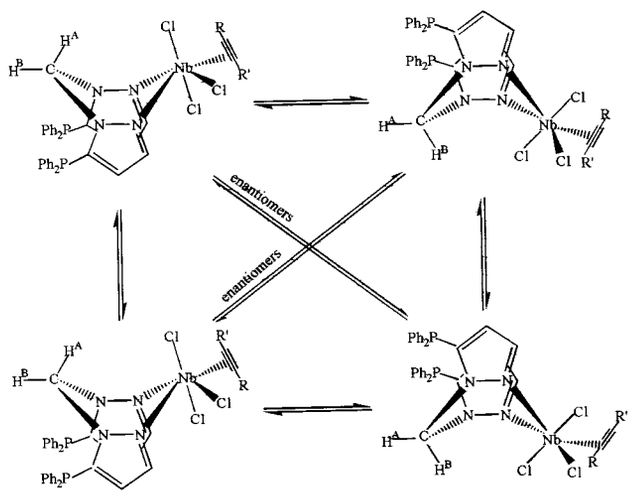
Scheme 2 Boat-to-boat inversion.

metallacycle (Scheme 2). A mechanism for this has been proposed for several complexes containing poly(pyrazol-1-yl)-alkane ligands.[4] In order to elucidate the dynamic behaviour of complexes **5**–**8** in solution, and to obtain NMR parameters for the static structure at the slow-exchange limit, variable-temperature NMR studies were carried out. In the different examples the presence of the PPh_2 moieties in the pyrazole rings creates steric hindrance that makes the boat-to-boat inversion more difficult and hence a static structure at moderately low temperature values was found. Complexes **5** and **6** (with symmetrical alkynes) and **7** and **8** (with unsymmetrical alkynes) will be discussed separately. In the case of complex **5**, when the temperature was lowered to 203 K two doublets corresponding to the AB system ($J_{AB} = 7.6$ Hz) of the CH_2 group was observed in the $^1H\{^{31}P\}$ NMR spectrum; however, in the ^1H NMR spectrum two triplets from an ABXX′ system, $J_{AX} = J_{BX'} = 7.8$ Hz; $J_{AX'} = J_{BX} = 0$ Hz, where each proton is coupled with a phosphorus atom, was observed. Similar behaviour was observed for complex **6** ($J_{AB} = 14.2$ Hz) in the $^1H\{^{31}P\}$ NMR spectrum at 213 K, but in the ^1H NMR spectrum an ABXX′ system, $J_{Ax} = J_{Ax'} = 4.7$ Hz; $J_{BX} = J_{BX'} = 0$ Hz, where only one proton is coupled to both phosphorus atoms was observed, giving rise to two triplets (relative intensities 2 : 1) for H^A and two singlets (relative intensities 2 : 1) for H^B. The coalescence temperatures were 258 and 265 K, respectively, for **5** and **6**. From these studies free activation energy values, $\Delta G^{\ddagger}$, of 12.82 and 13.12 kcal mol^{-1} for **5** and **6**, respectively, were calculated (1 cal = 4.184 J).[9] The results agree with the presence of the aforementioned boat-to-boat inversion in the six-membered metallacycle. At low temperature the process can be frozen, giving rise to two enantiomers, which are represented in Scheme 3.



Scheme 3 Proposed structures for the two enantiomers of complexes **5** and **6**.

These two enantiomers cannot be distinguished by means of NMR spectroscopy. As yet we do not have any conclusive explanation as to why the ABXX′ systems of both complexes are different, although we believe that a possible torsion of the boat could be responsible for the different couplings in **6** of H^A and H^B with the two phosphorus atoms. Modelling studies in order to clarify this point are in progress. In the case of complex **7**, when the temperature was lowered to 193 K two AB systems ($J_{AB} = 7.1$ and 14.1 Hz) for the CH_2 group were observed in the $^1H\{^{31}P\}$ NMR spectrum, but two different ABXX′ systems, $J_{AX} = J_{BX'} = 7.8$ Hz; $J_{AX'} = J_{BX} = 0$ Hz and $J_{AX} = J_{AX'} = 5.1$ Hz; $J_{BX} = J_{BX'} = 0$ Hz, were found in the ^1H NMR spectrum. Similar behaviour was found in the variable-temperature NMR study for **8** (at 230 K $J_{AB} = 6.6$ and 14.3 Hz; $J_{AX} = J_{BX'} = 7.8$ Hz; $J_{AX'} = J_{BX} = 0$ Hz and $J_{AX} = J_{AX'} = 4.8$ Hz; $J_{BX} = J_{BX'} = 0$ Hz). The coalescence temperatures were 243 K ($\Delta G^{\ddagger} = 11.91$ kcal mol^{-1}) and 253 K ($\Delta G^{\ddagger} = 12.55$ kcal mol^{-1}), respectively. Computer simulation studies of the all spin systems described were also carried out, and the spectra obtained agree very well with the corresponding experimental spectra. The next question that must be considered is, how can we explain the presence of two spin systems for the CH_2 group when the temperature is lowered? As discussed for complexes **5** and **6**, at low temperature the boat-to-boat inversion can be frozen in and now, as a consequence of the presence of unsymmetrical alkyne ligand, four stereoisomers, *i.e.* those with the most stable acetylene, are present in solution (Scheme 4) and there are two diastereo-



Scheme 4 Proposed structures for the four stereoisomers of complexes **7** and **8**.

isomers that give rise to a different response in the NMR spectra and are responsible for the two spin systems. We have confirmed the presence at low temperature of the proposed four stereoisomers by means of an experiment carried out on complex **7**. The addition of a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol, to a solution of **7** gives rise to the appearance in the $^1H\{^{31}P\}$ NMR spectrum at 193 K of four AB spin systems that correspond to the four diastereoisomers from the corresponding four stereoisomers.

The ^{13}C NMR resonances for the carbon atoms of the alkyne ligands appear at δ *ca.* 250, indicating that the alkyne ligand behaves as a four-electron donor (see Experimental section). An empirical correlation between the alkyne π donation and ^{13}C chemical shift for the bound alkyne carbons has been observed.[10] The NMR spectroscopic data of complexes **5**–**8** indicate that the alkyne ligand is fluxional, as was previously observed for other alkyne-containing niobium complexes.[5] In order to study this behaviour, variable-temperature ^1H-NMR studies were carried out for these complexes. We assume that a six-coordinate description of the complexes (see Fig. 2) in which the alkyne occupies a single site is preferable to the alternative seven-coordinate model in which each alkyne carbon is considered to occupy a separate coordination position. Based on this assumption we propose a simple rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle to explain the observed fluxional behaviour. Several examples have been described, mainly for d^4 alkyne complexes of Mo^{II} or W^{II}, where a fluxional behaviour by rotation of the alkyne ligand has been considered.[10] From these studies free energy values, $\Delta G^{\ddagger}$, of 9.72, 10.04 and 9.15 kcal mol^{-1} for **5**, **6** and **8**, respectively, were calculated[9] at the respective coalescence temperatures of 198, 210 and 193 K. It was not possible to calculate $\Delta G^{\ddagger}$ for complex **7**, in which the coalescence temperature was 178 K. The values allow us to establish a relationship between the steric demand of the alkyne and the rotation phenomenon. In fact, it can be seen that the higher $\Delta G^{\ddagger}$ and coalescence temperature values were found in the cases of the bulkier alkyne substituents. On the basis of these data we propose that steric effects may be implicated in the fluxional behaviour of the alkyne ligand in this class of complex. A good example of this behaviour is provided by the variable-

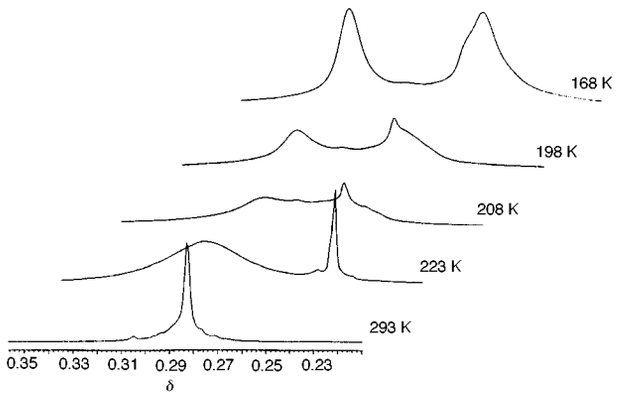


Fig. 3 Variable-temperature ^{1}H NMR spectra in the region of the $SiMe_3$ alkyne groups of the complex $[NbCl_3(bppzm)(Me_3SiC{\equiv}CSiMe_3)]$ **6**.

temperature NMR study of **6**. In Fig. 3 we can observe that in the variable-temperature ^{1}H NMR spectrum, when the temperature was lowered to below 168 K, distinct chemical shifts were observed for the $SiMe_3$ alkyne groups. In the complexes containing unsymmetrical acetylenes (**7** and **8**) two signals are observed for each of the substituents of the alkyne. This confirms the point discussed above in that there are four stereoisomers and two diastereoisomers present (Scheme 4).

Finally, we investigated the behaviour of the bppzm ligand towards late-metal centres, namely $[MCl_2(PhCN)_2]$ (M = Pd, Pt). A solution of $[MCl_2(PhCN)_2]$ in CH_2Cl_2 reacted with the bppzm ligand (in a 1:1 molar ratio) at room temperature to give, after 5 h of stirring, a solution from which the new compounds $[MCl_2(bppzm)]$ (M = Pd **9**, Pt **10**), were isolated after the appropriate work-up [eqn. (3)]. The complexes were isolated

$$MCl_2(PhCN)_2 + bppzm \longrightarrow MCl_2(bppzm) + 2PhCN \quad (3)$$
$$M = Pd\ \mathbf{9},\ Pt\ \mathbf{10}$$

as crystalline air-stable solids in good yields (see Experimental section) and were characterized spectroscopically. The H^4 resonance in the ^{1}H NMR spectrum appears only as doublet of doublets due to coupling with H^3 and P atoms in complex **9**, whereas a broad signal is observed for the corresponding proton in complex **10**, and H^3 exhibits one resonance as a doublet due to coupling with H^4 in complex **9** and a broad signal in complex **10**. These results indicate that both pyrazole rings of the bppzm are equivalent in both complexes. In addition, a broad signal, which corresponds to an unresolved triplet due to coupling with the phosphorus atoms, is observed in the spectrum of both complexes for the CH_2 group, indicating that a fluxional behaviour in solution of the eight-membered metallacycle occurs (see below). The $^{13}C\{^1H\}$ NMR spectra exhibit the signal for the methylene carbon atom as a triplet in **9**, due to coupling with the two phosphorus atoms (J_{PC} = 3.5 Hz), and as a singlet in **10**. In addition, two triplets and multiplets (probably due to the fact that the chemical shifts are close) are observed for C^3 and C^4 in **10** and **9**, respectively. The $^{31}P\{^1H\}$ NMR spectra show signals at δ 4.66 for **9** and δ −11.30 for **10**, indicating that both phosphine atoms are equivalent. It is noteworthy that both resonances appear at significantly lower fields than the corresponding signals in the free ligand and this behaviour is in contrast to that previously found in the niobium complexes described above, suggesting that in complexes **9** and **10** a coordination of the ligand through the phosphorus atoms takes place. Based on a square-planar geometry (see Fig. 4) the IR spectroscopic data allow us to propose a *cis*-geometry (C_{2v}) because two bands at *ca.* 330 and 300 cm^{-1}, which correspond to the ν(M–Cl) (M = Pd, Pt) are present.[11] The dynamic behaviour in solution of complexes **9** and **10**, involving a boat-to-boat inversion of the eight-membered metallacycle in a similar way to that shown in Scheme 2 for the six-membered metallacycle niobium complexes, was studied by means of variable-temperature NMR. From these studies we calculated the free activation energy values, $\Delta G^{\ddagger}$ of 10.82 and 10.12 kcal mol^{-1} for **9** and **10**, respectively, at the respective coalescence temperatures, 233 and 223 K. This behaviour contrasts with that observed in several MCl_2–diphosphine metallacycles (M = Pd, Pt) containing a bidentate phosphorus ligand, where a rigid boat–boat conformation in solution is found.[12] In order to confirm the proposed structure for **9** and **10** we have carried out a crystal structure analysis of complex **10**. A perspective view of the complex is shown in Fig. 5, and bond lengths and angles are listed in Table 1. The platinum complex exhibits a distorted square planar geometry. The distortion is reflected by the tetrahedral displacements of the following atoms from the mean coordination plane: Cl(2), −0.133(2); Cl(3), 0.123(2); P(4), −0.089(2) and P(5), 0.089(2) Å. The chelating behaviour of the bppzm ligand results in an eight-membered chelation ring, which presents a distorted boat–boat conformation as shown in Fig. 6.

The torsion angles are C(3)–N(6)–C(4)–N(8) and P(4)–Pt(1)–P(5)–C(7) of 111.9(8) and 90.5(3)°, which should be equal to zero in a non-distorted boat–boat conformation. The conformation of the metallacycle is such that H4B, the H_{endo} hydrogen atom of the methylene group, is oriented almost perpendicular to the coordination plane [P(1)···H4B, 2.750(1) Å], and the angle between the Pt(1)···H4B and the normal to the plane is 27.9°.

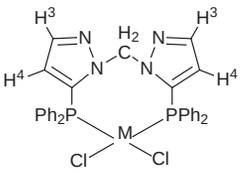


Fig. 4 Proposed structures for complexes **9** and **10**.

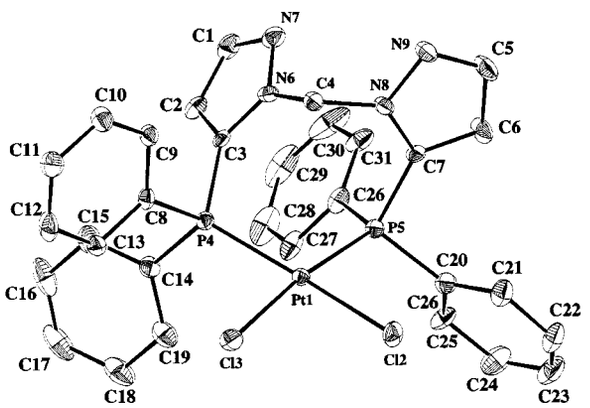


Fig. 5 ORTEP drawing of complex **10**.

Table 1 Selected bond lengths (Å) and angles (°) for **10**

Pt(1)–P(4)	2.252(2)	N(7)–C(1)	1.336(11)
Pt(1)–P(5)	2.269(5)	N(8)–C(7)	1.355(9)
Pt(1)–Cl(2)	2.332(2)	N(8)–N(9)	1.377(8)
Pt(1)–Cl(3)	2.337(5)	N(8)–C(4)	1.432(9)
P(4)–C(3)	1.811(7)	N(9)–C(5)	1.330(11)
P(5)–C(7)	1.795(7)	C(1)–C(2)	1.364(12)
N(6)–N(7)	1.343(8)	C(2)–C(3)	1.376(9)
N(6)–C(3)	1.365(9)	C(5)–C(6)	1.401(13)
N(6)–C(4)	1.465(9)	C(6)–C(7)	1.372(10)
P(4)–Pt(1)–P(5)	98.85(10)	Cl(2)–Pt(1)–Cl(3)	86.19(10)
P(4)–Pt(1)–Cl(2)	170.84(7)	C(3)–P(4)–Pt(1)	113.4(2)
P(5)–Pt(1)–Cl(2)	88.82(10)	C(7)–P(5)–Pt(1)	112.9(2)
P(4)–Pt(1)–Cl(3)	86.66(10)	N(8)–C(4)–N(6)	111.8(5)
P(5)–Pt(1)–Cl(3)	172.39(7)		

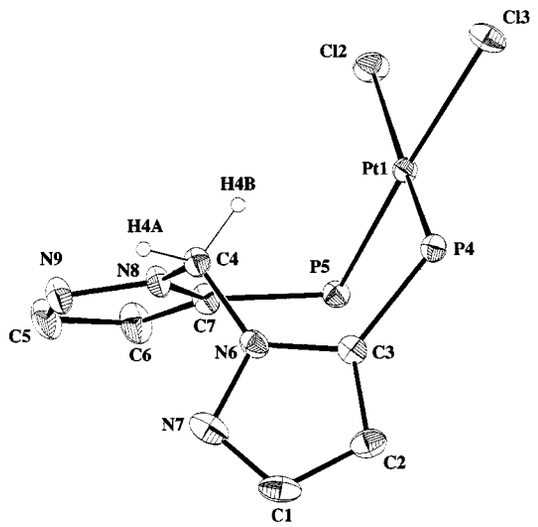


Fig. 6 Drawing showing the conformation of the chelation ring in complex **10**.

In conclusion, the preparation of new functionalized phosphorus-containing bis(pyrazol-1-yl)methane compounds has been carried out by means of a simple multistep synthesis. The coordination behaviour of one of the compounds synthesized, bis(5-diphenylphosphinopyrazol-1-yl)methane (bppzm), was considered towards metal centres of niobium, palladium and platinum. In the first case, new binuclear and mononuclear niobium species with an N,N-six-membered metallacycle were isolated. However, for the starting complexes $[MCl_2(PhCN)_2]$ (M = Pd, Pt), square-planar species with a P,P-eight-membered metallacycle were found. In both classes of complexes a dynamic behaviour in solution, which corresponds to a boat-to-boat inversion of the corresponding metallacycle, was considered to be present by variable-temperature NMR studies.

Experimental

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as matrix. Infrared spectra were obtained in the region 4000–200 cm^{-1}, using a Perkin-Elmer 883 spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Unity FT-300 spectrometer and referenced to the residual deuterated solvent. The NOE difference spectra were recorded with the following acquisition parameters: spectra width 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5–10 dB, number of scans 120. Two-dimensional NMR and simulated spectra were acquired using standard VARIAN-FT software, and processed using an IPC-Sun computer. The NMR probe temperatures were varied using an Oxford Instruments VTC 4 unit, measured by a thermocouple and calibrated with CD_3OD. The complexes $[\{NbCl_3(dme)\}_n]$, $[NbCl_3(dme)(RC{\equiv}CR')]$ and $[MCl_2(PhCN)_2]$ (M = Pd, Pt) and the compounds bis(pyrazol-1-yl)methane (bpzm) and bis(imidazol-1-yl)methane (bizm) were prepared as reported previously.[13–15]

Preparations

Bis(5-diphenylphosphinopyrazol-1-yl)methane (bppzm) 1. In a 250 cm^3 Schlenk tube, bpzm (3 g, 20 mmol) was dissolved in dry tetrahydrofuran (THF) (150 cm^3) and cooled to −70 °C. A 1.6 M solution of Bu^nLi (26.9 cm^3, 43 mmol) in hexane was added and the solution was stirred for 30 min. Ph_2PCl (7.27 cm^3, 41 mmol) was added and the reaction mixture was allowed to slowly reach room temperature. After 12 h the reaction was quenched with NH_4Cl (2.16 g, 41 mmol). The suspension was filtered and the solvent removed under vacuum. The orange oil obtained was washed with hexane and the residue was extracted with CH_2Cl_2. The solvent was removed and the orange oil obtained was washed with EtO. A colourless solid was obtained that was crystallized from CH_2Cl_2–Et_2O. Yield 63% (Found: C, 71.80; H, 5.09; N, 10.53. $C_{31}H_{26}N_4P_2$ requires C, 72.08; H, 5.07; N, 10.85%). ^1H NMR ($CDCl_3$, 295 K), δ 6.59 (t, 2 H, $^4J_{HP}$ = 1.5, CH_2), 7.42 (d, 2 H, $^3J_{HH}$ = 1.8, H^3), 5.91 (d, 2 H, $^3J_{HH}$ = 1.8 Hz, H^4), 7.29–7.17 (m, 20 H, Ph). ^{13}C-{^1H} NMR ($CDCl_3$), δ 62.27 (t, $^3J_{CP}$ = 10.4, CH_2), 140.17 (d, $^3J_{CP}$ = 6.1, C^3), 114.54 (d, $^2J_{CP}$ = 10.6, C^4), 140.56 (s, C^5), 133.35 (d, $^2J_{CP}$ = 10.4, C_o), 128.43 (d, $^3J_{CP}$ = 3.6 Hz, C_m), 128.99 (s, C_p), 135.30 (s, C_{ipso}). ^{31}P-{^1H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −31.37 (s, PPh_2).

Bis(5-diphenylphosphinopyrazol-1-yl)trimethylsilylmethane (bppztm) 2. In a 250 cm^3 Schlenk tube, bppzm (1 g, 1.94 mmol) was dissolved in dry tetrahydrofuran (THF) (100 ml) and cooled to −79 °C. A 1.6 M solution of Bu^nLi (2.03 cm^3, 3.25 mmol) in hexane was added and the solution was stirred for 1 h. $SiMe_3Cl$ (0.27 cm^3, 2.13 mmol) was added and the reaction mixture was allowed to slowly reach room temperature. After 12 h the reaction was quenched with NH_4Cl (104 mg, 1.94 mmol). The suspension was filtered and the solvent removed under vacuum to give a colourless solid. Yield 58% (Found: C, 69.02; H, 5.48; N, 9.87. $C_{34}H_{34}N_4P_2Si$ requires C, 69.38; H, 5.82; N, 9.51%). ^1H NMR ($CDCl_3$, 295 K), δ 7.06 (t, 1 H, $^4J_{HP}$ = 5.1, CH), 7.60 (d, 2 H, $^3J_{HH}$ = 1.9, H^3), 6.04 (d, 2 H, $^3J_{HH}$ = 2.0 Hz, H^4), 0.02 (s, 9 H, $SiMe_3$), 7.39–7.18 (m, 20 H, Ph). ^{13}C-{^1H} NMR ($CDCl_3$), δ 67.37 (t, $^3J_{CP}$ = 9.8, CH), 139.82 (d, $^3J_{CP}$ = 6.1, C^3), 114.06 (d, $^2J_{CP}$ = 10.6, C^4), 140.23 (s, C^5), 133.96, 132.97 (2d, $^2J_{CP}$ = 10.8, 10.1, C_o), 128.49, 128.09 (2d, $^3J_{CP}$ = 3.6, 3.3 Hz, C_m), 129.14, 128.31 (2s, C_p), 136.35, 136.03 (s, C_{ipso}). ^{31}P-{^1H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −37.85 (s, PPh_2).

Bis(2-diphenylphosphinoimidazol-1-yl)methane (bpizm) 3. The synthetic procedure was the same as for complex **1**, using bizm (3 g, 20 mmol), Bu^nLi (1.6 M, 26.50 cm^3, 43 mmol) and Ph_2PCl (7.27 cm^3, 41 mmol) to give compound **3** as a colourless solid. Yield 65% (Found: C, 71.97; H, 5.16; N, 10.64. $C_{31}H_{26}N_4P_2$ requires C, 72.08; H, 5.07; N, 10.85%). ^1H NMR ($CDCl_3$, 295 K), δ 6.58 (t, 2 H, $^4J_{HP}$ = 3,3, CH_2), 7.17 (d, 2 H, $^3J_{HH}$ = 1.3, H^4), 7.05 (d, 2 H, $^3J_{HH}$ = 1.3 Hz, H^5), 7.48–7.32 (m, 20 H, Ph). ^{13}C-{^1H} NMR ($CDCl_3$), δ 55.49 (t, $^3J_{CP}$ = 17.1, CH_2), 146.05 (d, $^1J_{CP}$ = 4.5, C^2), 132.28 (s, C^4), 121.94 (d, $^3J_{CP}$ = 3.0, C^5), 133.78 (d, $^2J_{CP}$ = 20.6, C_o), 128.66 (d, $^3J_{CP}$ = 4.0, C_m), 129.43 (s, C_p), 133.94 (s, $^1J_{CP}$ = 23.6 Hz, C_{ipso}). ^{31}P-{^1H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −34.51 (s, PPh_2).

$[\{NbCl_3(bppzm)\}_2]$ 4. To a THF (50 cm^3) suspension of $[\{NbCl_3(dme)\}_n]$ (0.250 g, 0.86 mmol) was added an equimolar quantity of bppzm (0.446 g, 0.86 mmol). The suspension was stirred for 20 h at room temperature. The solvent was removed *in vacuo* and a brown solid was obtained. Yield 77% (Found: C, 52.41; H, 3.37; N, 7.54. $C_{62}H_{52}Cl_6N_8P_4Nb_2$ requires C, 52.02; H, 3.66; N, 7.83%). ^1H NMR ($CDCl_3$, 295 K), δ 6.60 (s, 4 H, CH_2), 7.45 (s, 4 H, H^3), 5.85 (s, 4 H, H^4), 7.42–7.24 (m, 40 H, Ph). ^{13}C-{^1H} NMR ($CDCl_3$), δ 61.57 (s, CH_2), 134.44 (s, C^3), 114.03 (s, C^4), 139.52 (s, C^5), 134.04–127.87 (m, Ph). ^{31}P-{^1H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −34.19 (s, PPh_2). IR (Nujol, cm^{-1}) 320, 241 [ν(Nb–Cl)]. Mass spectrum: *m*/*z* 1429 (M + 1).

$[NbCl_3(bppzm)(PhC{\equiv}CPh)]$ 5. The synthetic procedure was the same as for complex **1**, using $[NbCl_3(dme)(PhC{\equiv}CPh)]$ (0.250 g, 0.53 mmol) and bppzm (0.280 g, 0.53 mmol), to give complex **5** as an orange solid. Yield 80% (Found: C, 60.18;

H, 4.22; N, 6.02. $C_{45}H_{36}Cl_3N_4P_2Nb$ requires C, 60.46; H, 4.06; N, 6.27%). ^{1}H NMR ($CDCl_3$, 295 K), δ 7.19 (t, $^4J_{HP}$ = 2.7, 2 H, CH_2), 8.74 (dd, $^3J_{HH}$ = 2.5, $^4J_{HP}$ = 1.2, 1 H, H^3), 7.42 (dd, 1 H, H$^{3'}$), 6.03 (dd, $^3J_{HH}$ = 2.5, $^3J_{HP}$ = 0.6, 1 H, H^4), 5.79 (dd, $^3J_{HH}$ = 2.5, $^3J_{HP}$ = 0.7, 1 H, H$^{4'}$), 7.63–7.21 (m, 20 H, PPh_2), 7.93 [dd, $^3J_{Ho,m}$ = 8.3, $^4J_{Ho,p}$ = 0.9 Hz, 4 H, H$_o$(PhC≡)], 7.63–7.21 [m, 6 H, H$_m$, H$_p$(PhC≡)]. ^{13}C-{^{1}H} NMR ($CDCl_3$), δ 58.92 (t, $^3J_{PC}$ = 15.0, CH_2), 147.41 (s, C^3), 144.42 (s, C$^{3'}$), 114.01 (s, C^4), 113.73 (s, C$^{4'}$), 146.69 (dd, $^1J_{PC}$ = 20.0, $^5J_{PC}$ = 3.0, C^5), 144.84 (dd, $^1J_{PC}$ = 18.8, $^5J_{PC}$ = 1.7 Hz, C$^{5'}$), 137.84–126.81 (m, Ph), 238.98 (s, C≡C). ^{31}P-{^{1}H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −32.65, −32.30 (AB, J_{AB} = 33.6, PPh_2, P′Ph_2). IR (Nujol, cm^{-1}) 1690 [ν(C≡C)], 393, 323 [ν(Nb–Cl)].

[$NbCl_3$(bppzm)(Me_3SiC≡$CSiMe_3$)] 6. The synthetic procedure was the same as for complex **1**, using [$NbCl_3$(dme)(Me_3SiC≡$CSiMe_3$)] (0.250 g, 0.54 mmol) and bppzm (0.281 g, 0.54 mmol), to give complex **6** as a blue solid. Yield 78% (Found: C, 52.56; H, 5.13; N, 6.03. $C_{39}H_{44}Cl_3N_4P_2Si_2Nb$ requires C, 52.86; H, 5.01; N, 6.32%). ^{1}H NMR ($CDCl_3$, 295 K), δ 6.85 (t, $^4J_{HP}$ = 2.6, 2 H, CH_2), 8.45 (dd, $^3J_{HH}$ = 2.2, $^4J_{HP}$ = 0.8, 1 H, H^3), 7.68 (dd, $^3J_{HH}$ = 2.4, $^4J_{HP}$ = 0.8, 1 H, H$^{3'}$), 6.01 (dd, $^3J_{HH}$ = 2.2, $^3J_{HP}$ = 0.5, 1 H, H^4), 5.99 (dd, $^3J_{HH}$ = 2.4, $^3J_{HP}$ = 0.7 Hz, 1 H, H$^{4'}$), 7.45–7.18 (m, 20 H, PPh_2), 0.28 (s, Me_3SiC≡). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ 58.82 (t, $^3J_{PC}$ = 14.8, CH_2), 146.13 (s, C^3), 144.69 (s, C$^{3'}$), 114.19 (s, C^4), 114.07 (s, C$^{4'}$), 146.28 (d, $^1J_{PC}$ = 22.7, C^5), 144.79 (d, $^1J_{PC}$ = 15.0 Hz, C$^{5'}$), 133.68–128.37 (m, Ph), 0.07 (s, Me_3Si), 265.62 (s, C≡C). ^{31}P-{^{1}H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −32.87, −32.35 (AB, J_{AB} = 34.2 Hz, PPh_2, P′Ph_2). IR (Nujol, cm^{-1}) 1710 [ν(C≡C)], 370, 322 [ν(Nb–Cl)].

[$NbCl_3$(bppzm)(PhC≡CMe)] 7. The synthetic procedure was the same as for complex **1**, using [$NbCl_3$(dme)(PhC≡CMe)] (0.250 g, 0.62 mmol) and bppzm (0.318 g, 0.62 mmol), to give complex **7** as a brown solid. Yield 75% (Found: C, 57.34; H, 3.96; N, 6.96. $C_{40}H_{34}Cl_3N_4P_2Nb$ requires C, 57.75; H, 4.12; N, 6.73%). ^{1}H NMR ($CDCl_3$, 295 K), δ 7.08 (t, $^4J_{HP}$ = 2.8, 2 H, CH_2), 8.63 (dd, $^3J_{HH}$ = 2.4, $^4J_{HP}$ = 0.9, 1 H, H^3), 7.39 (dd, 1 H, H$^{3'}$), 6.01 (dd, $^3J_{HH}$ = 2.4, $^3J_{HP}$ = 0.7, 1 H, H^4), 5.86 (dd, $^3J_{HH}$ = 2.5, $^3J_{HP}$ = 0.7, 1 H, H$^{4'}$), 7.45–7.21 (m, 20 H, PPh_2), 7.75 [dd, $^3J_{Ho,m}$ = 6.9, $^4J_{Ho,p}$ = 1.3 Hz, 2 H, H$_o$(PhC≡)], 7.45–7.21 [m, 3 H, H$_m$, H$_p$(PhC≡)], 3.58 (s, ≡CMe). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ 59.01 (t, $^3J_{PC}$ = 15.1, CH_2), 147.03 (s, C^3), 144.65 (s, C$^{3'}$), 114.24 (s, C^4), 113.93 (s, C$^{4'}$), 146.73 (d, $^1J_{PC}$ = 23.0, C^5), 144.92 (d, $^1J_{PC}$ = 19.6 Hz, C$^{5'}$), 136.94–128.44 (m, Ph), 24.23 (s, ≡C*Me*), 256.78, 235.24 (s, C≡C). ^{31}P-{^{1}H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −32.92, −32.36 (AB, J_{AB} = 33.9 Hz, PPh_2, P′Ph_2). IR (Nujol, cm^{-1}) 1692 [ν(C≡C)], 384, 320 [ν(Nb–Cl)].

[$NbCl_3$(bppzm)(PhC≡$CSiMe_3$)] 8. The synthetic procedure was the same as for complex **1**, using [$NbCl_3$(dme)(PhC≡C-$SiMe_3$)] (0.250 g, 0.54 mmol) and bppzm (0.278 g, 0.54 mmol), to give complex **8** as a brown solid. Yield 68% (Found: C, 57.05; H, 4.18; N, 5.98. $C_{42}H_{40}Cl_3N_4P_2SiNb$ requires C, 56.67; H, 4.53; N, 6.29%). ^{1}H NMR ($CDCl_3$, 295 K), δ 7.00 (t, $^4J_{HP}$ = 2.8, 2 H, CH_2), 8.58 (dd, $^3J_{HH}$ = 2.2, $^4J_{HP}$ = 0.7, 1 H, H^3), 7.49 (dd, $^3J_{HH}$ = 2.5, $^4J_{HP}$ = 0.8, 1 H, H$^{3'}$), 6.03 (dd, $^3J_{HH}$ = 2.2, $^3J_{HP}$ = 0.6, 1 H, H^4), 5.89 (dd, $^3J_{HH}$ = 2.5, $^3J_{HP}$ = 0.8, 1 H, H$^{4'}$), 7.47–7.20 (m, 20 H, PPh_2), 7.85 [dd, $^3J_{Ho,m}$ = 7.0, $^4J_{Ho,p}$ = 1.2 Hz, 2 H, H$_o$(PhC≡)], 7.47–7.20 [m, 3 H, H$_m$, H$_p$(PhC≡)], 0.39 (s, ≡$CSiMe_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ 58.89 (t, $^3J_{PC}$ = 14.8, CH_2), 146.70 (s, C^3), 144.55 (s, C$^{3'}$), 114.04 (s, C^4), 114.00 (s, C$^{4'}$), 146.56 (d, $^1J_{PC}$ = 21.0, C^5), 144.80 (d, $^1J_{PC}$ = 19.7 Hz, C$^{5'}$), 133.56–128.06 (m, Ph), −0.12 (s, ≡CSi*Me*$_3$), 260.43, 246.27 (s, C≡C). ^{31}P-{^{1}H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −32.80, −32.20 (AB, J_{AB} = 35.7 Hz, PPh_2, P′Ph_2). IR (Nujol, cm^{-1}) 1698 [ν(C≡C)], 382, 326 [ν(Nb–Cl)].

[$PdCl_2$(bppzm)] 9. To a CH_2Cl_2 (50 cm^3) solution of [$PdCl_2$(PhCN)$_2$] (0.371 g, 0.97 mmol) was added an equimolar quantity of bppzm (0.500 g, 0.97 mmol). The solution was stirred for 5 h at room temperature. The solvent was removed *in vacuo* and a yellow solid was obtained. Yield 85% (Found: C, 53.51; H, 3.98; N, 8.21. $C_{31}H_{26}Cl_2N_4P_2Pd$ requires C, 53.64; H, 3.78; N, 8.07%). ^{1}H NMR ($CDCl_3$, 295 K), δ 6.71 (s, 2 H, CH_2), 7.38 (d, $^3J_{HH}$ = 1.5, 2 H, H^3), 5.76 (dd, $^3J_{HH}$ = 1.4, $^3J_{HP}$ = 1.3 Hz, 2 H, H^4), 7.68–7.26 (m, 20 H, Ph). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ 62.68 (t, $^3J_{PC}$ = 3.5 Hz, CH_2), 140.28–140.14 (m, C^3), 118.98–118.89 (s, C^4), 134.41–128.26 (m, Ph). ^{31}P-{^{1}H} NMR ($CDCl_3$, H_3PO_4 as reference), δ 4.66 (s, PPh_2). IR (Nujol, cm^{-1}) 332, 309 [ν(Nb–Cl)].

[$PtCl_2$(bppzm)] 10. The synthetic procedure was the same as for complex **9**, using [$PtCl_2$(PhCN)$_2$] (0.457 g, 0.97 mmol) and bppzm (0.500 g, 0.97 mmol), to give complex **10** as a yellow solid. The crystals for X-ray diffraction were grown from a solution of CH_2Cl_2–Et_2O by slow evaporation of the solvent. Yield 80% (Found: C, 47.34; H, 3.11; N, 6.98. $C_{31}H_{26}Cl_2N_4P_2Pt$ requires C, 47.58; H, 3.35; N, 7.16%). ^{1}H NMR ($CDCl_3$, 295 K), δ 6.70 (s, 2 H, CH_2), 7.33 (s, 2 H, H^3), 5.70 (s, 2 H, H^4), 7.63–7.29 (m, 20 H, Ph). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ 62.44 (s, CH_2), 139.85 (t, $^3J_{PC}$ = 5.5, C^3), 118.46 (t, $^3J_{PC}$ = 4.0 Hz, C^4), 134.17–128.01 (m, Ph). ^{31}P-{^{1}H} NMR ($CDCl_3$, H_3PO_4 as reference), δ −11.30 (t, J_{PPt} = 3623.2 Hz, PPh_2). IR (Nujol, cm^{-1}) 328, 293 [ν(Nb–Cl)].

Crystal data for 10. Yellow crystals (0.50 × 0.30 × 0.23 mm) are triclinic with space group $P\bar{1}$ and lattice constants a = 10.32(2), b = 10.965(6), c = 17.486(8) Å, α = 94.04(5), β = 101.65(9), γ = 117.75(5)°, V = 6164(13) Å^3, Z = 2, D_c = 1.627 g cm^{-3}, μ = 45.27 cm^{-1}. Reflections were collected at 25 °C on a NONIUS-MACH3 diffractometer equipped with graphite monochromated radiation (λ = 0.7107 Å), 6201 reflections collected ($2 < \theta < 28$), 5450 reflections with $I > 2\sigma(I)$. Data were corrected in the usual fashion for Lorentz and polarization effects, and empirical absorption correction was based on a ψ scan (range of transmission factors 0.610–1.000).[16] Data/parameters 6201/382. The structure was solved by direct methods[17] and refinement on F^2 was carried out by full-matrix least squares analysis.[18] Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions but not refined. Final disagreement indices are R_1 = 0.0378, wR_2 = 0.1085, GOF = 0.953, largest difference peak and hole 2.024 and −1.490 e Å^{-3}.

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Paper 8/05683H