Synthetic and Structural Studies of Pd^{II} and Pt^{II} Complexes with Quincorine and Quincoridine Derivatives

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A series of Pd^{II}-quincorine and -quincoridine complexes in which the ligands are coordinated through *N*,*O*-donor atoms have been synthesised, and their structural features determined by X-ray crystallography. Additionally, new chiral tetradentate *N*,*P*-ligands containing two quinuclidine cores bridged through a *cis*-enediyne fragment have been obtained. The different coordinating properties of the new ligands, which contain two soft phosphorus and two hard nitrogen donors, to Pd^{II} and Pt^{II} are emphasised. Several typical complexes were structurally characterised by X-ray crystallography.

Introduction

The development of asymmetric catalysis using chiral organic compounds or chiral metal complexes has induced an increased interest in the synthesis of new optically active ligands.[1,2] In this context *cinchona* alkaloids, such as quinine and quinidine and their derivatives, readily available in both pseudo-enantiomeric forms, play an important role and are extensively used. Among asymmetric synthetic procedures in organic chemistry, one of the best known is the asymmetric dihydroxylation of olefins using various *cinchona* alkaloid derivatives as chiral monodentate amine ligands for OsO_4 as developed by Sharpless.[3] The mechanism of this reaction was also extensively analysed by Corey, and the most efficient ligands for promoting face-selective dihydroxylation of olefins were found to be bis-*cinchona* alkaloids such as the $(DHQD)_2PHAL$ system (Figure 1).[3−5]

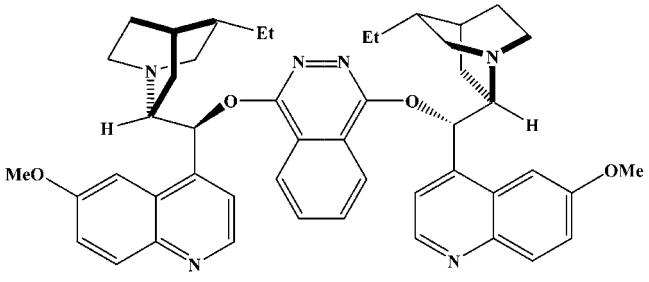

Figure 1. $(DHQD)_2PHAL$, a bis-*cinchona* alkaloid

Additionally, bidentate *N*,*P*-ligands have acquired a growing importance in the development of coordination chemistry and asymmetric catalysis.[6] A remarkable number of aminophosphane, -phosphite, -phosphonite and -phosphinite ligands have been developed and their complexes used for asymmetric catalytic reactions, such as cross-coupling, hydroformylation and hydrogenation.[7−9]

Beck et al. reported the first *N*,*O*-chelate complexes of cinchonidine and cinchonine, but only a few metal complexes of *cinchona* alkaloids have been described.[10] Quincoridine-based aminophosphite ligands and their Rh^{I} and Pd^{II} complexes have also been reported by Gavrilov and coworkers.[11] Recently, Lemaire et al. have developed a new family of *N*,*P*-ligands derived from quincorine (QCI) and quincoridine (QCD) with applications in hydroformylation, asymmetric hydrosilylation and asymmetric Grignard cross-coupling reactions.[12]

The chirality, in combination with the donor properties of QCI and QCD, should provide a useful ligand system for catalytic processes. QCI and QCD contain four stereogenic centres each, including the *N*-chiral 1*S*-configured bridgehead and also possess three potential donor sites: the OH group, a tertiary N-atom and an olefinic C=C bond (Figure 2).

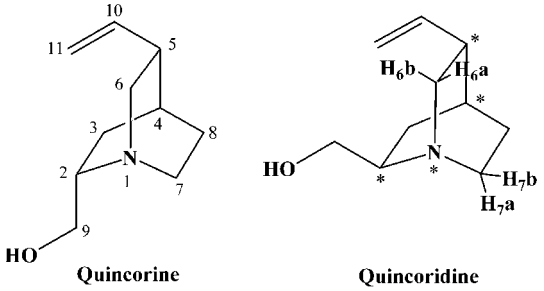

Figure 2. Atom numbering scheme and stereocentres in quincorine (QCI) and quincoridine (QCD)

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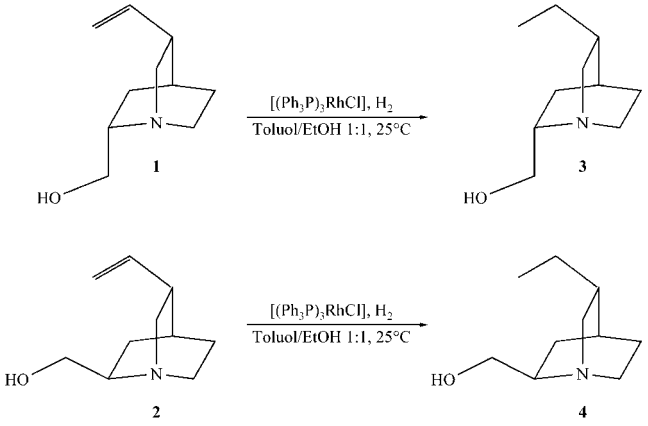
In the present work we report on new *N*,*O*-chelate and bis-*N*,*O*-chelate complexes of Pd^{II} with QCI and QCD and their corresponding saturated derivatives. New chiral aminophosphinites, containing two quinuclidine cores bridged through a *cis* enediyne fragment, are developed and their different coordination modes are described.

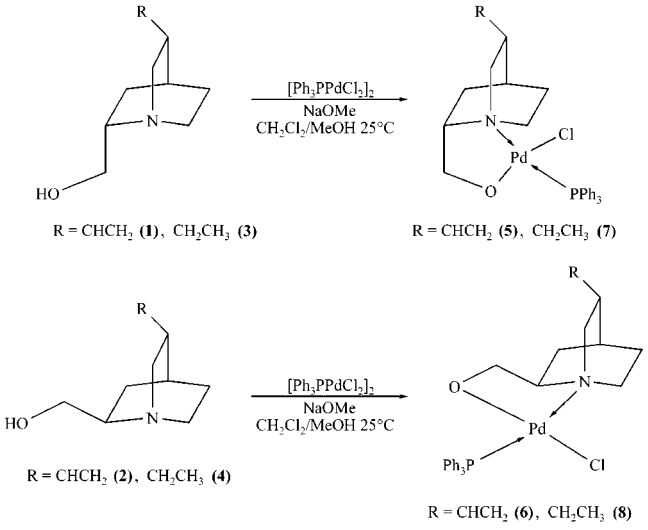
Results and Discussion

N,*O*-Chelate Complexes

In the course of this research program directed toward the synthesis and characterisation of new metal complexes, we have used QCI [(2*S*,4*S*,5*R*)-2-hydroxymethyl-5-vinyl-2-quinuclidine] (**1**) and QCD [(2*R*,4*S*,5*R*)-2-hydroxymethyl-5-vinyl-2-quinuclidine] (**2**) as ligands. The corresponding saturated derivatives [(2*S*,4*S*,5*R*)-5-ethyl-2-hydroxymethyl-2-quinuclidine] (**3**) and [(2*R*,4*S*,5*R*)-5-ethyl-2-hydroxymethyl-2-quinuclidine] (**4**) were prepared efficiently by hydrogenation, according to a known literature procedure (Scheme 1).[13]



Scheme 1. The synthesis of dihydro-QCI (**3**) and dihydro-QCD (**4**)



Scheme 2. The synthesis of phosphane Pd^{II}-QCI and -QCD complexes

Reactions of two equivalents of the ligands **1**−**4** with one equivalent of the chloro-bridged complex [$(Ph_3P)(Cl)Pd(\mu\text{-}Cl)_2Pd(Cl)(PPh_3)$] in the presence of NaOMe in CH_3OH/CH_2Cl_2 gave the corresponding five-membered ring chelate complexes **5**−**8** (Scheme 2).

All of the complexes **5**−**8** gave the expected fragmentation patterns in their positive FAB mass spectra. In the $^{31}P\{^1H\}$ NMR spectra of **5**−**8** all compounds display two singlets around δ = 26 (high intensity) and 23 ppm (low

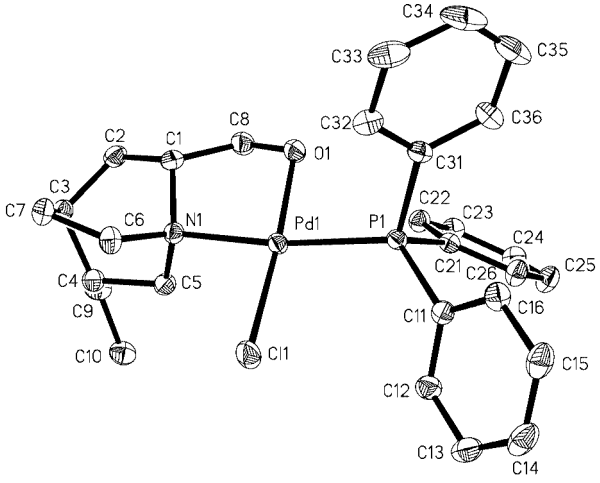


Figure 3. The molecular structure of **7**; H atoms omitted for clarity; ellipsoids at 50% probability level; selected bond lengths [Å] and angles [°]: Pd1−P1 2.2480(6), Pd1−Cl1 2.3020(6), Pd1−O1 1.9986(16), Pd1−N1 2.1043, O1−C8 1.407(3), N1−C1 1.496(3), N1−C5 1.495(3), N1−C6 1.494(3), C(aliph.)−C(aliph.) 1.508(3)−1.549(3); O1−Pd1−N1 84.69(7), N1−Pd1−Cl1 92.17(5), Cl1−Pd1−P1 95.99(2), P1−Pd1−O1 87.08(5), C8−O1−Pd1 108.87(13), O1−C8−C1 110.03(17), C8−C1−C2 115.78(18), C8−C1−N1 108.54(17), N1−C1−C2 109.90(17), C1−N1−C5 107.78(17), C1−N1−C6 110.55(17), C5−N1−C6 108.38(17), C3−C4−C5 107.86(18), C3−C4−C9 112.84(19), C5−C4−C9 112.99(18)

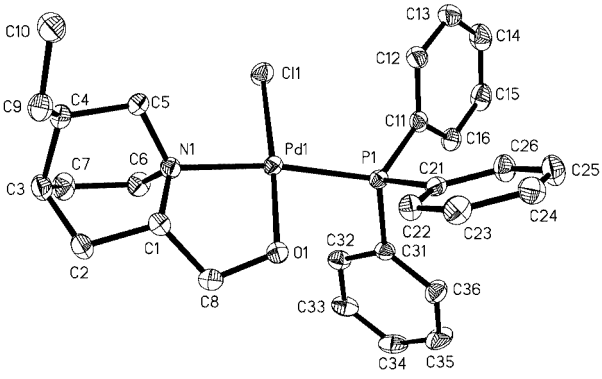


Figure 4. The molecular structure of **8**; H atoms omitted for clarity; ellipsoids at 50% probability level; selected bond lengths [Å] and angles [°]: Pd1−P1 2.2470(3), Pd1−Cl1 2.3082(3), Pd1−O1 2.0036(8), Pd1−N1 2.1101(9), O1−C8 1.4034(15), N1−C1 1.5103(14), N1−C5 1.4967(15), N1−C6 1.4940(15), C(aliph.)−C(aliph.) 1.5093(17)−1.5504(16); O1−Pd1−N1 85.27(4), N1−Pd1−Cl1 91.56(3), Cl1−Pd1−P1 97.409(11), P1−Pd1−O1 85.81(2), C8−O1−Pd1 107.79(7), O1−C8−C1 110.96(10), C8−C1−C2 116.19(10), C8−C1−N1 108.42(9), N1−C1−C2 109.30(10), C1−N1−C5 111.17(9), C1−N1−C6 106.98(9), C5−N1−C6 107.70(9), C3−C4−C5 106.62(10), C3−C4−C9 113.44(10), C5−C4−C9 111.40(10)

intensity ≈ 5%). The signal with the high intensity was assigned to the *trans*-P−M−N isomer whereas the low intensity signal corresponds to the *cis*-P−M−N isomer. The formation of the five-membered chelate rings in **5**−**8** was also confirmed in the ^{1}H NMR spectra by the diastereotopicity of the 9-H atoms: an upfield shift of ca. 0.5 ppm was observed for one of them. The H-6 and H-7 atoms suffer a small downfield shift probably because of interaction with the d_z^2 orbital of the metal atom and the coordination of the tertiary N-atom.

Deep yellow crystals of the QCI-Pd^{II} complex **7** and the QCD-Pd^{II} complex **8**, suitable for X-ray analysis, were obtained from diethyl ether solutions by layering with hexanes. Single-crystal X-ray structure determinations (Figure 3 and 4) proved that the *trans*-P−M−N isomers were formed as the main products because of the steric demands of the bulky ligands. The chirality at C-2 is retained in the complexes. The coordination geometry around Pd is virtually square planar in both cases (mean dev. in **7**: 1.86 pm; **8**: 2.86 pm). The Pd atoms are incorporated into five-membered chelate rings. In the case of **7**, the ring adopts a twist conformation, and in **8** an envelope conformation, with C-8 as the flap. The similarity in the bonding situation around

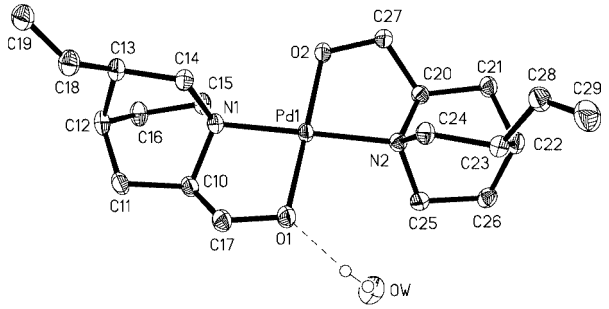
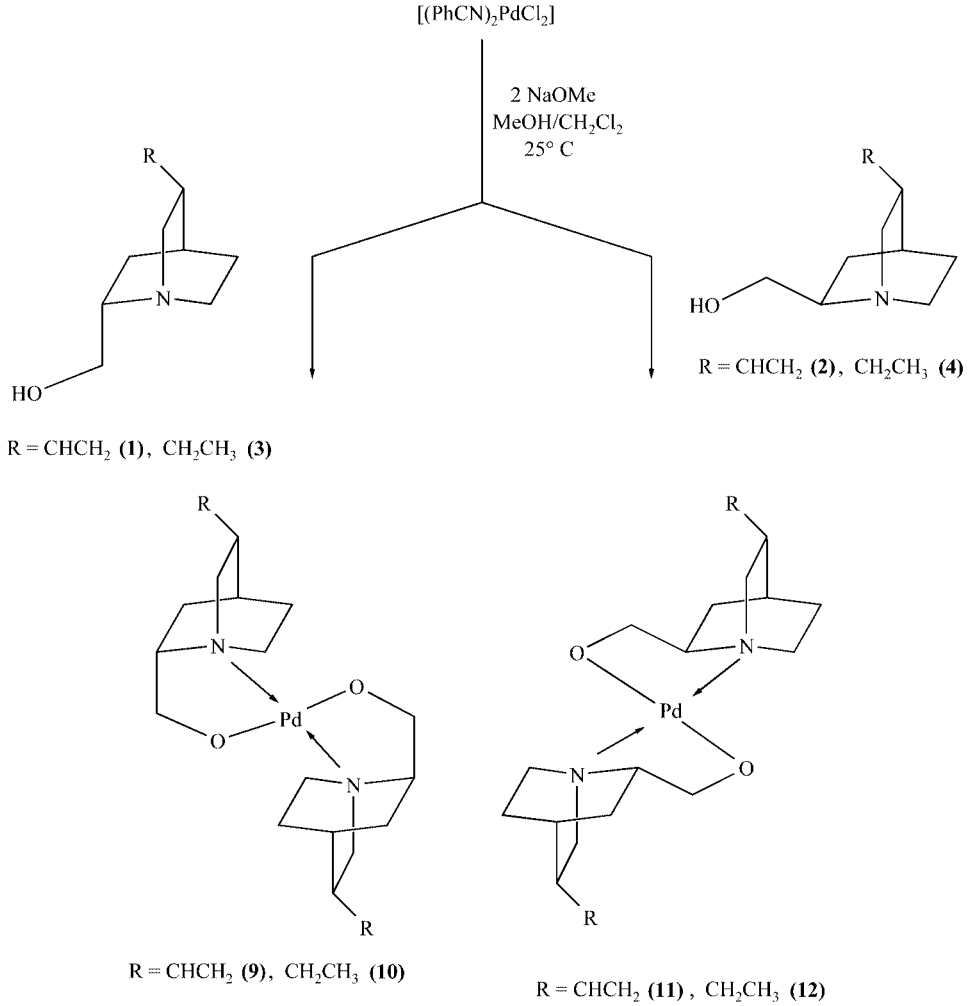


Figure 5. The molecular structure of **9** in the crystal; non-water hydrogens omitted for clarity; ellipsoids at 50% probability level; selected bond lengths [Å] and angles [°]: Pd1−O1 1.9852(14), Pd1−N1 2.0372(16), Pd1−O2 2.0006(14), Pd1−N2 2.0335(15), O1−C17 1.401(2), O2−C27 1.400(2), N1−C20 1.502(2), N1−C24 1.484(2), N1−C25 1.487(2), N2−C10 1.501(2), N2−C14 1.478(2), N2−C15 1.493(2), C13−C18 1.488(3), C18−C19 1.312(4), C23−C28 1.499(3), C28−C29 1.312(3), C(aliph.)−C(aliph.) 1.508(3)−1.556(3), O1···H99a 1.79(5), O2···H98a 1.92(3); O1−Pd1−N1 94.10(6), N1−Pd1−O2 85.24(6), O2−Pd1−N2 95.32(6), N2−Pd1−O1 85.49(6), C10−N2−Pd1 103.67(11), C14−N2−Pd1 115.40(11), C15−N2−Pd1 108.82(11), C20−N1−Pd1 106.48(11), C24−N1−Pd1 118.12(11), C25−N1−Pd1 104.60(11), C14−C13−C18 115.26(18), C24−C23−C28 117.56(16), C13−C18−C19 129.0(2), C23−C28−C29 129.2(2)



Scheme 3. The synthesis of homoleptic Pd^{II}-QCI and -QCD complexes

Pd is also reflected in nearly identical bond lengths at Pd in both cases. They match the typically observed range for Pd−P, Pd−Cl and Pd−N bond lengths.

When one equivalent of *trans*-[$PdCl_2(PhCN)_2$] was reacted with two equivalents of **1**−**4** in the presence of NaOMe in methanol/dichloromethane, the bis-*N*,*O*-chelate complexes **9**−**12** were obtained in excellent yields (90%; Scheme 3).

All of the compounds **9**−**12** show the expected fragmentation patterns and the molecular ions in their EI mass spectra. Again, the ^{1}H NMR spectra confirmed the formation of the spiro complexes **9**−**12** because of the diastereotopicity of the 9-H atoms. These exhibit a downfield shift and an upfield shift associated with the different environment obtained through the closure of the five-membered chelate rings. The H-6 and H-7 atoms suffer a small downfield shift, perhaps because of the coordination of the tertiary N-atom to Pd and the interaction with the d_z^2 orbital of the metal.

Yellow crystals of **9** and **11** suitable for X-ray analysis were obtained from Et_2O by layering with hexanes. As shown in Figure 5 and 6, the coordination geometry around Pd is square planar (mean dev. **9**: 2.29 pm; **11**: 4.73 pm), with N(1) and N(2) occupying the *trans* positions. Because of the chelating ligands, Pd is in both cases the spiro atom and therefore part of two five-membered ring systems that display approximately envelope conformations, with the quinuclidine-bound carbon atoms in the flap positions.

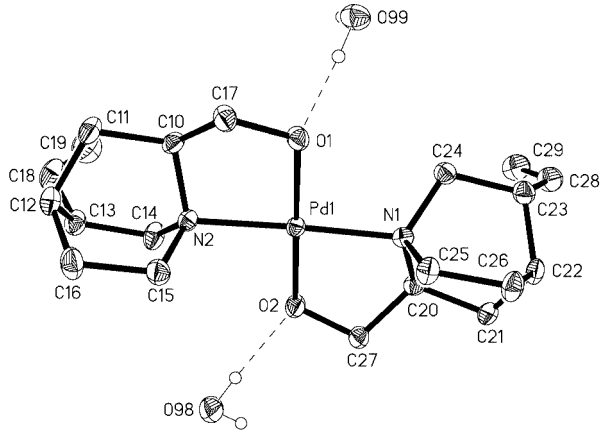


Figure 6. The molecular structure of **11** in the crystal; non-water hydrogens omitted for clarity; ellipsoids at 50% probability level; selected bond lengths [Å] and angles [°]: Pd1−O1 2.0054(10), Pd1−N1 2.0475(11), Pd1−O2 2.0037(10), Pd1−N2 2.0522(11), O1−C17 1.4048(17), O2−C27 1.4097(16), N1−C10 1.5149(17), N1−C14 1.4945(16), N1−C15 1.4915(19), N2−C20 1.5120(17), N2−C24 1.4978(18), N2−C25 1.4952(16), C13−C18 1.502(2), C18−C19 1.322(2), C23−C28 1.5070(19), C28−C29 1.311(2), C(aliph.)−(aliph.) 1.515(2)−1.5559(19), O1···Hw2 2.01(3); O1−Pd1−N1 85.99(4), N1−Pd1−O2 93.14(4), O2−Pd1−N2 85.94(4), N2−Pd1−O1 94.91(4), C10−N1−Pd1 104.87(8), C14−N1−Pd1 111.92(8), C15−N1−Pd1 114.12(8), C20−N2−Pd1 104.49(8), C24−N2−Pd1 111.81(8), C25−N2−Pd1 114.15(8), C14−C13−C18 112.03(12), C24−C23−C28 112.34(11), C13−C18−C19 125.93(19), C23−C28−C29 125.04(15)

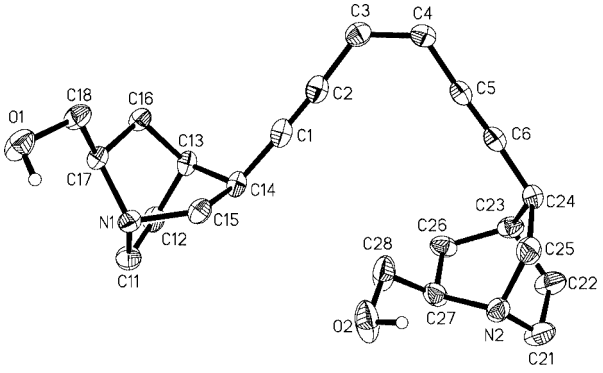
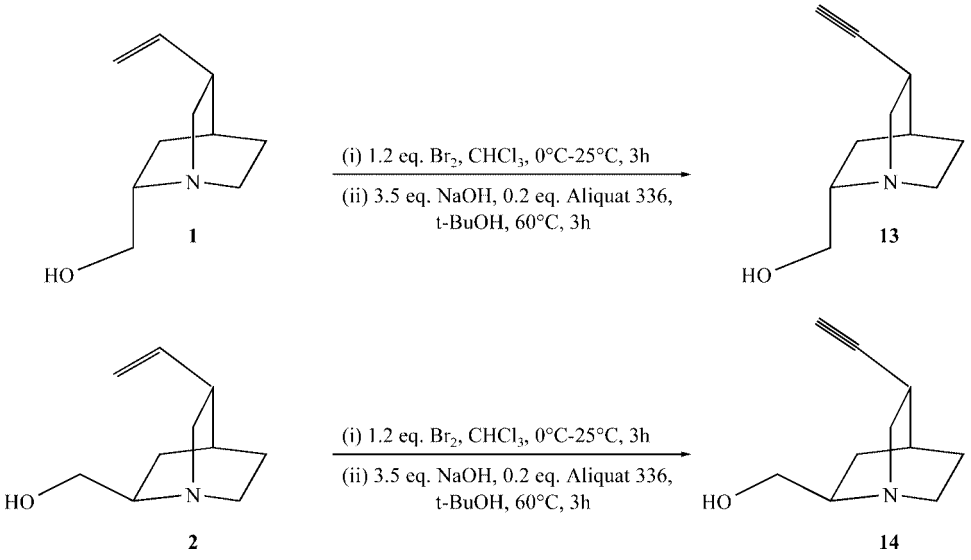


Figure 7. The molecular structure of **18** in the crystal; H-atoms omitted for clarity; ellipsoids at 50% probability level; selected bond lengths [Å] and angles [°]: C1−C2 1.199(2), C2−C3 1.429(2), C3−C4 1.343(2), C4−C5 1.428(2), C5−C6 1.197(2), C1−C14 1.467(2), C6−C24 1.467(2), N1−C11 1.4893(19), N1−C15 1.4732(18), N1−C17 1.4893(17), N2−C21 1.484(2), N2−C25 1.468(2), N2−C27 1.4804(19), C(aliph.)−C(aliph.) 1.507(3) to 1.573(2); C2−C1−C14 177.94(15), C1−C2−C3 176.98(15), C2−C3−C4 125.56(13), C3−C4−C5 125.16(13), C4−C5−C6 177.23(15), C5−C6−C24 176.72(15), C17−C18−O1 113.80(13), C27−C28−O2 113.97(16)



Scheme 4. The synthesis of didehydro-QCI (**13**) and didehydro-QCD (**14**)

Both compounds crystallised with water molecules (**9**: one; **11**: two). In complex **9** intra- and intermolecular hydrogen-bonding [O−H···O: H···O 207(2)[i], 201(3) pm; [i] x, $y + 1$, z] forms chains, which are also connected by non-classical C−H···O hydrogen-bonding [H···O 266[ii], 248 pm[iii]; [ii] $-x + 2$, $y - 0.5$, $-z + 1$, [iii] $-x + 1$, $y + 0.5$, $-z + 1$]. The hydrogen-bonding scheme in **11** is similar, but with stronger classical O−H···O bonds [H···O 179(5), 192(3), 203(3)[i], 201(5) pm[ii]; [i] $-x$, $y - 0.5$, $-z + 1.5$, [ii] x, $y + 1$, z] and comparable non-classical C−H···O bonds [H···O: 263[i], 233[i], 254[iii], 251 pm[iv]; [iii] $-x + 1$, $y + 0.5$, $-z + 1.5$, [iv] $-x$, $y + 0.5$, $-z + 1.5$]. Again, the bond lengths in the molecules are unexceptional and match the usual observed ranges.

N,P-Ligand Synthesis

For the synthesis of *N,P*-ligands we used 10,11-didehydroquincorine (**13**) and 10,11-didehydroquincoridine (**14**) as precursors. The terminal alkynes **13** and **14** were prepared efficiently from **1** and **2** according to a known literature procedure (Scheme 4).[13]

The symmetrical (*Z*)-enediynes **17** and **18** were obtained in good yields in a two-step procedure[14,15] involving two sequential $[Pd(PPh_3)_4]$- and $[PdCl_2(PhCN)_2]$-catalysed coupling reactions from (*Z*)-1,2-dichloroethene and **13** and **14**. Colourless single crystals of **18** were obtained by layering a CH_2Cl_2 solution with hexanes. A structure determination revealed a *cis*-arrangement in the molecule (Figure 7).

Classical hydrogen-bonding of the type O−H···N [H···N: 196(3)[i], 203(3) pm[ii]; [i] $-x + 1$, $y - 0.5$, $-z + 0.5$; [ii] $-x + 1$, $y + 0.5$, $-z + 0.5$] together with non-classical C−H···O hydrogen-bonding [H···O: 257[iii], 245 pm[iv]; [iii] $x + 1$, y, z; [iv] $-x + 2$, $y + 0.5$, $-z + 0.5$] leads to the formation of zigzag chains parallel to the crystallographic *b*-axis in the crystal packing (Figure 8).5

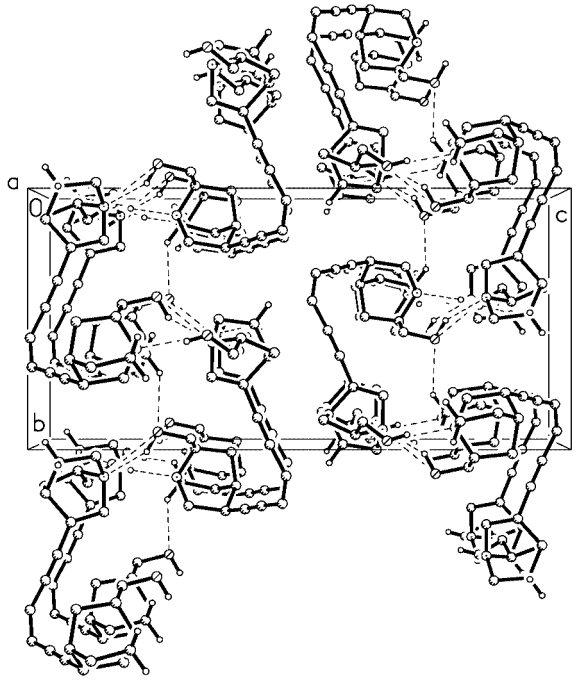


Figure 8. The packing of **18** in the crystal showing the hydrogen bonding; view along the *a* axis; molecules contain the OH group; other hydrogens omitted

Treatment of **17** and **18** with chlorodiphenylphosphane in dichloromethane, in the presence of triethylamine, gave the bis-aminophosphinites **19** and **20** in very good yields (Scheme 5).

These are pale yellow oils, which are stable under nitrogen atmosphere for a long time. In the $^{31}P\{^1H\}$ NMR spectra the resonances of the P atoms are found at $\delta = 115.29$ (**19**) and $\delta = 114.60$ ppm (**20**), respectively.

Platinum(II) and Palladium(II) Complexes

The bis-*N,P*-aminophosphinites **19** and **20**, having two soft electron-donating atoms and two hard electron-donating atoms, show different coordinating properties towards Pt^{II} and Pd^{II}. It is known that the formation of square-planar Pt^{II} complexes is strongly dependent on a number of factors, such as solvent polarity, the *trans* effect of the resident ligands, and the order of adding the reactants. When phosphorus is coordinated to ^{195}Pt, the geometry of the products can often be assigned from the magnitude of the coupling constants. These are strongly dependent on the

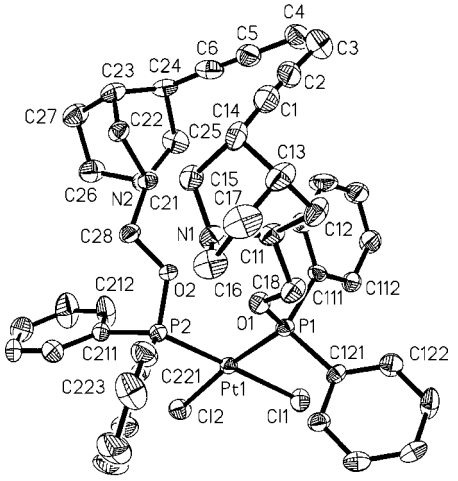
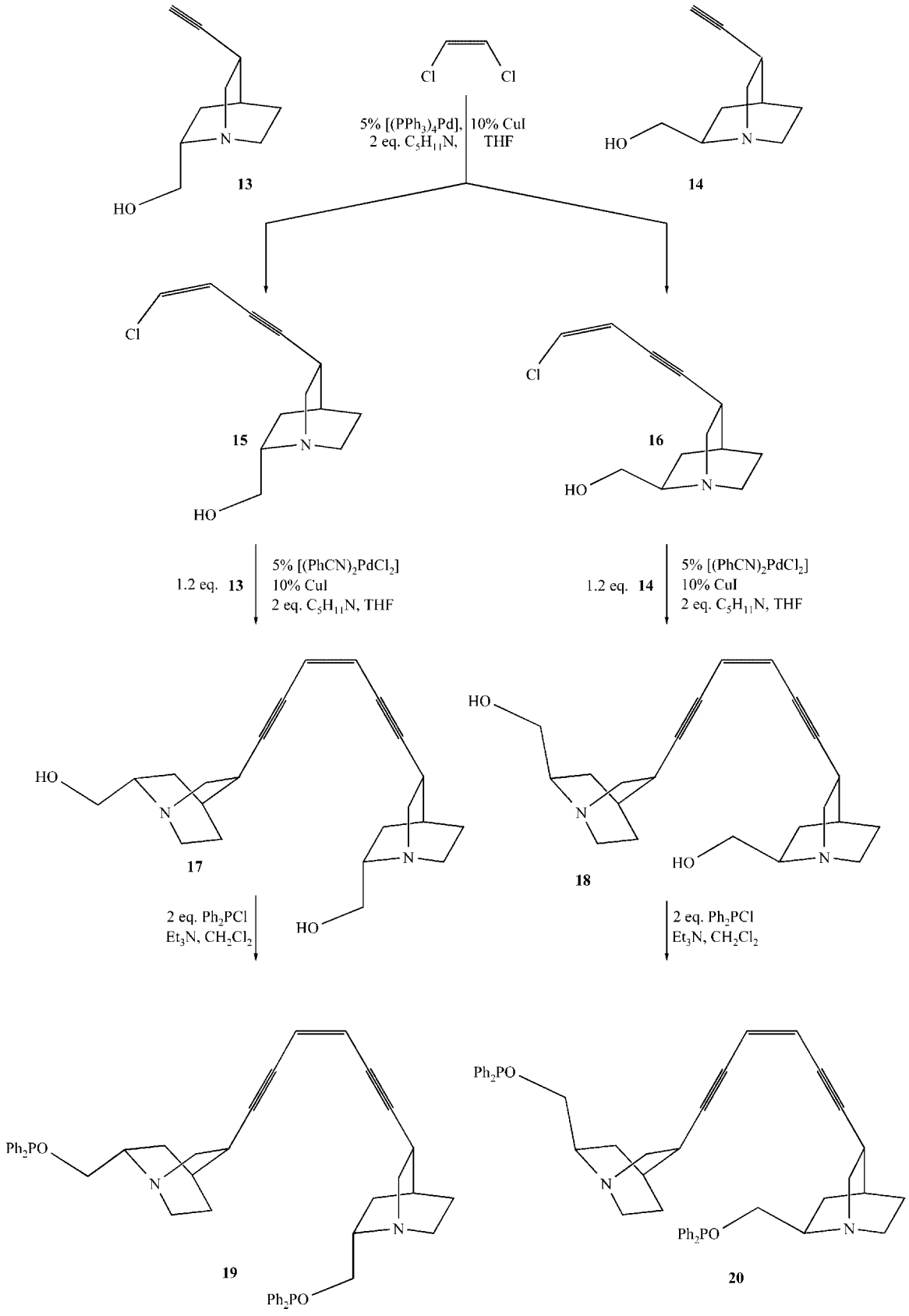
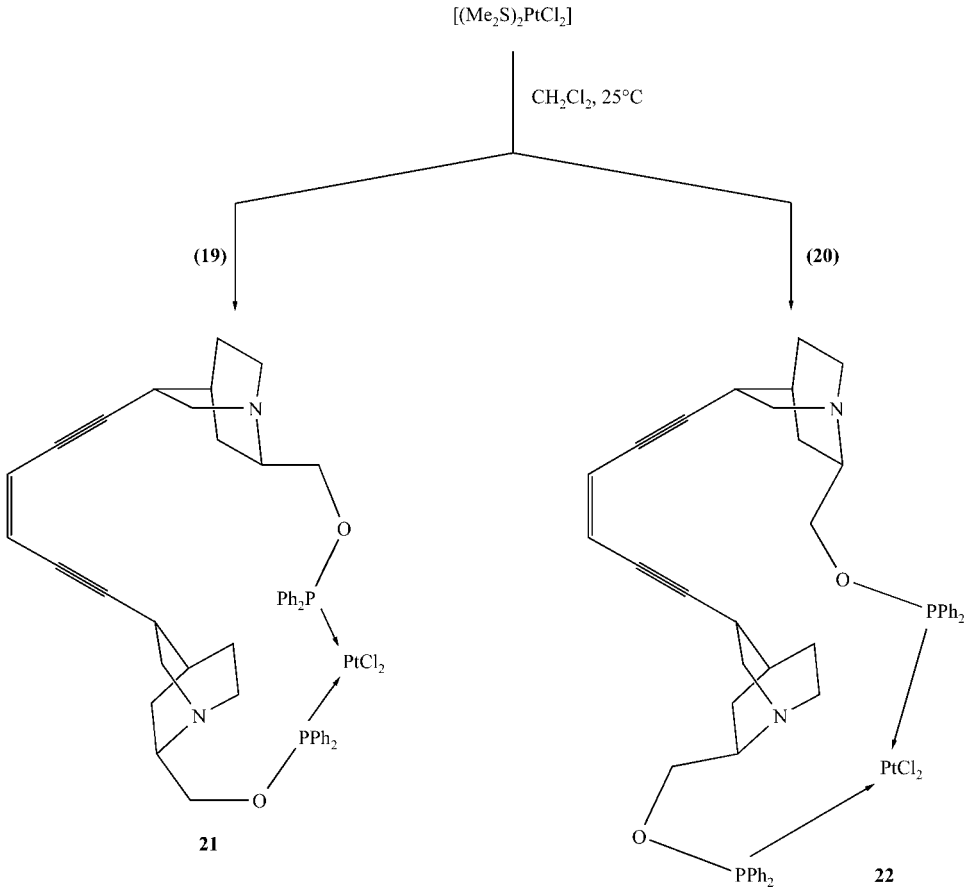


Figure 9. The molecular structure of **21**; hydrogen atoms and the disordered THF molecule are omitted for clarity; ellipsoids at 50% probability level; selected bond lengths [Å] and angles [°] (corresponding values of the second independent molecule in the asymmetric unit are given in brackets): Pt1−P1 2.2231(19) [2.2291(18)], Pt−1P2 2.229(2) [2.2349(18)], Pt1−Cl1 2.3642(19) [2.3564(18)], Pt1−Cl2 2.3532(19) [2.3536(18)], P1−O1 1.587(5) [1.597(5)], P2−O2 1.600(4) [1.601(4)], O1−C18 1.466(7) [1.459(6)], O2−C28 1.438(6) [1.442(6)], C1−C2 1.176(9) [1.204(9)], C2−C3 1.470(10) [1.473(11)], C3−C4 1.328(10) [1.299(14)], C4−C5 1.429(9) [1.363(15)], C5−C6 1.191(9) [1.227(15)], C1−C14 1.482(9) [1.459(8)], C6−C24 1.481(8) [1.415(15)], N1−C11 1.483(7) [1.456(6)], N1−C15 1.453(7) [1.461(7)], N1−C16 1.486(7) [1.490(8)], N2−C21 1.488(6) [1.515(8)], N2−C25 1.457(7) [1.478(10)], N2−C26 1.471(7) [1.501(12)], C(aliph.)−C(aliph.) 1.509(9)−1.580(7) [1.496(7)−1.583(11)]; P1−Pt1−P2 94.17(7) [93.23(7)], P1−Pt1−Cl1 85.41(7) [93.51(7)], P2−Pt1−Cl2 92.07(7) [85.85(7)], Cl1−Pt1−Cl2 88.29(7) [87.29(7)], C18−O1−P1 122.1(4) [116.2(3)], C28−O2−P2 127.5(4) [128.8(4)], O1−C18−C11 109.9(4) [111.0(4)], O2−C28−C21 107.9(4) [107.8(4)], C14−C1−C2 174.9(7) [177.3(7)], C1−C2−C3 176.0(7) [175.9(9)], C2−C3−C4 122.8(7) [126.3(10)], C3−C4−C5 128.6(7) [127.3(9)], C4−C5−C6 176.4(7) [176.9(10)], C5−C6−C24 175.9(6) [176.6(10)]



Scheme 5. The synthesis of the bis-*N*,*P*-aminophosphinites **19** and **20** from didehydro-QCI (**13**) and didehydro-QCD (**14**)



Scheme 6. Platinum(II) chelate complexes of the bis-*N*,*P*-aminophosphinites **19** and **20**

ligand *trans* to the phosphorus atom, because of the inductive effect of that ligand on the platinum-phosphorus bond. Ligands with a very strong σ-inductive character reduce the positive charge on the platinum atom and thus weaken the overlap of the phosphorus and the metal orbitals relative to the *trans*-ligands, which have weaker σ-inductive effects.[16]

When a solution of $[PtCl_2(SMe_2)_2]$ in dichloromethane was added to a solution of **19** or **20** in the same solvent, in a 1:1 molar ratio, the *cis* complexes **21** and **22** were obtained (Scheme 6).

In the $^{31}P\{^1H\}$ NMR spectra singlets, with ^{195}Pt satellites, at δ = 83.89 ppm ($^1J_{Pt,P}$ = 2099.28 Hz) (**21**) and δ = 85.10 ppm ($^1J_{Pt,P}$ = 2076.01 Hz) (**22**) are observed. The FAB mass spectra indicated that the complexes are monomeric. Slow diffusion of diethyl ether into a concentrated THF/dioxane solution of the complex **21** produced colourless crystals that crystallised in the non-centrosymmetric space group *P*1 with two independent molecules of **21** and one disordered and badly resolved THF molecule per formula unit (Figure 9).

The complex can be regarded as a 21-membered ring system with a $PtCl_2$ group that connects the phosphorus(III) ends of the ligand to form a macrocyclic complex with an essentially planar coordination geometry at platinum (mean dev. Pt1: 1.2; Pt2: 4.2 pm). Because of the steric demand of the aminophosphinite ligand, the bite angle at platinum is somewhat wider than 90° [94.17(7), 93.23(7)°]. The ligand is bound symmetrically with similar Pt−P bond lengths [222.31(19), 222.9(2); 222.91(18), 223.49(18) pm, respectively].

Attempts to synthesise the corresponding *trans* complex from **20** through the inverse addition of the reactants led, after 30 minutes at room temperature, to a complex mixture of products. The $^{31}P\{^1H\}$ NMR spectrum of this mixture displays many signals with different intensities and corresponding ^{195}Pt satellites, including the signal of the reactant. After 24 h at room temperature the *cis* complex **22** became the main product observed by ^{31}P NMR spectroscopy. Treatment of two equivalents of $[PtCl_2(SMe_2)_2]$ with one equivalent of **20**, in dichloromethane, again produced the *cis* complex **22**.

Armstrong and co-workers have reported recently that the bis-phosphane ligands 2,7-bis(3-diphenylphosphanylpropoxy)naphthalene (DPPN) and 2,7-bis(3-diphenylphosphanylethoxy)naphthalene (DPEN) form dimeric *cis*, *cis*/*trans* and *trans* complexes of platinum(II) depending on the conditions employed.[17] They have also demonstrated that an excess of the ligand catalyzes *trans*/*cis* isomerisation, either by adding an excess of the phosphane, or by having the excess present during the addition of the platinum precursor. Based on these and our results we conclude that the *cis* complexes **21** and **22** are the thermodynamic products.

The complex mixture formed by the inverse addition of the reactants should be a mixture of kinetic and thermodynamic products and thus the free unchanged ligand has catalysed a *trans*/*cis* isomerisation. The ligands **19** and **20** show a marked preference to form *cis*-P−M−P-monomeric metallamacrocycles with Pt^{II} centres, even though a 1:2 molar ratio was employed.

In view of the interesting complexes **21** and **22** we tried to obtain the corresponding complexes with Pd^{II}. The results were completely different. The reaction of one equivalent of **20** with one equivalent of $[(\eta^4\text{-}C_7H_8)PdCl_2]$ in dichloromethane produced a yellow solid. The $^{31}P\{^1H\}$ NMR spectrum of the crude product shows many singlets up to $\delta = 103$ ppm. Attempts to isolate a pure complex from the mixture were unsuccessful.

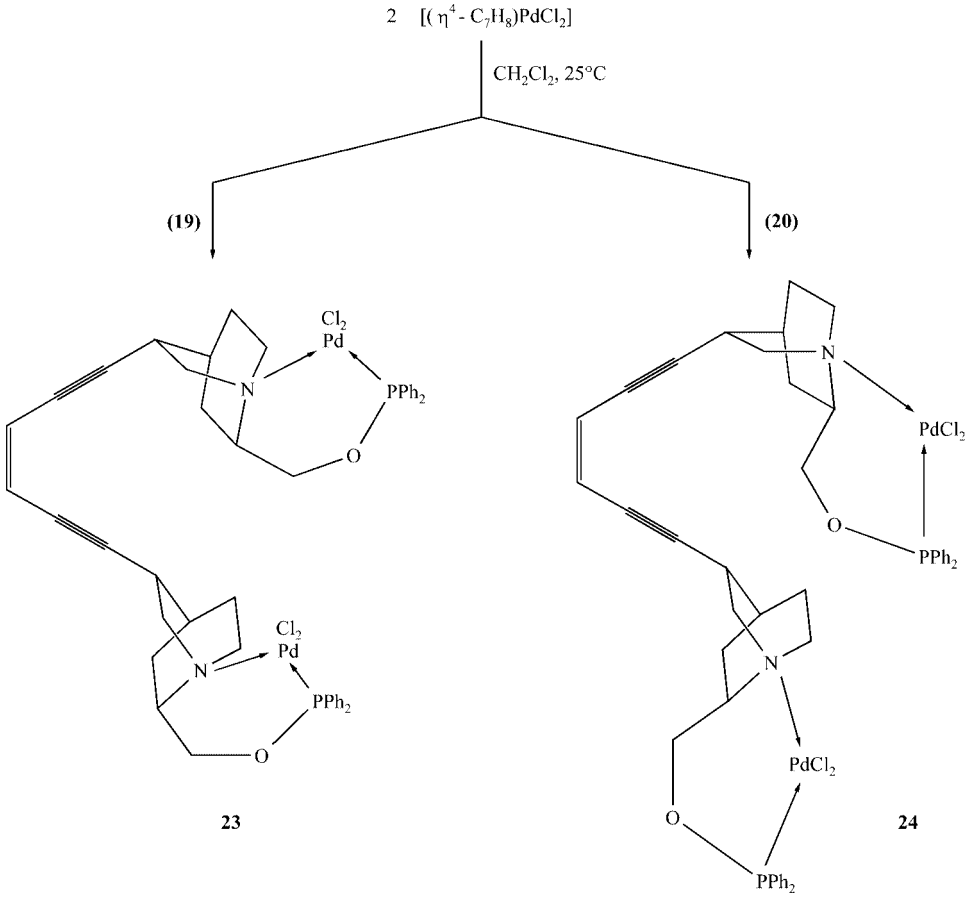
When one equivalent of **19** or **20** was allowed to react with two equivalents of $[(\eta^4\text{-}C_7H_8)PdCl_2]$ in dichloromethane yellow solids were again obtained (Scheme 7).

The $^{31}P\{^1H\}$ NMR spectra of these products show only one signal around $\delta = 103$ ppm. The ESI mass spectra indicated that the compounds are the bis-*N*,*P*-chelate complexes **23** and **24** (Scheme 5). The formation of the six-membered chelate rings in **23** and **24** is also confirmed by ^1H NMR spectra. The 6b-H and 7a-H atoms undergo downfield shifts of more than 1.5 ppm in comparison with the free ligands because of the anisotropy of the phenyl groups. Secondly, in the $^1H,^1H$-COSY spectra of **23** and **24** the cross-peaks corresponding to the vicinal correlations of the 2-H atom with the 9-H atoms disappear due to the changing of the dihedral angles through the closure of the six-membered rings.

In contrast to platinum(II), palladium(II) shows a marked preference to form bis-*N*,*P*-chelate complexes with ligands **19** and **20**.

Conclusion

We have shown that the *N*,*O*-chelate complexes and bis-*N*,*O*-chelate complexes of Pd^{II} with QCI and QCD and their saturated derivatives are easy to prepare. The syntheses of two new bis-*N*,*P*-aminophosphinite ligands, derived from QCI and QCD, have been developed. Both ligands have two soft and hard donor-atoms that can be exploited to form mononuclear and binuclear chelate complexes. Platinum(II) forms P−M−P metallamacrocycle complexes, but palladium(II) prefers to form bis-*N*,*P*-chelate complexes with these ligands.



Scheme 7. Dinuclear palladium(II) complexes of the bis-*N*,*P*-aminophosphinites **19** and **20**

Experimental Section

General Remarks: All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 was freshly distilled under nitrogen from P_4O_{10}, THF was dried over sodium/benzophenone and distilled prior to use. Et_3N was heated to reflux over sodium and distilled under nitrogen. Piperidine and nBuNH$_2$ were dried over NaOH and then distilled under nitrogen. Ph_2PCl and (*Z*)-1,2-dichloroethene were purchased from Aldrich. $Pd(PPh_3)_4$,[18] $[PdCl_2(PhCN)_2]$,[19] $[(\eta^4\text{-}C_7H_8)PdCl_2]$,[20] $[PdCl_2(PPh_3)]_2$ [21] and $[PtCl_2(SMe_2)_2]$[16] were prepared according to literature procedures. QCI (**1**) and QCD (**2**) were donated by Buchler GmbH. Dihydro-QCI (**3**), dihydro-QCD (**4**), didehydro-QCI (**13**), and didehydro-QCD (**14**) were prepared according to a literature procedure.[13] Preparative column chromatography was performed on Fluka silica gel (particle size 30−60 μm). Analytical TLC was carried out on Polygram Sil G/UV_{254} plates (0.2 mm silica gel). *tert*-Butyl methyl ether (MTBE) was purchased from Fluka.

NMR spectra were obtained from CD_2Cl_2, $CDCl_3$ and C_6D_6 solutions. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker DRX-400 spectrometer operating at 400, 100 and 162 MHz, respectively. Chemical shifts (δ) are given in ppm relative to residual $CHCl_3$ (δ = 7.27 ppm), CH_2Cl_2 (δ = 5.31 ppm) or C_6H_6 (δ = 7.16 ppm) for ^{1}H, $CDCl_3$ (δ = 77.0 ppm), CD_2Cl_2 (δ = 53.7 ppm) or C_6D_6 (δ = 128.7 ppm) for ^{13}C, and 85% H_3PO_4 (δ = 0.0 ppm, external) for ^{31}P. Coupling constants (*J*) are given in Hz. Mass spectra were obtained using a Finnigan MAT 90 spectrometer operating in FAB and ESI mode for coordination complexes (the isotope patterns matched calculated patterns in all cases), and in EI mode for the organic precursors. In all cases precision mass analyses confirmed the purity of the products. Melting points were determined on a Büchi 510 Melting Point apparatus and are uncorrected.

General Procedure for the Preparation of the Pd^{II}-Phosphane Complexes 5−8: A solution of ligand **1**−**4** and NaOMe in CH_2Cl_2/MeOH (1:1) was added dropwise to a suspension of $[PdCl_2(PPh_3)]_2$ in CH_2Cl_2 and the mixture was stirred for 3 h at room temperature. The solvent was then removed under vacuum and the residue was dissolved again in CH_2Cl_2 and stirred for 15 minutes. The suspension was filtered to removed NaCl and the resulting clear solution was concentrated to dryness. The crude product was recrystallised from diethyl ether and *n*-hexane.

5: From **1** (100 mg, 0.6 mmol), NaOMe (0.6 mmol) and $[PdCl_2(PPh_3)]_2$ (263 mg, 0.3 mmol). $C_{28}H_{31}ClNOPPd$ (570.41). M.p. 158−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96−1.02 (m, 1 H, H-3), 1.55−1.67 (m, 2 H, H-8), 1.76−1.79 (m, 1 H, H-4), 1.80−1.87 (m, 1 H, H-3), 2.32−2.43 (m, 1 H, H-5), 3.06−3.12 (m, 2 H, H-6, H-9), 3.16−3.24 (m, 1 H, H-2), 3.36−3.43 (m, 1 H, H-7), 3.61−3.69 (m, 1 H, H-7), 3.74 (t, *J* = 11.44 Hz, 1 H, H-9), 3.81 (dd, *J* = 13.7, *J* = 10.62 Hz, 1 H, H-6), 5.00−5.07 (m, 2 H, 11), 5.77−5.86 (m, 1 H, 10), 7.26−7.38 (m, 9 H, Ph), 7.56−7.61 (m, 6 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.26 (C-3), 27.13 (C-4), 27.72 (C-8), 39.62 (C-5), 43.50 (C-7), 58.09 (C-6), 67.96 (C-2), 73.57 (C-9), 115.22 (C-11), 128.03 (d, *J* = 10.85 Hz, Ph *o*-C), 129.51 (d, *J* = 51.52 Hz, Ph *i*-C), 130.56 (d, *J* = 2.63 Hz, Ph *p*-C), 134.67 (d, *J* = 10.98 Hz, Ph *m*-C), 140.57 (C-10) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.84 (*trans* to N), 23.95 (*cis* to N) ppm. FAB: *m*/*z* = 570 $[M + H]^+$, 534 $[M - Cl]^+$.

6: From **2** (100 mg, 0.6 mmol), NaOMe (0.6 mmol) and $[PdCl_2(PPh_3)]_2$ (263 mg, 0.3 mmol). $C_{28}H_{31}ClNOPPd$ (570.41). M.p. 152−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25−1.31 (m, 1 H, H-3), 1.49−1.56 (m, 1 H, H-3), 1.62−1.72 (m, 3 H, H-8, H-4), 2.38−2.45 (m, 1 H, H-5), 3.08 (dd, *J* = 11.98, *J* = 4.79 Hz, 1 H, H-9), 3.13−3.21 (m, 1 H, H-2), 3.24−3.31 (m, 2 H, H-7, H-6), 3.49−3.57 (m, 1 H, H-7), 3.65 (dd, *J* = 13.12, *J* = 10.23 Hz, 1 H, H-6), 3.73−3.79 (m, 1 H, 9), 5.00−5.04 (m, 2 H, 11), 5.70−5.79 (m, 1 H, 10), 7.26−7.38 (m, 9 H, Ph), 7.55−7.60 (m, 6 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.56 (C-3), 26.03 (C-8), 27.39 (C-4), 39.45 (C-5), 48.94 (C-6), 52.57 (C-7), 67.50 (C-2), 73.01 (C-9), 115.64 (C-11), 128.03 (d, *J* = 10.85 Hz, Ph *o*-C), 129.45 (d, *J* = 51.47 Hz, Ph *i*-C), 130.56 (d, *J* = 2.64 Hz, Ph *p*-C), 134.65 (d, *J* = 1 1.00 Hz, Ph *m*-C), 138.43 (C-10) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.83 (*trans* to N), 23.96 (*cis* to N) ppm. FAB: *m*/*z* = 570 $[M + H]^+$, 534 $[M - Cl]^+$.

7: From **3** (100 mg, 0.6 mmol), NaOMe (0.6 mmol) and $[PdCl_2(PPh_3)]_2$ (263 mg, 0.3 mmol). $C_{28}H_{33}ClNOPPd$ (572.42). M.p. 175−176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81−0.85 (t, *J* = 7.30 H, 3 H, CH_2CH_3), 0.95−1.00 (m, 1 H, H-3), 1.34−1.41 (m, 2 H, CH_2CH_3), 1.53−1.63 (m, 3 H, H-5, H-8), 1.72−1.81 (m, 2 H, H-3, H-4), 2.77−2.81 (m, 1 H, H-6), 3.07 (dd, *J* = 11.68, *J* = 4.32 Hz, 1 H, H-9), 3.13−3.24 (m, 1 H, H-2), 3.33−3.43 (m, 1 H, H-7), 3.61−3.68 (m, 1 H, H-7), 3.74 (t, *J* = 11.68 Hz, 1 H, H-9), 3.78 (dd, *J* = 13.38, *J* = 10.35 Hz, 1 H, H-6), 7.26−7.38 (m, 9 H, Ph), 7.56−7.62 (m, 6 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.00 (CH_2CH_3), 21.98 (C-3), 24.84 (C-4), 27.92 (CH_2CH_3), 28.35 (C-8), 37.84 (C-5), 43.56 (C-7), 59.97 (C-6), 68.02 (C-2), 73.69 (C-9), 128.05 (d, *J* = 10.84 Hz, Ph *o*-C), 129.14 (d, *J* = 51.31 Hz, Ph *i*-C), 130.56 (d, *J* = 2.60 Hz, Ph *p*-C), 134.71 (d, *J* = 11.00 Hz, Ph *m*-C), ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.82 (*trans* to N), 26.74 (*cis* to N) ppm. FAB: *m*/*z* = 572 $[M + H]^+$, 536 $[M - Cl]^+$.

8: From **4** (100 mg, 0.6 mmol), NaOMe (0.6 mmol) and $[PdCl_2(PPh_3)]_2$ (263 mg, 0.3 mmol). $C_{28}H_{33}ClNOPPd$ (572.42). M.p. 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80−0.84 (t, *J* = 7.39 Hz, 3 H, CH_2CH_3), 1.20−1.36 (m, 3 H, 3, CH_2CH_3), 1.45−1.52 (m, 1 H, H-3), 1.56−1.73 (m, 4 H, H-8, H-5, H-4), 2.99−3.26 (m, 4 H, H-7, H-2, H-9, H-6), 3.46−3.54 (m, 1 H, H-7), 3.58−3.64 (m, 1 H, H-6), 3.76 (t, *J* = 11.35 Hz, 1 H, H-9), 7.26−7.37 (m, 9 H, Ph), 7.56−7.61 (m, 6 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.74 (CH_2CH_3), 21.35 (C-3), 25.13 (CH_2CH_3), 25.80 (C-4), 26.74 (C-8), 37.36 (C-5), 51.05 (C-6), 52.74 (C-7), 67.85 (C-2), 73.22 (C-9), 128.00 (d, *J* = 10.86 Hz, Ph *o*-C), 129.57 (d, *J* = 51.18 Hz, Ph *i*-C), 130.50 (d, *J* = 2.62 Hz, Ph *p*-C), 134.66 (d, *J* = 10.99 Hz, Ph *m*-C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.78 (*cis* to N) 26.64 (*trans* to N) ppm. FAB: *m*/*z* = 572 $[M + H]^+$, 536 $[M - Cl]^+$.

General Procedure for the Preparation of the Homoleptic Pd^{II} Complexes 9−12: A solution of ligand **1**−**4** and NaOMe in CH_2Cl_2/MeOH (1:1) was added dropwise to a solution of $[PdCl_2(PhCN)_2]$ in CH_2Cl_2 and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed from the light yellow suspension under vacuum and the residue was dissolved again in CH_2Cl_2 and stirred for 15 minutes. The suspension was filtered to remove NaCl and the resulting yellow solution was concentrated to dryness. The crude product was recrystallised from diethyl ether and *n*-hexane.

9: From **1** (400 mg, 2.4 mmol), 2.4 mmol of NaOMe and $[PdCl_2(PhCN)_2]$ (460 mg, 1.2 mmol). $C_{20}H_{32}N_2O_2Pd$ (438.91). M.p. 152−155 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.93−0.98 (m, 2 H, H-3), 1.55−1.63 (m, 4 H, H-8), 1.73−1.83 (m, 4 H, H-H-3, H-4), 2.38−2.42 (m, 2 H, H-5), 2.92 (dd, *J* = 11.21, *J* = 5.17 Hz, 2 H, H-9), 3.00−3.18 (m, 8 H, H-6, H-7, H-2), 3.44−3.49 (m, 2 H, H-9), 3.69−3.78 (m, 2 H, H-7), 5.07−5.13 (m, 4 H, H-11), 5.93−5.84 (m, 2 H, H-10) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 22.35 (C-3), 27.11 (C-4), 27.79 (C-8), 39.63 (C-5), 45.60 (C-7),

58.89 (C-6), 69.38 (C-2), 70.95 (C-9), 115.14 (C-11), 140.96 (C-10). EI: *m/z* = 438 $[M]^+$, 408 $[M - CH_2O]^+$, 378 $[M - 2CH_2O]^+$.

10: From **3** (270 mg, 1.6 mmol), 1.6 mmol of NaOMe and $[PdCl_2(PhCN)_2]$ (300 mg, 0.8 mmol). $C_{20}H_{36}N_2O_2Pd$ (442.94). M.p. 144−147 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.85−0.89 (t, *J* = 7.34 Hz, 6 H, CH_2CH_3), 0.90−0.95 (m, 2 H, H-3), 1.37−1.45 (m, 4 H, CH_2CH_3), 1.48−1.78 (m, 10 H, H-3, H-4, H-8, H-5), 2.68−2.73 (m, 2 H, H-6), 2.91 (dd, *J* = 11.1, *J* = 5.16 Hz, 2 H, H-9), 3.04−3.14 (m, 6 H, H-6, H-7, H-2), 3.44 (t, *J* = 11.1 Hz, 2 H, H-9), 3.76−3.68 (m, 2 H, H-7) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 11.98 (CH_2CH_3), 22.04 (C-3), 24.63 (C-4), 28.04 (CH_2CH_3), 28.38 (C-8), 37.76 (C-5), 45.65 (C-7), 60.88 (C-6), 69.34 (2), 70.99 (C-9). EI: *m/z* = 442 $[M]^+$, 412 $[M - CH_2O]^+$, 382 $[M - 2CH_2O]^+$.

11: From **2** (400 mg, 2.4 mmol), 2.4 mmol of NaOMe and $[PdCl_2(PhCN)_2]$ (460 mg, 1.2 mmol). $C_{20}H_{32}N_2O_2Pd$ (438.91). M.p. 155−160 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.21−1.26 (m, 2 H, H-3), 1.45−1.52 (m, 2 H, H-3), 1.58−1.76 (m, 6 H, H-8, H-2), 2.36−2.42 (m, 2 H, H-5), 2.88−2.95 (m, 4 H, H-9, H-7), 2.98−3.07 (m, 2 H, H-9), 3.16−3.23 (m, 2 H, H-7), 3.33 (dd, *J* = 13.34, *J* = 10.21 Hz, 2 H, H-6), 3.38−3.44 (ddd, *J* = 13.34, *J* = 8.42, *J* = 2.18 Hz, 2 H, H-6), 3.50 (t, *J* = 10.96 Hz, 2 H, H-9), 5.05−5.10 (m, 4 H, H-11), 5.84−5.75 (m, 2 H, H-10) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 21.66 (C-3), 25.95 (C8), 27.84 (C-4), 39.78 (C-5), 50.93 (C-6), 53.34 (C-7), 69.20 (C-2), 70.88 (C-9), 115.45 (C-11), 138.97 (C-10). EI: *m/z* = 438 $[M]^+$, 408 $[M - CH_2O]^+$, 378 $[M - 2CH_2O]^+$.

12: From **4** (100 mg, 0.6 mmol), 0.6 mmol of NaOMe and $[PdCl_2(PhCN)_2]$ (113 mg, 0.3 mmol). $C_{20}H_{36}N_2O_2Pd$ (442.94). M.p. 180−182 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.77−0.81 (t, *J* = 7.39 Hz, CH_2CH_3), 1.10−1.32 (m, 6 H, 3, CH_2CH_3), 1.36−1.42 (m, 2 H, H-3), 1.45−1.55 (m, 6 H, H-5, H-4, H-8), 1.61−1.68 (m, 2 H, H-8), 2.84−2.91 (m, 2 H, H-7), 2.95−3.10 (m, 6 H, H-6, H-2, H-9), 3.16−3.22 (m, 2 H, H-7), 3.3 (dd, *J* = 13.13, *J* = 9.84 Hz, 2 H, H-6), 3.5 (t, *J* = 12.43 Hz, 2 H, H-9) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 11.62 (CH_2CH_3), 21.21 (C-3), 25.12 (CH_2CH_3), 25.39 (C-4), 26.33 (C-8), 37.36 (C-5), 52.92 (C-6), 53.25 (C-7), 68.72 (C-2), 70.59 (C-9). EI: *m/z* = 442 $[M]^+$, 412 $[M - CH_2O]^+$, 382 $[M - 2CH_2O]^+$.

General Procedure for the Preparation of the Chloroenynes 15 and 16: A mixture of $[Pd(PPh_3)_4]$ (0.05 equiv.), (*Z*)-1,2-dichloroethene (3 equiv.), alkyne (1 equiv.), and piperidine or $nBuNH_2$ (2 equiv.) in absolute THF was stirred for 15 minutes at room temperature under a nitrogen atmosphere, and CuI (0.1 equiv.) was then added. The stirring was continued until TLC analysis indicated complete consumption of the alkyne (3−5 h). The reaction mixture was treated with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by column chromatography [MTBE/MeOH/NH_3(25%)] to yield the desired chloroenyne.

15: From **13** (2 g, 12 mmol), $[Pd(PPh_3)_4]$ (0.69 g, 0.59 mmol), CuI (0.23 g, 1.2 mmol), $nBuNH_2$ (1.75 g, 23.9 mmol) and (*Z*)-1,2-dichloroethene (3.49 g, 36 mmol). $C_{12}H_{16}ClNO$ (225.5). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.74−0.80 (m, 1 H, H-3), 1.34−1.49 (m, 2 H, H-8), 1.89−1.93 (m, 1 H, H-4), 2.04−2.11 (m, 1 H, H-3), 2.49−2.57 (m, 1 H, H-7), 2.65−2.68 (m, 1 H, H-5), 2.85−2.93 (m, 2 H, H-7, H-6), 3.06−3.11 (m, 2 H, H-2, OH), 3.23 (dd, *J* = 13.17, *J* = 9.95 Hz, 1 H, H-6), 3.38−3.45 (m, 2 H, H-9), 5.79 (dd, *J* = 7.33, *J* = 2.23 Hz, 1 H, H-12), 6.26 (d, *J* = 7.33 Hz, 1 H, H-13) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.91 (C-3), 26.18 (C-8), 26.56 (C-4), 28.95 (C-5), 39.55 (C-7), 56.82 (C-2), 56.88 (C-6), 62.61 (C-9), 75.09 (C-11), 102.02 (C-10), 112.20 (C-12), 127.39 (C-13) ppm. MS-EI (43 °C): *m/z* (%) = 227 (18) $[M^+]$, 225 (48) $[M^+]$, 194 (78), 190 (100), 162 (12), 159 (30), 132 (78), 126 (31), 103 (24), 82 (16), 77 (26), 72 (29), 63 (14), 55 (21), 51 (10), 44 (44). EI: *m/z* = 225 $[M]^+$, 194 $[M - CH_2OH]^+$, 190 $[M - Cl]^+$.

16: From **13** (2 g, 12 mmol), $[Pd(PPh_3)_4]$ (0.69 g, 0.59 mmol), CuI (0.23 g, 1.2 mmol), $nBuNH_2$ (2.06 g, 23.95 mmol) and (*Z*)-1,2-dichloroethene (3.49 g, 36 mmol). $C_{12}H_{16}ClNO$ (225.5). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38−1.62 (m, 4 H, H-8, H-3), 1.87−1.91 (m, 1 H, H-4), 2.59−2.63 (m, 1 H, H-5), 2.74−3.00 (m, 5 H, H-6, H-2, H-7), 3.31 (s, 1 H, OH), 3.57 (t, *J* = 11.24 Hz, 1 H, H-9), 5.78 (dd, *J* = 7.34, *J* = 2.23 Hz, 1 H, H-12), 6.26 (d, *J* = 7.34 Hz, 1 H, H-13) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.19 (C-13), 25.45 (C-8), 27.28 (C-4), 29.33 (C-5), 47.83 (C-6), 48.42 (C-7), 57.23 (C-2), 62.03 (C-9), 75.60 (C-11), 101.37 (C-10), 112.14 (C-12), 127.46 (C-13) ppm. MS-EI (55 °C): *m/z* (%) = 227 (24) $[M^+]$, 225 (79) $[M^+]$, 208 (4), 194 (100), 190 (88), 158 (22), 132 (48), 126 (64), 117 (16), 112 (25), 103 (34), 82 (32), 77 (31), 72 (49), 63 (14), 55 (35), 51 (16), 44 (48), 42 (68). EI: *m/z* = 225 $[M]^+$, 194 $[M - CH_2OH]^+$, 190 $[M - Cl]^+$.

General Procedure for the Preparation of the Enediynes 17 and 18: $[PdCl_2(PhCN)_2]$ (0.05 equiv.), piperidine (2 equiv.) and terminal alkyne (1.2 equiv.) were added to a solution of pure chloroenyne (1 equiv.) in absolute THF, at room temperature, under a nitrogen atmosphere. CuI (0.1 equiv.) was then added to the stirred solution. The stirring was continued until TLC analysis indicated complete consumption of the chloroenyne. The reaction mixture was treated with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography [MTBE/MeOH/NH_3(25%)] to afford the desired enediyne.

17: From **15** (2.32 g, 10.28 mmol), $[PdCl_2(PhCN)_2]$ (197 mg, 0.5 mmol), CuI (196 mg, 1.02 mmol), piperidine (1.76 g, 20.46 mmol) and **13** (1.86 g, 11.27 mmol). $C_{22}H_{30}N_2O_2$ (354). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.74−0.80 (m, 2 H, H-3), 1.34−1.49 (m, 4 H, H-8), 1.86−1.90 (m, 2 H, H-4), 2.03−2.10 (m, 2 H, H-3), 2.49−2.56 (m, 2 H, H-7), 2.66−2.68 (m, 2 H, H-5), 2.82−2.92 (m, 4 H, H-7, H-6), 3.02−3.10 (m, 2 H, H-2), 3.23 (dd, *J* = 13.15, *J* = 9.94 Hz, 2 H, H-6), 3.31−3.46 (m, 6 H, H-9, OH), 5.70 (s, 2 H, H-12) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.08 (C-3), 26.18 (C-8), 26.65 (C-4), 29.03 (C-5), 39.64 (C-7), 56.95 (C-2), 57.12 (C-6), 62.76 (C-9), 78.69 (C-11), 100.91 (C-10), 118.96 (C-12) ppm. MS-EI (163 °C): *m/z* (%) = 354 (100) $[M^+]$, 337 (2), 323 (45), 297 (25), 295 (12), 277 (8), 265 (16), 242 (10), 238 (12), 224 (7), 210(17), 184 (14), 177 (7), 165 (11), 141 (8), 128 (13), 115 (12), 100 (9), 96 (10), 86 (12), 70 (14), 55 814), 44 (27), 42 (24). EI: *m/z* = 354 $[M]^+$, 323 $[M - CH_2OH]^+$.

18: From **16** (1.05 g, 4.65 mmol), $[PdCl_2(PhCN)_2]$ (90 mg, 0.2 mmol), CuI (88 mg, 0.46 mmol), piperidine (0.8 g, 9.3 mmol) and **14** (0.92 g, 5.57 mmol). $C_{22}H_{30}N_2O_2$ (354). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.36−1.62 (m, 8 H, H-8, H-3), 1.87−1.88 (m, 2 H, H-4), 2.62−2.66 (m, 2 H, H-5), 2.74−3.00 (m, 10 H, H-6, H-2, H-7), 3.07 (s, 2 H, OH), 3.39 (dd, *J* = 11.1, *J* = 5 Hz, 2 H, H-9), 3.55 (t, *J* = 11.1 Hz, 2 H, H-9), 5.69 (s, 2 H, H-12) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.35 (C-3), 25.55 (C-8), 27.43 (C-4), 29.45 (C-5), 48.01 (C-6), 48.43 (C-7), 57.13 (C-2), 62.14 (C-9), 79.24 (C-11), 100.17 (C-10), 118.99 (C-12), ppm. MS-EI (132 °C): *m/z* (%) = 354 (100) $[M^+]$, 323 (21), 297 (9), 295 (13), 279 (16), 268 (5), 252 (3), 242 (8), 222 (6), 210 (9), 196 (9), 182 (11), 167 (29), 149 (47), 126 (11), 115 (10), 108 (7), 96 (11), 86 (8), 71 (13), 57 (17), 44 (19), 42 (12). EI: *m/z* = 354 $[M]^+$, 323 $[M - CH_2OH]^+$.

General Procedure for the Preparation of the Bis-*N*,*P*-aminophosphinites 19 and 20: A solution of Ph_2PCl (2.05 equiv.) in dry CH_2Cl_2 was cooled to 0 °C and then a solution of (*Z*)-enediyne (1 equiv.) and NEt_3 (4 equiv.) in the same solvent was added dropwise. After the addition, the reaction mixture was allowed to warm up to room temperature and stirred until TLC analysis indicated complete consumption of the reactant **17** and **18**. The solution was concentrated in vacuo and the residue was dissolved in CH_2Cl_2/*n*-hexane (1:2) and stirred for 15 minutes. The suspension was filtered to remove $Et_3N{\cdot}HCl$ and the resulting clear solution was concentrated to dryness. The crude product was purified by column chromatography under a nitrogen atmosphere (MTBE/acetonitrile/NEt_3) to afford the desired bis-aminophosphinite in very good yield.

19: From **17** (1.22 g, 3.44 mmol), Ph_2PCl (1.52 g, 6.8 mmol) and NEt_3 (13.7 mmol). $C_{46}H_{48}N_2O_2P_2$ (722.85). ^1H NMR (400 MHz, C_6D_6): δ = 0.75−0.80 (m, 2 H, H-3), 0.88−0.96 (m, 2 H, H-8), 1.00−1.08 (m, 2 H, H-8), 1.74−1.75 (m, 2 H, H-4), 2.13−2.18 (m, 2 H, H-3), 2.24−2.31 (m, 2 H, H-7), 2.43−2.45 (m, 2 H, H-5), 2.74−2.82 (m, 2 H, H-7), 2.92−3.04 (m, 4 H, H-6), 3.29−3.36 (m, 2 H, H-2), 3.64−3.70 (m, 2 H, H-9), 3.77−3.84 (m, 2 H, H-9), 5.59 (s, 2 H, H-12), 7.01−7.05 (m, 4 H, Ph), 7.09−7.13 (m, 8 H, Ph), 7.61−7.64 (m, 8 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 25.75 (C-3), 26.46 (C-8), 27.65 (C-4), 29.32 (C-5), 41.04 (C-7), 56.68 (d, *J* = 7.23 Hz, C-2), 71.71 (d, *J* = 18.3 Hz, C-9), 57.81 (C-6), 79.41 (C-11), 101.79 (C-10), 119.47 (C-12), 128.43 (d, *J* = 6.97 Hz, Ph *m*-C), 128.50 (d, *J* = 6.97 Hz, Ph *m*-C), 129.21 (d, *J* = 3.35 Hz, Ph *p*-C), 130.62 (d, *J* = 8.32 Hz, Ph *o*-C), 130.83 (d, *J* = 8.14 Hz, Ph *o*-C), 143.31 (d, *J* = 8.40 Hz, Ph *i*-C), 143.49 (d, *J* = 7.83 Hz, Ph *i*-C) ppm. ^{31}P NMR (162 MHz, C_6D_6): δ = 115.29 ppm. EI: *m*/*z* = 722 $[M]^+$, 521 $[M - Ph_2PO]^+$, 201 $[Ph_2PO]^+$.

20: From **18** (1.36 g, 3.84 mmol), Ph_2PCl (1.78 g, 8.00 mmol) and NEt_3 (15.36 mmol). $C_{46}H_{48}N_2O_2P_2$ (722.85). ^1H NMR (400 MHz, C_6D_6): δ = 0.96−1.12 (m, 4 H, H-8), 1.18−1.25 (m, 2 H, H-3), 1.62−1.67 (m, 2 H, H-3), 1.74 (br. s, 2 H, H-4), 2.31−2.48 (m, 6 H, H-7, H-5), 2.86−2.93 (m, 4 H, H-6, H-2), 3.12 (ddd, *J* = 14.02, *J* = 6.68, *J* = 2.01 Hz, 2 H, H-6), 3.77−3.84 (m, 2 H, H-9), 4.05−4.12 (m, 2 H, H-9), 5.58 (s, 2 H, H-12), 7.01−7.05 (m, 4 H, Ph), 7.09−7.13(m, 8 H, Ph), 7.60−7.66 (m, 8 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 25.22 (C-3), 25.53 (C-8), 28.31 (C-4), 29.96 (C-5), 48.58 (C-7), 49.63 (C-6), 56.78 (d, *J* = 6.28 Hz, C-2), 71.22 (d, *J* = 18.57 Hz, C-9), 79.94 (C-11), 101.20 (C-10), 119.39 (C-12), 128.37 (d, *J* = 6.70 Hz, Ph *m*-C), 128.46 (d, *J* = 6.55 Hz, Ph *m*-C), 129.10 (d, *J* = 1.80 Hz, Ph *p*-C), 130.55 (d, *J* = 11.36 Hz, Ph *o*-C), 130.76 (d, *J* = 11.32 Hz, Ph *o*-C), 143.63 (d, *J* = 14.51 Hz, Ph *i*-C), 143.82 (d, *J* = 14.69 Hz, Ph *i*-C) ppm. ^{31}P NMR (162 MHz, C_6D_6): δ = 114.60 ppm. EI: *m*/*z* = 722 $[M]^+$, 645 $[M - C_6H_5]^+$, 521 $[M - Ph_2PO]^+$, 201 $[Ph_2PO]^+$.

General Procedure for the Preparation of the Platinacycles 21 and 22: A solution of $[PtCl_2(SMe_2)_2]$ in CH_2Cl_2 (4 mL) was added dropwise to a stirred solution of **19** and **20** in CH_2Cl_2 (5 mL). After 15 minutes, the solvent was removed to give a pale-yellow solid. Recrystallisation from THF and toluene gave a white solid.

21: From **19** (370 mg, 0.51 mmol) and $[PtCl_2(SMe_2)_2]$ (200 mg, 0.51 mmol). M.p. 195−197 °C. $C_{46}H_{48}Cl_2N_2O_2P_2Pt$ (988.83). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86−0.91 (m, 2 H, H-3), 1.37−1.44 (m, 4 H, H-8), 1.97 (br. s, 2 H, H-4), 2.04−2.10 (m, 2 H, H-3), 2.24−2.32 (m, 2 H, H-7), 2.48−2.50 (m, 2 H, H-7), 2.71−2.74 (m, 2 H, H-5), 2.86−2.89 (m, 2 H, H-6), 3.07−3.11 (m, 2 H, H-2), 3.21 (dd, *J* = 13.22, *J* = 10.07 Hz, 2 H, H-6), 3.28 (br. s, 2 H, H-9), 3.47−3.49 (m, 2 H, H-9), 5.88 (s, 2 H, H-12), 7.37−7.53 (m, 12 H, Ph), 7.70−7.74 (m, 4 H, Ph), 8.04−8.09 (m, 4 H, Ph), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.57 (C-8), 25.61 (C-3), 26.27 (C-4), 28.57 (C-5), 40.44 (C-7), 54.89 (d, *J* = 8.02 Hz, C-2), 56.86 (C-6), 68.42 (C-9), 78.42 (C-11), 100.81 (C-10), 118.77 (C-12), 127.85 (d, *J* = 11.73 Hz, Ph *m*-C), 128.25 (d, *J* = 12.05 Hz, Ph *m*-C), 131.40 (d, *J* = 69.43, Ph *i*-C), 131.56 (Ph *p*-C), 131.75 (Ph *p*-C), 132.41 (d, *J* = 12.34 Hz, Ph *o*-C), 132.45 (d, *J* = 77.80 Hz, Ph *i*-C), 132.70 (d, *J* = 11.58 Hz, Ph *o*-C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 83.89 ($^1J_{Pt,P}$ = 2099.28 Hz) ppm. FAB: *m*/*z* = 988 $[M]^+$, 953 $[M - Cl]^+$.

22: From **20** (250 mg, 0.346 mmol) and $[PtCl_2(SMe_2)_2]$ (135 mg, 0.346 mmol). M.p. 215 °C. $C_{46}H_{48}Cl_2N_2O_2P_2Pt$ (988.83). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.46−1.56 (m, 8 H, H-8, H-3), 1.92 (br. s, 2 H, H-4), 2.28−2.32 (m, 2 H, H-2), 2.62−2.75 (m, 8 H, H-7, H-5, H-6), 2.94−3.01 (m, 2 H, H-6), 3.73−3.82 (m, 2 H, H-9), 4.07−4.09 (m, 2 H, H-9), 5.79 (s, 2 H, H-12), 7.25−7.36 (m, 12 H, Ph), 7.66−7.71 (m, 4 H, Ph), 7.81−7.86 (m, 4 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.70 (C-8), 25.34 (C-3), 27.13 (C-4), 29.09 (C-5), 48.39 (C-7), 49.06 (C-6), 54.53 (d, *J* = 6.93 Hz, C-2), 70.27 (C-9), 79.12 (C-11), 100.10 (C-10), 119.03 (C-12), 127.84 (d, *J* = 12.06 Hz, Ph *m*-C), 128.10 (d, *J* = 11.89 Hz, Ph *m*-C), 131.40 (d, *J* = 7.15 Hz, Ph *p*-C), 131.90 (d, *J* = 11.86 Hz, Ph *o*-C), 132.47 (d, *J* = 11.56 Hz, Ph *o*-C), 132.56 (d, *J* = 74.00 Hz, Ph *i*-C), 133.47 (d, *J* = 75.00 Hz, Ph *i*-C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 85.10 ($^1J_{Pt,P}$ = 2076.01 Hz) ppm. FAB: *m*/*z* = 988 $[M]^+$, 953 $[M - Cl]^+$.

General Procedure for the Preparation of the Binuclear Pd^{II}-*N*,*P*-aminophosphinite Complexes 23 and 24: $[(\eta^4\text{-}C_7H_8)PdCl_2]$ was added to a solution of **19** or **20** in CH_2Cl_2 (20 mL) and the reaction mixture was stirred overnight at room temperature. The solvent of the clear yellow solution was removed under vacuum and the remaining yellow solid was washed twice with *n*-hexane and dried in vacuo for two days.

23: From **19** (160 mg, 0.22 mmol) and $[(\eta^4\text{-}C_7H_8)PdCl_2]$ (120 mg, 0.44 mmol). M.p. 210−214 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.06−1.12 (m, 2 H, H-3), 1.49−1.67 (m, 4 H, H-8), 2.03 (br. s, 2 H, H-4), 2.25−2.31 (m, 2 H, H-3), 2.94−3.01 (m, 4 H, H-7, H-5), 3.19−3.24 (m, 4 H, H-6, H-2), 3.62−3.69 (m, 2 H, H-9), 3.84−3.95 (m, 2 H, H-9), 4.25−4.31 (m, 2 H, H-7), 5.09 (dd, *J* = 13.56, *J* = 10.4 Hz, 2 H, H-6), 5.80 (s, 2 H, H-12), 7.31−7.35 (m, 4 H, Ph), 7.42−7.47 (m, 6 H, Ph), 7.53−7.56 (m, 2 H, Ph), 7.59−7.65 (m, 4 H, Ph), 7.95−8.00 (m, 4 H, Ph) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 26.09 (C-4), 26.64 (C-8), 27.18 (C-3), 30.16 (C-5), 46.74 (C-7), 60.90 (d, *J* = 4.18 Hz, C-2), 62.07 (C-6), 67.85 (C-9), 79.83 (C-11), 98.95 (C-10), 119.87 (C-12), 128.39 (d, *J* = 12.46 Hz, Ph *m*-C), 128.96 (d, *J* = 12.07 Hz, Ph *m*-C), 130.85 (d, *J* = 62.07 Hz, Ph *i*-C), 131.86 (d, *J* = 49.16 Hz, Ph *i*-C), 132.42 (Ph *m*-C), 132.90 (d, *J* = 11.39 Hz, Ph *o*-C), 133.13 (Ph *p*-C), 134.61 (d, *J* = 13.04 Hz, Ph *o*-C) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 102.90 ppm. ESI: *m*/*z* = 1101 $[M + Na]^+$, 1043 $[M - Cl]^+$.

24: From **19** (200 mg, 0.27 mmol) and $[(\eta^4\text{-}C_7H_8)PdCl_2]$ (150 mg, 0.55 mmol). M.p. 238−240 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44−1.50 (m, 2 H, H-3), 1.73−1.77 (m, 4 H, H-8), 1.85−1.92 (m, 2 H, H-3), 2.01 (br. s, 2 H, H-4), 2.78−2.83 (m, 2 H, H-6), 2.90−2.95 (m, 2 H, H-5), 3.05−3.09 (m, 2 H, H-2), 3.27−3.29 (m, 2 H, H-7), 3.91−4.01 (m, 2 H, H-9), 4.56−4.64 (m, 2 H, H-7), 4.86 (dd, *J* = 12.46, *J* = 10.40 Hz, 2 H, H-6), 5.64 (s, 2 H, H-12), 7.30−7.35 (m, 4 H, Ph), 7.37−7.47 (m, 6 H, Ph), 7.50−7.54 (m, 2 H, Ph), 7.66−7.71 (m, 4 H, Ph), 7.98−8.03 (m, 4 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.64 (C-8), 26.16 (C-3), 27.27 (C-4), 30.02 (C-5), 52.96 (C-6), 54.79 (C-7), 61.02 (C-2), 67.40 (C-9), 80.14 (C-11), 96.91 (C-10), 119.45 (C-12), 128.27 (d, *J* = 12.50 Hz, Ph *m*-C), 128.61 (d, *J* = 12.10 Hz, Ph *m*-C), 131.32 (d, *J* = 78.90 Hz, Ph *i*-C), 131.85 (d, *J* = 60.71 Hz, Ph *i*-C), 132.16 (Ph *p*-C), 132.68 (d, *J* = 11.50 Hz, Ph *o*-C), 132.74 (Ph *p*-C), 134.30 (d,

Table 1. Crystal data for the crystal structures of **7**, **8**, **9**, **11**, **18** and **21**

	7	**8**	**9**	**11**	**18**	**21**
Formula	$C_{28}H_{33}ClNOPPd$	$C_{28}H_{33}ClNOPPd$	$C_{20}H_{34}N_2O_3Pd$	$C_{20}H_{36}N_2O_4Pd$	$C_{22}H_{30}N_2O_2$	$C_{50}H_{56}Cl_2N_2O_3P_2Pt$
M_r	572.37	572.37	456.89	474.91	354.48	1060.90
Habit	yellow prism	yellow prism	yellow prism	yellow block	colourless prism	colourless tablet
Dimensions (mm)	0.46 × 0.22 × 0.16	0.43 × 0.26 × 0.17	0.35 × 0.21 × 0.12	0.38 × 0.37 × 0.27	0.46 × 0.26 × 0.14	0.25 × 0.21 × 0.1
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P1$
a (Å)	8.7380(14)	8.9083(6)	11.3948(6)	8.4067(14)	7.7902(9)	11.3323(10)
b (Å)	16.900(3)	16.6224(10)	7.3436(4)	10.0958(18)	10.9628(12)	12.8787(10)
c (Å)	17.208(3)	17.1522(10)	12.3835(8)	23.817(4)	22.772(2)	17.6247(14)
α (°)	90	90	90	90	90	92.556(3)
β (°)	90	90	99.917(3)	90	90	108.556(3)
γ (°)	90	90	90	90	90	104.543(3)
V (Å^3)	2541.3(7)	2539.9(3)	1020.75(10)	2021.4(6)	1944.8(4)	2338.6(3)
Z	4	4	2	4	4	2
D_x (Mg·m^{-3})	1.497	1.497	1.487	1.560	1.211	1.507
μ (mm^{-1})	0.92	0.92	0.93	0.95	0.08	3.23
F(000)	1176	1176	476	992	768	1072
T (°C)	−140	−140	−140	−140	−140	−140
$2\theta_{max}$	60	60	60	60	60	60
Transmission	0.56−0.83	0.69−0.86	0.74−0.89	0.43−0.75	no correction	0.59−0.80
No. of reflections:						
measured	53471	51018	18924	40178	22535	48900
independent	7430	7423	5947	5912	3225	25501
R_{int}	0.0686	0.0192	0.0177	0.0776	0.0329	0.0322
Parameters	299	299	243	260	243	1031
Restraints	0	0	1	0	0	952
wR (F^2, all refl.)	0.0699	0.0369	0.0397	0.0643	0.0934	0.0763
R (F, >4σ(F)]	0.0266	0.0139	0.0154	0.0245	0.0342	0.0333
S	1.07	1.05	1.04	1.03	1.02	0.98
Max. Δ/σ	<0.001	0.001	0.001	0.001	0.001	0.001
Max. Δρ (e·Å^{-3})	1.18	0.48	0.43	0.76	0.25	2.25
Flack parameter	−0.036(17)	−0.012(10)	0.011(13)	0.00(2)		0.005(4)

J = 12.97 Hz, Ph *o*-C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 103.76 ppm. ESI: m/z = 1101 [M + Na]$^+$, 1043 [M − Cl]$^+$.

Crystal Structure Analyses: The crystal-structure data for **7**, **8**, **9**, **11**, **18 and 21** were collected on a Bruker SMART 1000CCD area detector (graphite-monochromated Mo-K_α radiation, λ = 71.073 pm) at −140 °C in the ω- and φ-scan mode. Empirical absorption corrections were applied using the program SADABS. The structures were solved by direct methods using SHELXS-86/97,[22] and subjected to full-matrix least-squares refinement on F^2 using SHELXL-93/97,[23] with anisotropic displacement parameters for non-H atoms. The crystal structure of **21** contains one disordered THF molecule per formula unit, which could not be resolved satisfactorily. This led to a residual electron density of 2.25 e·Å^{-3}. The crystal structure was therefore refined using the restraints SIMU and DELU for the carbon, nitrogen and oxygen atoms. Additionally, the restraint FLAT was added to describe the local symmetry of the phenyl rings. Methyls were treated as rigid groups and O-bonded hydrogens were refined freely. All other hydrogen atoms were included using a riding model.

CCDC-216416 (**7**), -216417 (**8**), -216418 (**9**), -216419 (**11**), -216420 (**18**) and -216421 (**21**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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