A novel hemilabile calix[4],quinoline-based P,N-ligand: coordination chemistry and complex characterisation†

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The synthesis of the calix[4]arene-based P,N-ligand **3** (5,11,17,23-tetra-*tert*-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene), in which the nitrogen atom-containing moiety has been introduced at the lower rim of the cavity prior to P-functionalisation, is described and its coordination properties investigated. In the crystal structure, the calix[4]-cavity adopts a *cone* conformation with an *exo* orientation of the phosphorus lone pair enabling P-N chelation. ^{1}H, ^{13}C, ^{31}P and ^{1}H{^{15}N} HMQC NMR spectra indicated that, in complexes [PdCl(CH_3)(**3**)] (**4**) and [Rh(CO)Cl(**3**)] (**5**), ligand **3** coordinates in a chelating fashion, while in *cis*-[$PtCl_2$(**3**)$_2$] (**6**) and [Rh(acac)(CO)(**3**)] (**7**) it behaves as a monodentate ligand, coordinating *via* the phosphorus atom only. X-Ray crystal structure determinations were performed for [PdCl(CH_3)(**3**)] (**4**) and *cis*-[$PtCl_2$(**3**)$_2$] (**6**). The cationic Pd complex [Pd(CH_3)(CH_3CN)(**3**)][PF_6] (**8**) was found to be active in a CO/ethylene copolymerisation reaction. Good selectivities were observed for the Pd-catalysed allylic alkylation of cinnamyl acetate with *in situ* prepared catalysts. [Rh(acac)$(CO)_2$] modified with ligand **3** catalyses the hydroformylation of 1-octene with low selectivities towards linear aldehydes. High-pressure NMR experiments on the hydrido carbonyl rhodium(**3**) were inconclusive, different species were formed.

Introduction

In organometallic chemistry, the use of a heteroditopic type ligand provides several advantages. Such heterofunctionalised systems are characterised by an intrinsic and electronic dissymmetry. Their versatility lies mainly in the wide range of catalytic transformations that can be optimised by varying, for example, the steric and electronic properties of the two donor atoms and the structure of the bridge between them. In particular, unsymmetrical bidentates, which combine nitrogen and phosphorus donor atoms, have been investigated extensively. When they behave as hemilabile ligands by reversible dissociation of one arm of the ligand, they can selectively liberate a coordination site at the metal centre and thus, favour the formation and stabilisation of intermediate species. Mixed P,N-chelates have found to be efficient ligands for important catalytic reactions,[1] including hydrogenation,[2] allylic alkylation,[3] CO/olefin copolymerisation,[4] and the Heck reaction.[5] In several cases, due to their specific properties, catalytic activities and selectivities higher than those observed with diphosphines or dinitrogen donor ligands have been achieved.[6] This cannot be generalized, as for instance in polyketone formation using palladium catalysts the symmetrical diphosphines and dipyridyl ligands both afford more active catalysts than the mixed pyridyl phosphine ligands.[7]

Although many sp^2-N donors have been used for the design of P,N-ligands, less attention has been paid to the variation of the phosphorus moiety, the great majority of P,N-ligands bearing diphenylphosphino fragments. This, together with our current investigations on bulky calixarene-based phosphite ligands,[8] prompted us to incorporate calixarene moieties in multifunctional structures, thus leading to a unique type of P,N-chelate. Pyridine phosphite ligands[9] have been used before in asymmetric allylic alkylation[10] and 1,4-conjugate addition reactions.[11]

It is well-established that the presence of transition metal centres bound to calixarene scaffolds may perturb the shape and the structural properties of such macrocycles leading to potential shape-selective catalysts.[12] Nevertheless, many aspects of the coordination chemistry of calixarenes still remain to be explored and, only recently, their potential, especially for transition metal catalysed reactions, has been recognised. In the last decade numerous publications appeared dealing with mono- and bidentate phosphite ligands based on calix[4]- and calix[6]arene building blocks,[8,13] but only in few cases unsymmetrical chelates have been discussed.[9,14]

Attracted by such systems we developed the synthesis of the first heteroditopic P,N-calix[4]arene-modified ligand in which the properties of a hard and soft donor atom are associated with the unique structure of the calix[4]arene matrix.

This paper deals with a new P,N-ligand **3** in which the N-containing moiety has been introduced at the lower rim of the calix[4]-cavity prior to P-functionalisation and the π-acceptor

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character of the phosphorus donor centre has been increased by using a μ_3-bridging phosphite unit. Note that the latter, when linked to three proximal phenolic oxygen atoms at the lower rim of a calix[4]arene cavity, displays the unique air-robustness and stability previously reported for other calix[4]arene-based phosphites, thus representing a suitable ligand to be applied in homogeneous catalysis.[6,15] The coordination properties of the P,N-ligand **3** towards Pd(II), Pt(II) and Rh(I) metal precursors have been investigated and the resulting complexes structurally characterised by means of ^{1}H, ^{13}C, ^{31}P and ^{1}H{^{15}N} HMQC NMR spectroscopy and X-ray diffraction studies. The new hemilabile P,N-chelate has been evaluated as ligand in the Pd-catalysed CO/ethylene copolymerisation, in the Pd-catalysed allylic alkylation and in the Rh-catalysed hydroformylation of 1-octene.

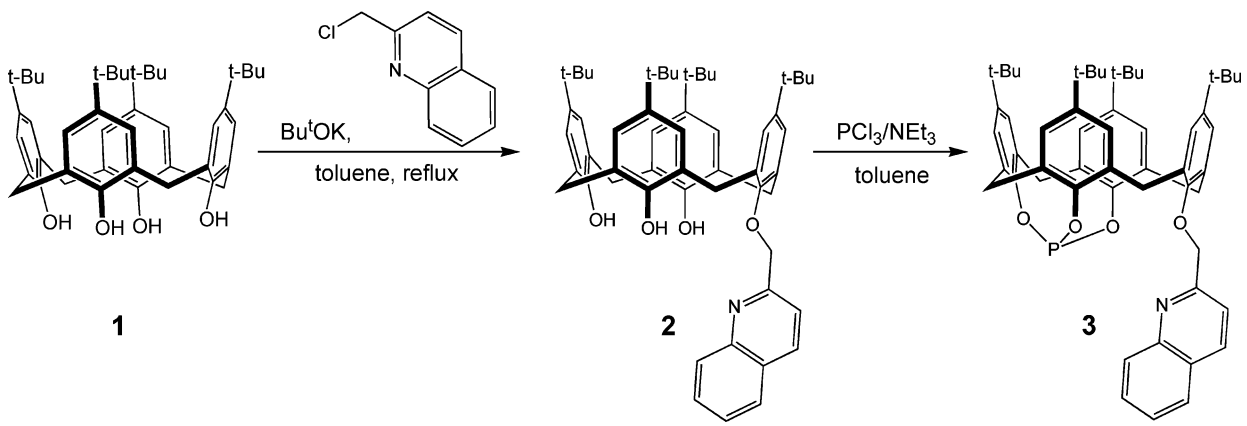
Results and discussion

Synthesis

The calix[4]arene-based P,N-ligand **3** was obtained through a two-step synthesis starting from *p-tert*-butylcalix[4]arene **1** (Scheme 1). The latter was first monofunctionalised at the lower rim by reaction with 2-(chloromethyl)-quinoline hydrochloride in the presence of *t*BuOK as a base. Unfortunately this reaction is non-selective towards monofunctionalisation and gives rise to the formation of a distal 1,3-disubstituted calix[4]arene as by-product, yielding only 15% of product **2**. Subsequently, the monoprotected *cone*-calix[4]arene **2** was reacted with PCl_3 in the presence of NEt_3 to give selectively the phosphito,quinoline-based ligand **3** in which the μ_3-bridging phosphorus atom is tethered to three neighbouring phenolic oxygen atoms of the calixarene scaffold.

Both steps are accessible from well-established calixarene alkylation and phosphorylation procedures.[14,16] The sequence in which the two steps are conducted is crucial in order to obtain calixarene structures in a *cone* conformation and thus, bidentate ligands with chelating properties.[17] The presence of the quinoline moiety at the lower rim of the cavity prevents *trans* annulus inversion and hence leads, once the product has been formed, to the selective formation of a potential P,N-chelating system in which the phosphorus atom and the N-heterocyclic fragment are oriented towards the same side of the calix[4]arene main plane (defined by the bridging methylene units $ArCH_2Ar$).

The phosphito, quinoline-based ligand **3** is characterised by one singlet in the ^{31}P NMR at $\delta = 103.9$ ppm (see Table 1). This value is in accordance with other reported monoalkylated calix[4]arene monophosphites adopting a so-called *up-up-out-up* conformation and characterised by an *exo* orientation of the phosphorus lone pair.[8a] It has been established before that the phosphorylation reaction performed with PCl_3/NEt_3 on a lower rim monofunctionalised calix[4]arene affords quantitatively and exclusively phosphites in which the phosphorus lone pair is pointing outwards to the cavity and this can be deduced also from ^{13}C NMR chemical shifts of the methylene groups connecting each pair of aromatic rings of the cavity ($ArCH_2Ar$). Studies showed that for *syn*-arranged $ArCH_2Ar$ moieties the ^{13}C NMR chemical shift of the methylene bridge lies between *ca.* 29 and 33 ppm, while for an *anti* arrangement a shift to 37–39 ppm is observed. Steric effects are believed to be the main cause of such a large difference.[18] For ligand **3**, one of these signals appears in the expected range for *syn*-oriented phenolic neighbours (at 34.52 ppm), while the other one falls in an intermediate range of values (at 36.86 ppm). It should be noted that the *up-up-out-up* conformation adopted by the calix[4]arene-based phosphite **3** is the result of the strain imposed by the very short μ_3-phosphite unit and thus, the observation of a signal with an intermediate chemical shift might be interpreted in terms of partial flattening of the calixarene core.



Scheme 1 Synthetic route to calix[4],quinoline-based P,N-ligand (**3**).

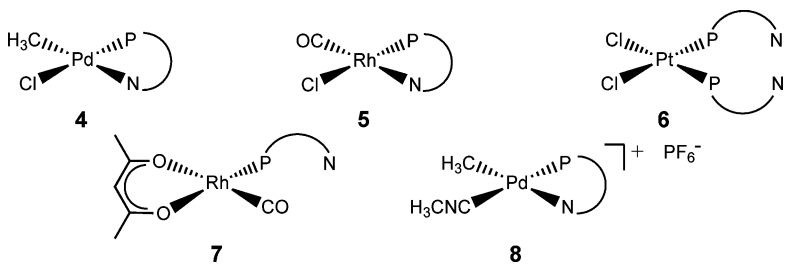


Table 1 Selected ^{31}P, ^{1}H and ^{15}N NMR data for transition metal complexes obtained with ligand **3** in CD_2Cl_2[a]

Compound	δ (^{31}P)[b]	CIS ($\Delta\delta$)[c]	δ (H^8)[d]	CIS ($\Delta\delta$)[c]	δ (^{15}N)[e]	CIS ($\Delta\delta$)[c]
Free **3**	103.9	—	8.03	—	–75.3	—
[PdCl(CH_3)(**3**)] (**4**)	85.7	–18.2	9.75	1.72	–110.6	–35.3
[Rh(CO)Cl(**3**)] (**5**)	102.6	–1.3	10.09	2.06	n.d.[f]	—
[$PtCl_2$(**3**)$_2$] (**6**)	33.2	–70.7	8.23	0.20	–70.8	4.5
[Rh(acac)(CO)(**3**)] (**7**)	105.8	1.9	8.12	0.09	–69.8	5.5
[Pd(CH_3)(CH_3CN)(**3**)][PF_6] (**8**)	81.4	–22.5	9.76	1.73	n.d.[f]	—

[a] T = 20 °C. δ in ppm. [b] Measured at 121.5 MHz. [c] Coordination Induced Shift = δ(complex)–δ(ligand). [d] Measured at 300.1 MHz. [e] Measured at 30.42 MHz. [f] Not determined.

The ^{1}H NMR spectrum shows three signals for the Bu^t groups in a 1 : 1 : 2 ratio and two AB patterns for the methylene units of the calix[4]-scaffold, indicating that in solution the ligand is C_s symmetric with a mirror plane containing the phosphorus atom and the quinoline moiety. This is in accordance with the facile dynamics (*up-up-out* ↔ *out-up-up* interconversion) already evidenced for μ_3-bridging phosphite moieties, which exchange the two distal aryl units between an *up* and an *out* position.[8]

The resonances for the protons of the quinoline unit were assigned using HH COSY experiments, while the ^{15}N NMR chemical shift (see Table 1) was obtained *via* PFG HMQC $^{1}H\{^{15}N\}$ measurements at natural abundance of the ^{15}N isotope (see Experimental). For ligand **3**, a correlation between the ^{15}N nucleus and the protons of the methylene bridge (ArOCH_2-quinoline) was observed at δ = –75.3 ppm. This value is in good agreement with ^{15}N NMR chemical shifts reported in literature for nitrogen donor ligands based on a phenanthroline skeleton.[19]

Single crystals of ligand **3** as a CH_2Cl_2 solvate were grown from a CH_2Cl_2/hexane solution. The X-ray crystal structure (Fig. 1) further corroborates the spectroscopic data reported above, showing the overall *cone* conformation of the calix[4]-scaffold and the *exo* orientation of the phosphorus lone pair. As already deduced from the ^{1}H, ^{13}C and ^{31}P NMR spectra, the presence of a short μ_3-P capping unit at the lower rim of the cavity determines an *up-up-out-up* conformation of the calixarene scaffold with one aryl-OP ring strongly tilted with respect to the reference plane of the molecule (*out* refers to the phenol unit containing O(13); dihedral angle 10.07(5)°).

Although ligand **3** appears to be C_1-symmetric in the solid state, the structural *up-up-out* ↔ *out-up-up* rearrangement discussed above and previously evidenced by Parlevliet *et al.* for μ_3-bridging phosphite moieties,[8a] renders the O(11) and O(13) phenol rings equivalent on the NMR time scale. Furthermore, the phosphorus and the nitrogen donor atoms are oriented in a distant conformation in the solid state and hence, rotation of the quinoline moiety around the C*ipso*-CH_2Ar bond is required to form chelating complexes.

Coordination chemistry

Several transition metal precursors have been chosen in order to study the coordination modes of ligand **3**, which may coordinate in a monodentate fashion, most likely *via* the phosphorus atom, or act as an N–P bidentate ligand.[20] Because of their many applications in metal-catalysed transformations, Rh(I) precursors such as [$Rh(CO)_2Cl]_2$ and [Rh(acac)($CO)_2$], as well as Pd(II) complexes such as [$PdCl_2$(cod)] and [PdCl(CH_3)(cod)],[21] and

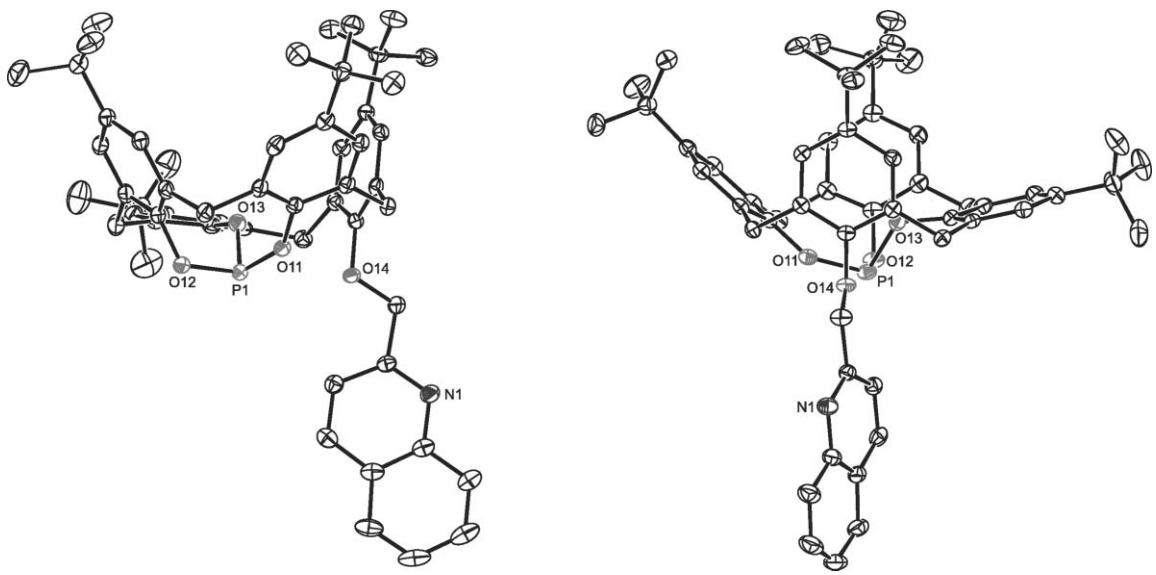


Fig. 1 Different views of calix[4]-based P,N-ligand **3** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Only the major conformations of the disordered ^{t}butyl groups are shown.

[$PtCl_2$(cod)] (acac = acetylacetonato, cod = 1,5-cyclooctadiene) were chosen as models for the coordination chemistry studies.

All complexes have been isolated and structurally characterised by NMR spectroscopy, elemental analysis and two of them by X-ray diffraction analysis.

Ligand **3** reacts with an equimolar amount of [$PdCl(CH_3)$(cod)] to form selectively the chelate complex [$PdCl(CH_3)$(**3**)] (**4**). The ^{31}P NMR spectrum shows one singlet at δ = 85.7 ppm (CIS¶ = −18.2 ppm) and in the ^{1}H NMR the methyl group Pd-CH_3 is characterised by one doublet at δ = 0.90 ppm with ^3J(P,H) = 3.0 Hz, in keeping with the presence of only one phosphorus ligand in *cis* position. The resonances for the methylene bridges of the calix[4]arene cavity (ArCH_2Ar) appear as two broad signals at room temperature. This indicates that the activation energy for the fluxional process involving the aryl fragments increases upon complexation, due to the loss of mobility of the calix[4]-moiety. Cooling a sample of palladium complex **4** to T = −20 °C resulted in a resolved ^{1}H NMR spectrum which allowed a clear attribution of four distinct AB patterns for the ArCH_2Ar of the cavity and one AB pattern for the ArOCH_2-quinoline bridge (Fig. 2).

COSY experiments were performed in order to assign the resonances of the quinoline unit, which are well separated at 20 °C. Fig. 3 shows for comparison the aromatic regions of the ^{1}H NMR spectra for the free **3** and the coordinated P,N-ligand in the palladium complex **4**. It should be noted that the low-field resonance (δ = 9.75 ppm) corresponds to the doublet assigned to H^8 of the heterocyclic aromatic ring and it is remarkably downfield shifted with respect to the same signal in the free ligand (CIS = 1.72 ppm; Table 1).

In order to substantiate the coordination of the nitrogen donor atom to the palladium centre, we carried out ^{15}N NMR measurements performed by recording PFG HMQC ^{1}H{^{15}N} spectra at natural abundance of the ^{15}N isotope.

Together with a cross peak between the ^{15}N nucleus and proton H^4 of the quinoline, the correlation with the protons of the methyl group *trans* to the N atom (Fig. 4) was also observed, further corroborating the chelating nature of the P,N-ligand in complex **4**. The ^{15}N NMR chemical shift of −110.6 ppm (Table 1) found for the quinoline fragment falls within the expected range, with a CIS value of −35.3 ppm similar to previously reported N *trans* to C in parent palladium complexes with coordinated nitrogen donor ligands.[19]

The crystal structure depicted in Fig. 5 proves the mononuclear structure of **4** and shows that the calixarene core adopts an *up-up-out-up* cone conformation ['*out*' refers to the phenol ring bearing O(3); dihedral angle *ca.* 12.42(7)°].

All metal–ligand bond distances fall in the expected range of values (Table 2) but, as frequently observed in chelate complexes, the palladium geometry deviates somewhat from an ideal square plane. Thus, the larger P(1)–Pd(1)–N(1) angle (97.88(5)°) reflects the strain imposed on the rigid 12-membered P,N-chelate ring by the coordination of the quinoline fragment to the metal centre. In fact, the Pd–N bond formation forces the quinoline plane to be perpendicular to the coordination plane, inducing an increased

¶ Coordination Induced Shift = δ(complex) − δ(ligand)

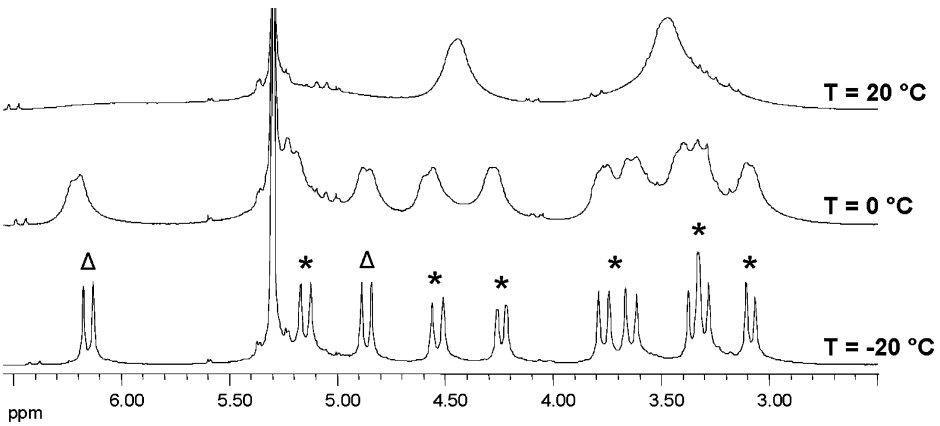


Fig. 2 Low temperature ^{1}H NMR experiments performed with [$PdCl(CH_3)$(**3**)] (**4**) (CD_2Cl_2; * = CH_2 groups of the calix[4]-cavity (ArCH_2Ar), Δ = CH_2 groups of the bridging unit (ArOCH_2-quinoline)).

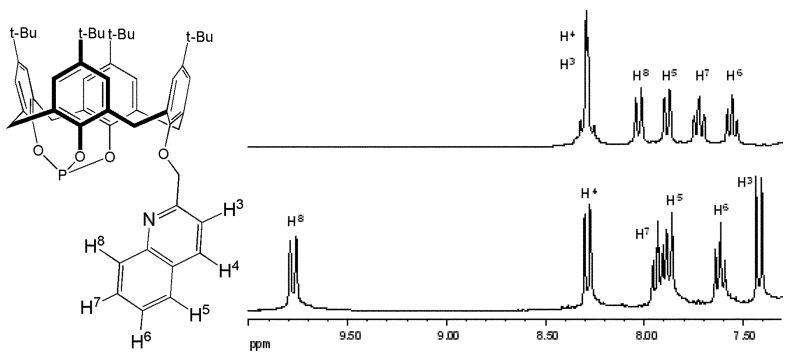


Fig. 3 Quinoline region of the ^{1}H NMR spectrum for the free ligand (**3**) (above) and complex [$PdCl(CH_3)$(**3**)] (**4**) (below) (CD_2Cl_2, T = 20 °C).

Table 2 Selected bond lengths and angles for [PdCl(CH_3)(**3**)] (**4**)

Bond lengths (Å)		Bond angles (°)	
Pd(1)–P(1)	2.1892(6)	P(1)–Pd(1)–N(1)	96.88(5)
Pd(1)–N(1)	2.2237(19)	Cl(1)–Pd(1)–N(1)	89.08(5)
Pd(1)–Cl(1)	2.3534(6)	C(55)–Pd(1)–P(1)	86.08(6)
Pd(1)–C(55)	2.075(2)	C(55)–Pd(1)–Cl(1)	88.01(6)
P(1)–O(1)	1.5819(16)	Pd(1)–P(1)–O(1)	110.97(6)
P(1)–O(2)	1.6049(17)	Pd(1)–P(1)–O(2)	111.63(6)
P(1)–O(3)	1.6185(17)	Pd(1)–P(1)–O(3)	121.62(6)
		O(1)–P(1)–O(2)	105.77(9)
		O(1)–P(1)–O(3)	103.02(9)
		O(2)–P(1)–O(3)	102.38(8)

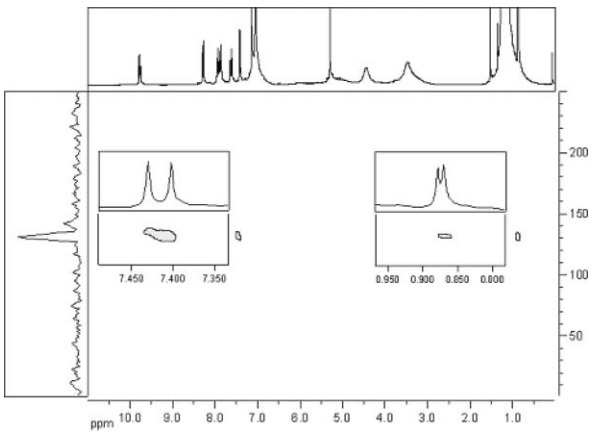


Fig. 4 $^{1}H,^{15}N$ PFG HMQC spectrum of complex [PdCl(CH_3)(**3**)] (**4**) recorded at natural abundance of ^{15}N (CD_2Cl_2, T = 20 °C).

distortion of the calixarene shape as revealed by the strong inclination of the O(4) phenol plane with respect to the calixarene reference plane, defined by the bridging methylene units (dihedral angle *ca.* 74.70(8)° for O(4) *vs.* 61.58(8)° for the O(2) phenol plane). Furthermore, the particular orientation of the quinoline moiety favours the approach of proton H^8 to the palladium centre, with a resulting $H^8 \cdots Pd$ distance of 2.66 Å. This evidence, together with the large downfield ^{1}H NMR shift of 1.72 ppm observed for this proton (*vide supra*), suggests the presence in complex **4** of a weak M←H–C interaction.

In addition to the so-called 'agostic interaction', which shows high-field ^{1}H NMR shifts and $H \cdots M$ separations (X-ray crystal structures) of *ca.* 1.8–2.2 Å,[22] Albinati *et al.* have suggested a much weaker variation of this interaction for a series of *trans*-[$PtCl_2R(L)$] complexes (R = PR_3, AsR_3, C_2H_4, $PhCH{=}CH_2$; L = nitrogen donor ligand) containing coordinated nitrogen donor ligands.[23] These molecules revealed downfield ^{1}H NMR shifts[24] but larger $H \cdots Pt$ separations of *ca.* 2.3–2.9 Å, as typical values for this type of interaction. The ligands were specifically chosen so that one or more C–H bonds would be situated above the coordination plane defined by the Pt atom, the P atom and the two Cl atoms, and have restricted motional freedom due to built-in rigidity and/or bulky substituents on the nitrogen donor ligand, which increase the energy barrier for rotation about the Pt–N bond.

Addition of ligand **3** to 0.5 equivalents of $[Rh(CO)_2Cl]_2$ resulted in the formation of the mononuclear chelate species [Rh(CO)Cl(**3**)] (**5**), as suggested by the spectroscopic data similar to those observed for [PdCl(CH_3)(**3**)] (**4**). The structure of complex **5** is supported both by the ^{31}P NMR spectrum, showing a doublet at δ = 102.6 ppm with $^{1}J(P,Rh)$ = 307 Hz and by the ν(CO) frequency in the IR spectrum at 2012 cm^{-1}. These values are in good agreement with other reported square planar chelate Rh(I) complexes [Rh(CO)Cl(P^N)] containing *cis* coordinated P,N-ligands.[25] Analogous to the Pd(II) complex **4**, a large downfield shift for the resonance of H^8 of the quinoline is observed in the ^{1}H NMR spectrum (CIS = 2.06 ppm; Table 1). Again, this NMR evidence may be attributed to the presence of a weak interaction M←H–C as a result of proton H^8 approaching the metal centre in a pseudoaxial position. Furthermore, the broadening of the $ArCH_2Ar$ and the $ArOCH_2$-quinoline signals, observed also for **4**, indicates that the P,N-ligand acts as a bidentate ligand and upon coordination, through both the phosphorus and the nitrogen atoms, generates a rigid structure with limited flexibility. Similarly, the singlet found for the free ligand at δ = 5.51 ppm, which was assigned to the methylene bridge ($ArOCH_2$-quinoline), splits into two broad signals of two non-equivalent protons, further corroborating the increased rigidity of the P,N-ligand induced by the coordination of the quinoline fragment to the metal centre.

Low temperature NMR experiments performed for [Rh(CO)Cl(**3**)] (**5**) showed that the fluxional process in which the aryl rings of the cavity are involved can be halted at T = 0 °C. At this temperature de-coalescence is reached and the ^{1}H NMR spectrum again shows five AB patterns, which can be assigned to

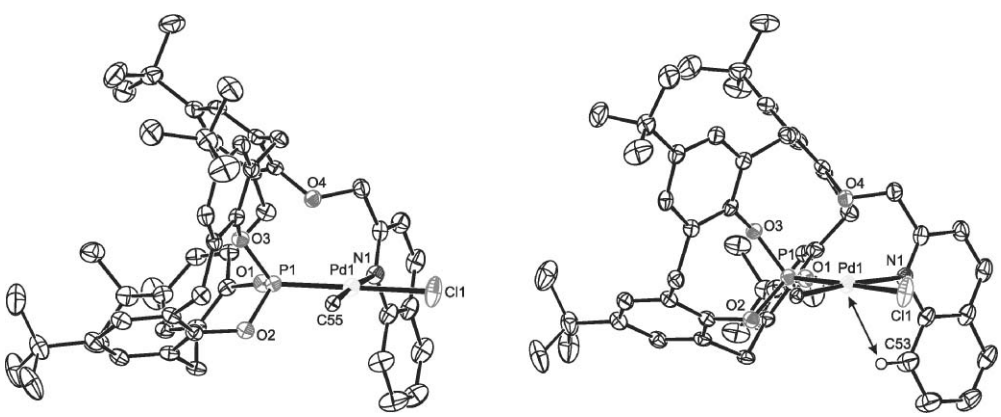


Fig. 5 Different views of the chelate complex [PdCl(CH_3)(**3**)] **4** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Only the major conformation of the disordered ^{t}butyl group is shown.

the bridging ArCH_2Ar and the ArOCH_2-quinoline protons (see Experimental).

Mixing the Pt(II) precursor with two equivalents of **3** leads to the formation of complex [$PtCl_2$(**3**)$_2$] (**6**). The ^{31}P NMR spectrum shows one singlet with Pt satellites (δ = 33.2 ppm, ^1J(Pt, P) = 6833 Hz) indicating coordination of the phosphite moiety to the metal centre. The magnitude of the Pt–P coupling constant, nearly identical to values reported for other *cis*-[$PtCl_2$(phosphite)$_2$] complexes containing calix[4]-based phosphites, suggests the formation of a species with two phosphorus atoms coordinated in a *cis*-position.[14,15] In contrast to the previous examples, the signal of H^8 in the quinoline unit is only slightly shifted compared to the free ligand (Table 1) and no broadening of the signals for the methylene bridges of the calix[4]arene cavity is observed and most likely **3** is acting as a monodentate ligand.

The PFG ^{1}H{^{15}N}-HMQC NMR spectrum recorded for complex **6** evidenced a ^{15}N chemical shift of $\delta = -70.8$ ppm as a result of two correlations: one between the ^{15}N nucleus and the bridging ArOCH_2-quinoline and a second one between the ^{15}N nucleus and proton H^3 of the quinoline unit. The observed ^{15}N chemical shift of complex **6** is almost identical to the one reported for the free ligand, thus a negligible CIS value was obtained in this case upon coordination (Table 1). This, together with the other NMR data, supports the fact that in complex **6** the N-containing unit behaves as non-coordinating pendant arm. Furthermore, the two AB patterns typical of the ArCH_2Ar in the free ligand, split into four AB patterns once **6** is formed, indicating that upon complexation the calix[4]arene fragment is no longer C_s-symmetric on the NMR time scale. The high steric crowding resulting from the *cis* coordination of the two calix[4]-based phosphite moieties prevents the rotation of the backbone through the Pt–P bond. The equivalence of the two phosphorus atoms, indicated by the ^{31}P NMR, may be due to the presence of a two-fold axis, as found in the X-ray structure (*vide infra*).

The nature of complex [$PtCl_2$(**3**)$_2$] was further corroborated by X-ray crystal structure determination carried out on single crystals obtained from a CH_2Cl_2/CH_3CN solution of **6** (Fig. 6). The platinum centre has, as expected, a planar coordination environment and the Pt–P bond lengths (Table 3) are comparable to those found in other [$PtCl_2$(phosphite)$_2$] complexes.[14,26] Analogous to complex **4** reported above, in complex **6** both calix[4]arene cores adopt an *up-up-out-up cone* conformation ['*out*' refers to the phenol rings bearing O(11) and O(21); dihedral angles 23.6(3)° and 16.6(3)°, respectively] with an *out* phenol ring whose orientation approaches that of the calixarene reference plane. The large P(1)–Pt(1)–P(2) angle of 95.25(7)° clearly reflects the high steric crowding generated by the two calix[4]arene frameworks when *cis*-coordinated. Due to the spatial expansion of each ligand, particularly important when considering the region containing the quinoline pendent arm, the rotation of one particular phosphite around its Pt–P axis is hindered by the neighbouring phosphite ligand.

When [Rh(acac)$(CO)_2$] is treated with one equivalent of P,N-ligand **3** in dichloromethane, the ^{31}P NMR spectrum of the reaction mixture shows a doublet at $\delta = 105.8$ ppm with a rhodium–phosphorus coupling constant ^1J(P,Rh) of 311 Hz, which is similar to values reported for analogous rhodium complexes with coordinated phosphites.[14] The presence, in the ^{1}H NMR spectrum, of two AB patterns for the methylene bridging units (ArCH_2Ar) indicates that, upon complexation, ligand **3** retains its C_s symmetry. This suggests that only one P,N-ligand is coordinated to the rhodium centre giving rise to the formation of complex [Rh(acac)(CO)(**3**)] (**7**), in which the steric congestion derived from the presence of only one bulky calixarene scaffold still allows free rotation of the phosphite moiety around the Rh–P bond. The monodentate coordination of ligand **3** in complex **7** was inferred by the presence of the ν(CO) frequency in the IR spectrum at 2002 cm^{-1} and the slight shift of the signal of proton H^8 of the quinoline compared to the signal in the free ligand (Table 1). This was further corroborated by the PFG ^{1}H{^{15}N}-HMQC NMR spectrum, which showed a ^{15}N NMR chemical shift of –69.8 ppm with negligible CIS value (Table 1), resulting from one correlation of the ^{15}N nucleus with the methylene bridge ArOCH_2-quinoline and a second correlation with proton H^3 of the quinoline moiety.

Table 3 Selected bond lengths and angles for [$PtCl_2$(**3**)$_2$] (**6**)

Bond lengths (Å)		Bond angles (°)	
Pt(1)–P(1)	2.210(2)	P(1)–Pt(1)–P(2)	95.25(7)
Pt(1)–P(2)	2.215(2)	P(2)–Pt(1)–Cl(2)	89.92(7)
Pt(1)–Cl(1)	2.3387(19)	Cl(2)–Pt(1)–Cl(1)	87.34(7)
Pt(1)–Cl(2)	2.3420(19)	Cl(1)–Pt(1)–P(1)	87.79(7)
P(1)–O(11)	1.577(6)	Pt(1)–P(1)–O(11)	119.6(2)
P(1)–O(12)	1.599(6)	Pt(1)–P(1)–O(12)	108.1(2)
P(1)–O(13)	1.569(5)	Pt(1)–P(1)–O(13)	113.0(2)
P(2)–O(21)	1.596(5)	O(11)–P(1)–O(12)	105.1(3)
P(2)–O(22)	1.601(6)	O(12)–P(1)–O(13)	107.2(3)
P(2)–O(23)	1.580(6)	O(11)–P(1)–O(13)	103.1(3)
		Pt(1)–P(2)–O(21)	120.1(2)
		Pt(1)–P(2)–O(22)	108.8(2)
		Pt(1)–P(2)–O(23)	112.3(2)
		O(21)–P(2)–O(22)	105.0(3)
		O(22)–P(2)–O(23)	106.9(3)
		O(21)–P(2)–O(23)	102.9(3)

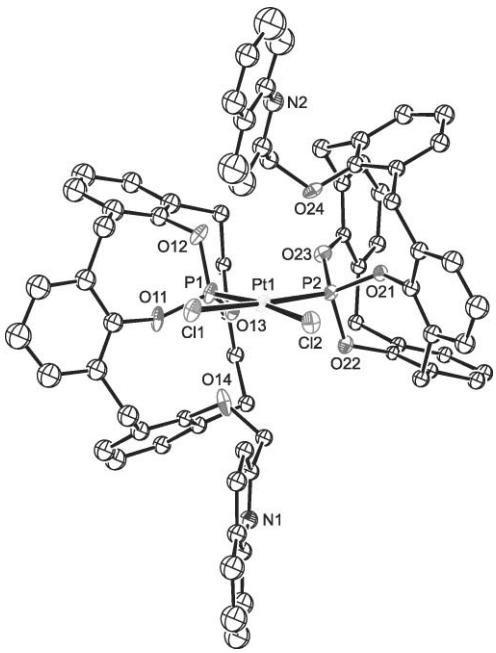


Fig. 6 Complex *cis*-[$PtCl_2$(**3**)$_2$] **6** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. ^{t}Butyl groups, hydrogen atoms and solvent molecules are omitted for clarity.

Catalytic investigations

The calix[4]-based P,N-ligand **3** was employed in three different metal-catalysed transformations: the palladium-catalysed CO/olefin co- and terpolymerisation, the palladium-catalysed allylic alkylation of cinnamyl ester and the rhodium-catalysed hydroformylation of 1-octene.

CO/ethylene copolymerisation

In the early 1990s several groups and chemical companies reported on the palladium-catalysed alternating copolymerisation of olefins with carbon monoxide to yield copolymers with very attractive physical properties.[27] Catalysts are usually of the type $[Pd(solvent)_2(L)]^{2+}$ or $[Pd(CH_3)(solvent)(L)]^{+}$ where L is a diphosphine, a bipyridine or diimine ligand, but interest in searching for new catalysts with unsymmetrical bidentate ligands has also been increasing, particularly with P,N-ligands.[4,7]

Phosphite ligands have not found wide application in the CO/olefin copolymerisation reaction, the limitation of their use being mainly due to two reasons: (i) phosphites promote side reactions to palladium(0) complexes and thus, decrease the concentration of the active catalyst in the reaction mixture, (ii) phosphites are sensitive to alcoholysis, and the use of methanol, the solvent in industrial CO/ethylene copolymerisation, leads to decomposition. To avoid this problem, the catalysis can be performed in dichloromethane or other non-protic solvents.[28] Nozaki *et al.* have studied the use of a bisnaphthol-based diphosphite in CO/propene copolymerisation, but no polymer was obtained.[28b] Only when the calix[6]arene-based diphosphite reported by Parlevliet *et al.* was employed, was the corresponding cationic palladium complex found to be active in the palladium-catalysed CO/ethylene copolymerisation reaction.[8b]

As higher activities are obtained when weakly coordinating anions[29] are used, the catalyst precursor $[Pd(CH_3)(CH_3CN)(\mathbf{3})][PF_6]$ (**8**) was chosen as the catalyst. It was synthesized by chloride abstraction using $AgPF_6$ in a coordinating solvent such as acetonitrile. Complex **8** was isolated prior to use and characterised by NMR spectroscopy. The broad signals displayed in the ^{1}H NMR spectrum for the bridging methylene groups ArCH_2Ar and ArOCH_2-quinoline, and the low-field shift (CIS = 1.73 ppm; Table 1) observed for proton H^8 of the quinoline unit, are indicative of the chelating nature of complex **8**, in which the P,N-ligand is coordinated *via* both the phosphorus and the nitrogen atoms (see Experimental). Furthermore, the singlet found in the ^{1}H NMR at $\delta = 2.02$ ppm corroborates the presence of acetonitrile in the coordination sphere of the palladium centre.[4a]

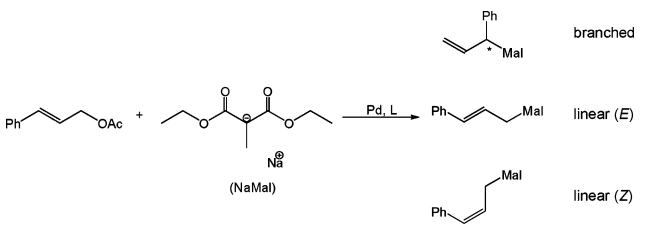
Complex $[Pd(CH_3)(CH_3CN)(\mathbf{3})][PF_6]$ (**8**) was tested in the CO/ethylene copolymerisation reaction that was performed in dichloromethane, in the presence of 1,4-benzoquinone and at the pressure of 30 bar (p(CO)/p(ethylene) = 1). An appreciable amount of copolymer, corresponding to a productivity of 17 g of copolymer per gram of palladium, could be isolated. The polymer structure was confirmed by the ^{13}C NMR spectrum, which showed the characteristic signals for the carbonyl and methylene groups. Catalytic runs performed with varying CO/ethylene pressure, indicated that a minimum pressure of 30 bar is required to obtain copolymer in isolable amounts. It is important to mention that in neither case formation of palladium metal, resulting from catalyst decomposition, was observed.

CO/styrene copolymerisation experiments performed with complex **8** did not lead to product formation. This corroborates the general observation that, apart from a few exceptions, nitrogen-donor ligands are the ligands of choice for obtaining CO/vinylarene copolymers in high yields and with high molecular weight values.[30] Attempts were also undertaken to perform CO/ethylene/styrene terpolymerisation reactions, but no product was obtained.

To the best of our knowledge, ligand **3** is the first phosphito-based P,N-ligand to find successful application in the copolymerisation of CO/ethylene under mild conditions, albeit with low activity.

Allylic alkylation of cinnamyl ester

Transition metal-catalysed allylic alkylation is a useful tool in synthetic organic chemistry. In many cases, palladium-based catalysts are the systems of choice and thus, the most widely studied. When substrates giving symmetrical substituted Pd(allyl) complexes are used (cyclopent-2-enyl acetate or 1,3-diphenylprop-2-enyl 1-acetate), high enantioselectivities can be obtained. When other types of allylic substrates are used, such as crotyl acetate or cinnamyl acetate, non–symmetrical substituted Pd(allyl) complexes are formed and regiocontrol becomes an issue prior to enantiocontrol. Three products can be formed: the achiral (*E*) and (*Z*) linear products and the chiral branched product, which is the product of interest for applications in asymmetric synthesis (Scheme 2).



Scheme 2 Regioselectivity in the palladium-catalysed allylic alkylation of cinnamyl acetate.

Although palladium complexes have a preference for the formation of the linear achiral product, it was recently shown that, in combination with P,N-ligands, they can also direct the regioselectivity towards the preferential formation of the branched product with excellent enantioselectivities.[31]

Ligand **3** was used in the palladium-catalysed allylic alkylation of cinnamyl acetate using diethyl 2-methylmalonate as a nucleophile. The catalyst precursor was formed *in situ* by mixing $[Pd(allyl)Cl]_2$ with two equivalents of ligand **3** in THF solution under an inert atmosphere. Subsequently, the substrate and the internal standard (decane) were added and the reaction started upon addition of the nucleophile to the mixture.

Quantitative conversion was reached after 20 h reaction time providing only two products: the linear (*E*) and the branched product. The linear *cis* product was not observed under the employed reaction conditions. Similarly to other P,N-ligands reported in literature, ligand **3** shows a preference for the *trans* species, affording a product distribution of 44% for the branched

and 56% for linear (*E*) product. The observed regioselectivity is in the range of values reported for chiral P,N-ligands used in asymmetric allylic alkylation but superior to achiral P,N-ligands.[30c]

Hydroformylation of 1-octene

The catalyst precursor was formed *in situ* by mixing three equivalents of ligand **3** with [Rh(acac)(CO)$_2$] in toluene solution under an inert atmosphere. Experiments were run by means of a semiautomated autoclave (AMTEC SPR16, see Experimental) equipped with sixteen independent reactors and an automated sampling under reaction conditions. After 2 h reaction time, full conversion of 1-octene was reached, affording a linear/branched ratio of 1.4[32] and isomerisation of about 13%. The corresponding activity (turnover frequency (TOF) = (mol aldehyde) · (mol Rh)$^{-1}$ · h^{-1}), determined at *ca.* 30% conversion, was 650 which is much lower than the activities reported for calix[4]arene-based monophosphite ligands.[8a] It should be recalled that the heterofunctionalised P,O-ligands reported by Steyer *et al.* have also found to be less active than the parent monoalkylated calix[4]-monophosphites reported by Parlevliet *et al.*[14]

In the present work, bidentate coordination of ligand **3** and formation of chelate complexes have been observed and unambiguously demonstrated for Pd(II) and Rh(I) metal precursors and thus, cannot be discarded even when discussing the coordination mode of **3** under catalytic conditions. Additionally, the low selectivity obtained in the catalytic experiment might be attributed to the hemilabile nature of the P,N-ligand **3** and to the possible formation of different rhodium species in solution in which **3** coordinates in a monodentate fashion or acts as a chelating system.

High-pressure (HP) NMR studies

High-pressure NMR experiments have been carried out to investigate the composition of the catalyst solution in the rhodium-catalysed hydroformylation of olefins and elucidate the coordination mode of the P,N-ligand **3** under syngas pressure. The complexation reaction was studied *in situ* upon addition of two equivalents of ligand **3** to a toluene solution of the [Rh(acac)(CO)$_2$] precursor and then by pressurising the NMR tube with 20 bar of syngas (CO/H$_2$ 1:1). The ^{31}P NMR of the mixture, recorded at room temperature under argon, displayed one singlet corresponding to the free ligand ($\delta = 104.3$ ppm) and one doublet at $\delta = 104.7$ ppm with ^1J(Rh,P) = 217 Hz in a 1:1 ratio. This, together with the spectroscopic data previously discussed, indicates the formation of the species [Rh(acac)(CO)(**3**)] (**7**), in which the P,N-ligand **3** is coordinated to the rhodium centre exclusively *via* the phosphorus atom. The solution was then pressurised with 20 bar of syngas and subjected to 5 h activation period at 40 °C. The reaction was found to proceed unselectively. Thus, the resulting ^{31}P NMR spectrum showed several signals corresponding to the presence of at least four different rhodium complexes in solution.

The doublet at $\delta = 127.8$ ppm with ^1J(Rh,P) = 240 Hz and the broad double triplet in the hydride region ($\delta = -9.58$ ppm) of the ^{1}H NMR proved the formation of a rhodium hydride complex with two equivalent phosphorus atoms. Hydride complexes [HRh(diphosphite)(CO)$_2$] generated in the presence of chelating diphosphites, bisequatorially coordinated to the rhodium centre, have been found to display similar ^1J(Rh,P) values.[33] This, together with the characteristic multiplicity displayed by the hydride signal, suggests that two calix[4]-based P,N-ligands are coordinated to the rhodium centre through the phosphorus atoms, both equatorially positioned, generating [HRh(**3**)$_2$(CO)$_2$] (**9**). A second doublet, found at higher fields ($\delta = 97.9$ ppm), showed a rhodium–phosphorus coupling constant ^1J(Rh,P) = 225 Hz, which could be attributed to monohydrido species [HRh(**3**)(CO)$_3$] (**10**), in which only one P,N-ligand is coordinated to the rhodium centre. The hydride region of the ^{1}H NMR spectrum showed for this complex a weak broad singlet at $\delta = -9.87$ ppm, as a result of small phosphorus–hydride ^2J(H,P) and rhodium–hydride ^1J(H,Rh) coupling constants, which could not be resolved completely. This indicates that, in the trigonal bipyramidal structure, the rhodium centre has an apical hydride with a phosphite moiety *cis*-positioned, thus suggesting the equatorial coordination of ligand **3**. In this species, **3** is considered to behave most likely as a monodentate ligand, coordinating exclusively through the phosphorus atom, but at this stage of investigation the formation of chelates, in which **3** acts as a bidentate ligand, cannot be discarded *a priori.*

Species **9** and **10** are the only hydrides present in solution since no additional hydrides are visible in the ^{1}H NMR spectrum.

The third signal at $\delta = 117.5$ ppm, which is characterised by a second-order multiplicity, could be resolved at 0 °C. The pattern of signals obtained, consistent with an AA'XX' spin system, could be satisfactorily simulated leading to the coupling constants: ^1J(Rh,P) = 277 Hz, ^2J(Rh,P) = 15 Hz and ^3J(P,P) = 18 Hz (Fig. 7). The values found for ^1J(Rh,P) are similar to those reported for rhodium(0) dimers containing diphosphite ligands.[34,35] Hence, we assume that the compound at $\delta = 117.5$ ppm corresponds to a Rh(0) dimeric species which can be formulated as [Rh(μ-CO)(CO)$_2$(**3**)]$_2$ (**11a**) or [Rh(μ-CO)(CO)(**3**)$_2$]$_2$ (**11b**).

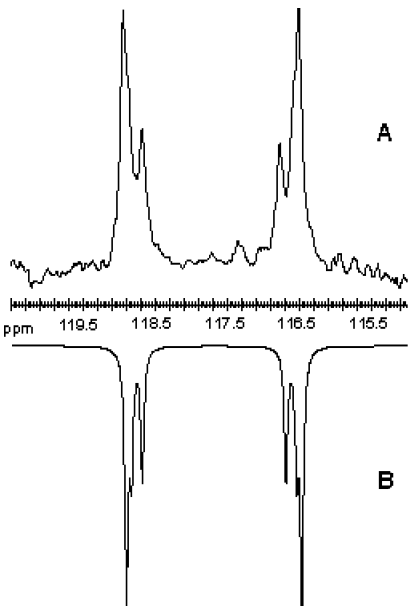


Fig. 7 ^{31}P{^{1}H} NMR spectra of species **11**: (**A**) experimental (toluene-d_8, T = 0 °C); (**B**) simulated for a AA'XX' system.

Analysis of chemical shifts and coupling constants allowed the attribution of all the resonances displayed in the ^{31}P NMR spectrum, with the exception of a complex pattern of signals

found at $\delta = 111$ ppm, which could not be resolved even at low temperature. Due to the spectroscopic similarities displayed in HP NMR experiments performed with DIOP-based P,N-ligands reported by Aghmiz *et al.*,[36] we might attribute these signals to dimeric rhodium species formulated as $[(P\wedge N)_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)(P\wedge N)]$.

Conclusions

We have described the synthesis of the first hybrid P,N-ligand based on a calix[4]arene platform. Due to the *cone* conformation of the calixarene cavity, the bidentate P,N-ligand becomes a potential chelating system. In the presence of $[PdCl(CH_3)(cod)]$ and $[Rh(CO)_2Cl]_2$ metal precursors, it readily forms 12-membered chelate P,N-rings, while with $[PtCl_2(cod)]$ and with $[Rh(acac)(CO)_2]$ shows monodentate coordination exclusively *via* the phosphorus atom, affording a 2:1 and a 1:1 complex, respectively. The nature of these species was confirmed by ^1H, ^{31}P and ^{15}N NMR spectroscopy and X-ray crystal structure determination. Interestingly, due to the particular orientation of the quinoline moiety in the chelate complexes, a detectable weak M←H–C interaction was observed, which was supported by downfield ^1H shifts and crystallographic H···M separation.

P,N-ligands have not been widely studied in the hydroformylation of olefins and not many investigations have been carried out to elucidate their coordination mode under syngas pressure. Coordination of a pyridyl group to a rhodium hydrido carbonyl may be interesting for photochemical activation of the catalyst, but so far no indications have been found that such species form. We tested the new P,N-ligand in three metal catalysed transformations. Under the employed reaction conditions, poor activities were obtained in the palladium-catalysed CO/ethylene copolymerisation, while good regioselectivities towards the branched product were observed in the palladium-catalysed allylic alkylation of cinnamyl acetate. When employed in the rhodium-catalysed hydroformylation of 1-octene, ligand **3** showed low activities and very poor selectivities towards linear aldehydes. Most likely, if P–N coordinated species are formed, they are not carbonyl hydrides and inactive as hydroformylation catalysts.

Experimental

General considerations

Unless otherwise stated, all preparations were carried out under an inert atmosphere of argon using standard Schlenk techniques. Materials were obtained from commercial suppliers and used without further purification. Solvents were dried over suitable reagents and freshly distilled under nitrogen prior to use. Calix[4]arene-based P,N-ligand (**3**) was obtained in pure form by preparative, centrifugally accelerated, radial, thin layer chromatography (Chromatotron®, Harrison Research, model 7924T). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Mercury 300 and Bruker DRX-300 spectrometers (300.1 MHz for ^1H NMR, 75.5 MHz for $^{13}C\{^1H\}$ NMR and 121.5 MHz for $^{31}P\{^1H\}$). The deuterated solvents used are indicated in the experimental part; shifts are given, relative to TMS (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). The nomenclature '*m*-H' specifically refers to aromatic protons in *meta* position on phenolic rings of the calix[4]arene backbone. The ^{15}N NMR spectra were recorded using the PFG HMQC (Pulse Field Gradient Heteronuclear Multiple-Quantum Correlation) sequence in a Bruker DRX-300 equipped with a 5 mm triple resonance inverse probe with *z*-gradient, operating at 30.42 MHz ^{15}N frequency and a second 300 W X decoupler giving a 90° ^{15}N pulse of 10 μs.[19c] Chemical shifts were referenced to external nitromethane = 0 ppm, negative chemical shifts are reported for lower frequencies. Gas chromatographic analysis were performed on a Shimadzu GC-17A apparatus (split/splitless, equipped with a FID detector and a DB-1 column, internal diameter of 0.32 mm, film thickness 3 μm, carrier gas 80 kPa He). Elemental analyses data were performed at the H. Kolbe Mikroanalytisches Laboratorium in Mülheim (Germany).

Catalytic experiments

CO/ethylene copolymerisation experiments. CO/olefins copolymerisation reactions were performed in a stainless steel autoclave equipped with a temperature controller and a mechanical stirrer. In a typical CO/ethylene copolymerisation experiment, dichloromethane (50 ml), 1,4-benzoquinone ([BQ]/[Pd] = 40) and the catalyst (12.7 μmol of $[Pd(CH_3)(CH_3CN)(\mathbf{3})][PF_6]$ (**8**)) were introduced in an autoclave that was purged with 30 bar of CO/ethylene (p(CO)/p(ethylene) = 1) for 10 min. The autoclave was then closed, charged with 30 bar of CO/ethylene and heated to 50 °C. After 24 h, the autoclave was cooled to room temperature, the pressure was released and the reaction mixture was poured into methanol, affording the precipitation of a white solid that was filtered, washed with methanol and dried under vacuum.

Allylic alkylation reaction. The alkylation experiments were performed at room temperature (20 °C) in THF (10 ml), using 0.1 mol% of catalyst prepared *in situ* (0.5 μmol of $[Pd(allyl)Cl]_2$ and 1 μmol of P,N-ligand **3** in THF under stirring for 30 min), 1 mmol of cinnamyl acetate as substrate and 2 mmol of sodium diethyl 2-methymalonate as nucleophile. The reaction was monitored by taking samples which, after aqueous work up, were analysed by GC using decane as the internal standard.

Hydroformylation reaction. The hydroformylation experiments were performed in a semiautomated autoclave (AMTEC – Slurry Phase Reactor – SPR16) equipped with sixteen stainless steel 15 ml reactors and an automated sampling under reaction conditions. All reactors are connected *via* a valve system with gas and liquid supply and equipped with individually adjustable stirring (magnetic stirrer bars – 500 to 2000 rpm) and heating (external electrical heating jacket, up to 220 °C).

In a typical run, the autoclave was charged with 5 ml of a 1.8 mM toluene solution of $[Rh(acac)(CO)_2]$ and 3 eq of ligand (0.043 mmol). Once closed, the autoclaves were purged with 30 bar of syngas (CO/H_2 1:1 v/v) five times at 90 °C and five times at 30 °C, then pressurised with 10 bar of syngas and heated for 3 h at 80 °C to preform the catalysts. After releasing the pressure, 3 ml of a stock solution (internal standard (decane, 1.5 ml, 7.75 mmol), substrate (1-octene, 7.5 ml, 0.048 mol) and toluene (6.0 ml)) were added to the catalyst mixtures and the total pressure raised to 20 bar (stirring rate 1000 rpm). Progress of the reaction was checked by monitoring the pressure decrease. During

the experiments, several samples were taken, which were diluted with toluene and analysed by GC.

High-pressure NMR experiments. High-pressure NMR experiments were performed in a 10 mm outer diameter/8 mm inner diameter sapphire tube glued into a Ti (6A1–4V) alloy pressure head, which allows measurements up to 140 bar.[37] In a typical experiment, 10 mg (0.039 mmol) of [Rh(acac)(CO)$_2$] and 63.41 mg (0.077 mmol) of P,N-ligand **3** were dissolved in 2.0 ml of toluene-d_8 under argon atmosphere. The solution was then transferred, *via* cannula, to the NMR tube which was purged three times with 10 bar syngas (CO/H$_2$ 1:1), pressurised to 20 bar and incubate at 40 °C. Spectroscopic measurements were then performed at variable temperature on a Bruker Avance DRX-300 MHz. Samples in the high-pressure NMR tube could not be spun during measurements as a consequence of technical set-up of the NMR spectrometer.

Syntheses

5,11,17,23-tetra-*tert*-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-trihydroxycalix[4]arene (2). *p-tert*-butyl-calix[4]arene (**1**) (5.00 g, 7.7 mmol) and 2-(chloromethyl)-quinoline hydrochloride (3.30 g, 15.4 mmol) were refluxed in dry toluene (250 ml) for about 20 h in the presence of *t*BuOK (3.46 g, 30.8 mmol) as a base. The reaction mixture was then partitioned between water and CHCl$_3$ and the organic layer washed twice with water and dried over Na$_2$SO$_4$. After evaporation of the solvent to dryness the crude product was purified by column chromatography (CH$_2$Cl$_2$/pentane/AcOEt eluent).Yield: 0.91 g, 1.15 mmol (15%). ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): δ = 1.23 (s, 36H; C(C*H*$_3$)$_3$), 3.45 and 4.30 (AB q, ^{2}J = 13.7 Hz, 4H; ArC*H*$_2$Ar), 3.45 and 4.65 (AB q, ^{2}J = 13.2 Hz, 4H; ArC*H*$_2$Ar), 5.54 (s, 2H; ArOC*H*$_2$quinoline), 7.0 (s, 2H; *m*-Ar*H*), 7.07 (s, 2H; *m*-Ar*H*), 7.10 (s, 2H; *m*-Ar*H*), 7.14 (s, 2H; *m*-Ar*H*), 7.60 (t, ^{2}J = 7.8 Hz, 1H; *quinoline-H*), 7.77 (t, ^{2}J = 7.8 Hz, 1H; *quinoline-H*), 7.91 (d, ^{2}J = 7.2 Hz, 1H; *quinoline-H*), 8.26 (d, ^{2}J = 8.4 Hz, 1H; *quinoline-H*), 8.36 (d, ^{2}J = 9.0 Hz, 1H; *quinoline-H*), 9.94 (bs, 3H; O*H*).

5,11,17,23-tetra-*tert*-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene (3). Monoalkylated calix[4]-arene **2** (0.91 g, 1.15 mmol) was azeotropically dried twice with dry toluene and then dissolved in 60 ml of dry toluene. Distilled NEt$_3$ (2.4 ml, 17.3 mmol) was added and the solution was cooled to −78 °C. PCl$_3$ (0.1 ml, 1.15 mmol) in toluene (10 ml) was then added dropwise and the solution was allowed to come to room temperature whilst stirring under argon atmosphere. After 20 h at 80 °C, the salts formed were removed by filtration through a layer of SiO$_2$ and washed with toluene. The filtrate and washing solutions were then evaporated under vacuum giving **3** in a pure form.Yield: 1.03 mmol (90%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ = 1.17 (s, 9H; C(C*H*$_3$)$_3$), 1.26 (s, 9H; C(C*H*$_3$)$_3$), 1.32 (s, 18H; C(C*H*$_3$)$_3$), 3.50 and 4.43 (AB q, ^{2}J = 13.8 Hz, 4H; ArC*H*$_2$Ar), 3.57 and 4.67 (AB q, ^{2}J = 13.8 Hz, 4H; ArC*H*$_2$Ar), 5.51 (s, 2H; ArOC*H*$_2$-quinoline), 7.06 (s, 2H; *m*-Ar*H*), 7.13 and 7.19 (AB q, ^4J = 2.3 Hz, 4H, *m*-Ar*H*), 7.19 (s, 2H; *m*-Ar*H*), 7.57 (t, ^{2}J = 7.4 Hz, 1H; *quinoline-H*^{6}), 7.74 (t, ^{2}J = 7.4 Hz, 1H; *quinoline-H*^{7}), 7.90 (d, ^{2}J = 8.0 Hz, 1H; *quinoline-H*^{5}), 8.03 (d, ^{2}J = 8.4 Hz, 1H; *quinoline-H*^{8}), 8.30 (m, 2H; *quinoline-H*^{3},H^4).^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$, 293 K): δ = 31.52 (s, C(*C*H$_3$)), 31.60 (s, C(*C*H$_3$)), 31.64 (s, C(*C*H$_3$)), 34.34 (s, *C*(CH$_3$)), 34.52 (s, Ar*C*H$_2$Ar), 34.62 (s, *C*(CH$_3$)), 34.72 (s, *C*(CH$_3$)), 36.86 (s, Ar*C*H$_2$Ar), 78.95 (s, ArO*C*H$_2$-quinoline), 120.59–137.13 and 145.29–158.80 (aryl C). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 293 K): δ = 103.9 (s, P(OAr)$_3$).

***cis*-Chloromethyl-{5,11,17,23-tetra-tert-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}-palladium(II) (4).** Ligand **3** (200 mg, 0.24 mmol) was added to a solution of [PdCl(CH$_3$)(cod)][21b] (64.8 mg, 0.24 mmol) in dry CH$_2$Cl$_2$ (3 ml). After stirring for 30 min at room temperature, the solution was concentrated under vacuum and the product precipitated as a white solid by addition of diethyl ether and cooling to −20 °C. Yield: 181 mg, 0.19 mmol (76%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 253 K): δ = 0.79 (d, ^{3}J = 1.59 Hz, 3H; Pd-C*H*$_3$), 1.09 (s, 9H; C(C*H*$_3$)$_3$), 1.11 (s, 9H; C(C*H*$_3$)$_3$), 1.16 (s, 9H; C(C*H*$_3$)$_3$), 1.32 (s, 9H; C(C*H*$_3$)$_3$), 3.09 and 3.38 (AB q, ^{2}J = 12.5 Hz, 2H; ArC*H*$_2$Ar), 3.31 and 4.26 (AB q, ^{2}J = 13.3 Hz, 2H; ArC*H*$_2$Ar), 3.64 and 4.56 (AB q, ^{2}J = 15.1 Hz, 2H; ArC*H*$_2$Ar), 3.77 and 5.18 (AB q, ^{2}J = 14.2 Hz, 2H; ArC*H*$_2$Ar), 4.86 and 6.18 (AB q, ^{2}J = 13.8 Hz, 2H; ArOC*H*$_2$-quinoline), 6.86 (bd, 1H; *m*-Ar*H*), 6.93 (bd, 1H; *m*-Ar*H*), 7.03 (bd, 2H; *m*-Ar*H*), 7.10 (bd, 1H; *m*-Ar*H*), 7.12 (s, 2H; *m*-Ar*H*), 7.28 (bd, 1H; *m*-Ar*H*), 7.42 (d, ^{2}J = 8.3 Hz, 1H; *quinoline-H*^{3}), 7.61 (t, ^{2}J = 7.4 Hz, 1H; *quinoline-H*^{6}), 7.88 (d, ^{2}J = 7.9 Hz, 1H; *quinoline-H*^{5}), 7.92 (t,^2J = 8.4 Hz, 1H; *quinoline-H*^{7}), 8.29 (d, ^{2}J = 8.3 Hz, 1H; *quinoline-H*^{4}), 9.75 (d, ^{2}J = 8.6 Hz, 1H; *quinoline-H*^{8}). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 293 K): δ = 85.7 (s, P(OAr)$_3$). Anal. Calcd. for C$_{55}$H$_{63}$ClNO$_4$PPd: C, 67.76; H, 6.51. Found: C, 67.83; H, 7.02%.

***cis*-Chlorocarbonyl-{5,11,17,23-tetra-tert-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}-rhodium(I) (5).** Ligand **3** (203 mg, 0.25 mmol) was added to a solution of [Rh(CO)$_2$Cl]$_2$ (52.2 mg, 0.12 mmol) in dry CH$_2$Cl$_2$ (3 ml). After stirring for 30 min at room temperature, dry Et$_2$O was added to precipitate the product as a yellow solid. Yield: 0.17 mmol (72%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 273 K): δ = 1.10 (s, 9H; C(C*H*$_3$)$_3$), 1.12 (s, 9H; C(C*H*$_3$)$_3$), 1.16 (s, 9H; C(C*H*$_3$)$_3$), 1.33 (s, 9H; C(C*H*$_3$)$_3$), 3.16 and 3.42 (AB q, ^{2}J = 12.5 Hz, 2H; ArC*H*$_2$Ar), 3.28 and 4.21 (AB q, ^{2}J = 11.5 Hz, 2H; ArC*H*$_2$Ar), 3.63 and 4.38 (AB q, ^{2}J = 15.3 Hz, 2H; ArC*H*$_2$Ar), 3.83 and 5.22 (AB q, ^{2}J = 14.5 Hz, 2H; ArC*H*$_2$Ar), 4.86 and 6.05 (AB q, ^{2}J = 13.6 Hz, 2H; ArOC*H*$_2$-quinoline), 6.90 (bs, 1H; *m*-Ar*H*), 6.94 (bs, 1H; *m*-Ar*H*), 7.06 (bs, 2H; *m*-Ar*H*), 7.12 (bs, 1H; *m*-Ar*H*), 7.14 (bs, 2H; *m*-Ar*H*), 7.32 (bs, 1H; *m*-Ar*H*), 7.43 (d, ^{2}J = 8.3 Hz, 1H; *quinoline-H*^{3}), 7.64 (t, ^{2}J = 7.5 Hz, 1H; *quinoline-H*^{6}), 7.87 (d, ^{2}J = 8.0 Hz, 1H; *quinoline-H*^{5}), 7.94 (t,^2J = 7.8 Hz, 1H; *quinoline-H*^{7}), 8.32 (d, ^{2}J = 8.3 Hz, 1H; *quinoline-H*^{4}), 10.09 (d, ^{2}J = 8.7 Hz, 1H; *quinoline-H*^{8}). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ = 102.6 (d, ^{1}J$_{PRh}$ = 307 Hz, P(OAr)$_3$). IR(CH$_2$Cl$_2$): ν(cm^{-1}) 2012 (CO). Anal. Calcd. for C$_{55}$H$_{60}$ClNO$_5$PRh: C, 67.11; H, 6.14. Found: C, 67.18; H, 6.52%.

***cis*-Dichlorobis-{5,11,17,23-tetra-tert-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(μ_3-phosphorustrioxy)calix[4]arene}-platinum-(II) (6).** Ligand **3** (98.7 mg, 0.12 mmol) was added to a solution of [PtCl$_2$(cod)] (22.5 mg, 0.06 mmol) in dry CH$_2$Cl$_2$ (2 ml). After stirring for 30 min at room temperature, the solution was concentrated under vacuum and the product precipitated as a white solid by addition of CH$_3$CN and cooling to −20 °C. Yield:

0.052 mmol (87%). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 1.04 (s, 9H; C(C*H*$_3$)$_3$), 1.15 (s, 18H; C(C*H*$_3$)$_3$), 1.21 (s, 9H; C(C*H*$_3$)$_3$), 2.54 and 3.95 (AB q, ^{2}J = 13.0 Hz, 2H; ArC*H*$_2$Ar), 2.65 and 4.47 (AB q, ^{2}J = 13.0 Hz, 2H; ArC*H*$_2$Ar), 3.48 and 4.57 (AB q, ^{2}J = 13.5 Hz, 2H; ArC*H*$_2$Ar), 3.56 and 4.79 (AB q, ^{2}J = 12.0 Hz, 2H; ArC*H*$_2$Ar), 4.98 and 6.41 (AB q, ^{2}J = 11.9 Hz, 2H; ArOC*H*$_2$-quinoline), 6.61 (bs, 1H; *m*-Ar*H*), 6.69 (bs, 1H; *m*-Ar*H*), 6.87 (bs, 1H; *m*-Ar*H*), 6.98 (bs, 1H; *m*-Ar*H*), 7.05 (bs, 2H; *m*-Ar*H*), 7.18 (bs, 2H; *m*-Ar*H*),7.51 (t, ^{2}J = 7.2 Hz, 1H; *quinoline-H*^{6}), 7.62 (t, ^{2}J = 7.2 Hz, 1H; *quinoline-H*^{7}), 7.82 (m, 2H; *quinoline-H*^{4},H^5), 8.23 (d, ^{2}J = 8.3 Hz, 1H; *quinoline-H*^{8}), 8.77 (d, ^{2}J = 8.3 Hz, 1H; *quinoline-H*^{3}). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ = 33.2 (s with Pt satellites, $^1J_{PtP}$ = 6833 Hz, P(OAr)$_3$). Anal. Calcd. for $C_{108}H_{120}Cl_2N_2O_8P_2Pt$: C, 68.20; H, 6.36. Found: C, 68.31; H, 6.57%.

Acetylacetonato(carbonyl)-{5,11,17,23-tetra-*tert*-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(*μ*$_3$-phosphorustrioxy)calix[4]arene}-rhodium(I) (7). Ligand **3** (0.24 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (0.24 mmol) in 3 ml of dichloromethane. After stirring for 30 min, the volatiles were evaporated under vacuum to give **7** as a yellow solid. Owing to its high solubility in all common organic solvents, complex **7** was not purified further. Yield: 0.23 mmol (95%). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 0.73 (s, 9H; C(C*H*$_3$)$_3$), 0.98 (s, 9H; C(C*H*$_3$)$_3$), 1.28 (s, 18H; C(C*H*$_3$)$_3$), 1.31 (s, 3H; *acac*-C*H*$_3$), 1.74 (s, 3H; *acac*-C*H*$_3$), 3.27 and 4.64 (AB q, ^{2}J = 14.2 Hz, 4H; ArC*H*$_2$Ar), 3.43 and 5.19 (AB q, ^{2}J = 14.2 Hz, 4H; ArC*H*$_2$Ar), 4.97 (s, 1H; *acac*-C*H*), 5.37 (s, 2H; ArOC*H*$_2$-*quinoline*), 6.80 (s, 2H; *m*-Ar*H*), 6.96 (s, 2H; *m*-Ar*H*), 7.04 and 7.14 (AB q, ^4J = 2.4 Hz, 4H, *m*-Ar*H*), 7.13 (t, ^{2}J = 7.0 Hz, 1H; *quinoline-H*^{6}), 7.33 (t, ^{2}J = 7.0 Hz, 1H; *quinoline-H*^{7}), 7.46 (d, ^{2}J = 8.1 Hz, 1H; *quinoline-H*^{5}), 7.91 (d, ^{2}J = 8.5 Hz, 1H; *quinoline-H*^{4}), 8.12 (d, ^{2}J = 8.3 Hz, 2H; *quinoline-H*^{8}), 8.67 (d, ^{2}J = 8.5 Hz, 2H; *quinoline-H*^{3}). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ = 105.8 (d, $^1J_{PRh}$ = 311 Hz, P(OAr)$_3$). IR(CH_2Cl_2): ν(cm^{-1}) 2002 (CO).

***cis*-Acetonitrile(methyl)-{5,11,17,23-tetra-tert-butyl-25-[(2-quinolylmethyl)oxy]-26,27,28-(μ$_3$-phosphorustrioxy)calix[4]arene}-palladium(II) hexafluorophosphate (8).** To a solution of complex [PdCl(CH$_3$)(**3**)] (**4**) (100 mg, 0.103 mmol) in a CH_2Cl_2/CH_3CN (10:1) mixture, a solution of NH_4PF_6 (16.7 mg, 0.103 mmol) in 1 ml of CH_3CN was added dropwise. The precipitated NH_4Cl was filtered off, and the filtrate was evaporated to dryness. The compound, obtained as a white solid, was spectroscopically pure and was used without further purification. Yield: 100 mg, 0.094 mmol (92%). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 0.98 (s, 3H; Pd-C*H*$_3$), 1.15 (s, 9H; C(*CH*$_3$)$_3$), 1.20 (s, 9H; C(*CH*$_3$)$_3$), 1.25 (s, 18H; C(C*H*$_3$)$_3$), 2.02 (s, 3H; C*H*$_3$CN), 3.52 (bd, ^{2}J = 13.8 Hz, 4H; ArC*H*$_2$Ar), 4.42 (bd, ^{2}J = 13.8 Hz, 4H; ArC*H*$_2$Ar), 5.62 (bs, 2H; ArOC*H*$_2$-quinoline), 7.06–7.16 (m, 8H; *m*-Ar*H*), 7.46 (d, ^{2}J = 8.4 Hz, 1H; *quinoline-H*^{3}), 7.66 (t, ^{2}J = 7.4 Hz, 1H; *quinoline-H*^{6}), 7.88 (m, ^{2}J = 7.9 Hz, 2H; *quinoline-H*^{5},H^7), 8.35 (d,^2J = 8.1 Hz, 1H; *quinoline-H*^{4}), 9.76 (d, ^{2}J = 8.4 Hz, 1H; *quinoline-H*^{8}). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ = 81.4 (s, P(OAr)$_3$).

X-Ray crystal structure determinations

Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å). Absorption correction was based on multiple measured reflections (**3** and **4**). The structures were solved with Direct Methods (SIR-97[38] for **3**; SHELXS-97[39] for **6**) or automated Patterson methods (DIRDIF-97[40] for **4**) and refined with SHELXL-97[41] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters (**3** and **4**). All hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[42]

X-Ray crystal structure determination of 3. $C_{54}H_{60}NO_4P\cdot CH_2Cl_2$ + disordered solvent, Fw = 902.93 [*], colourless plate, 0.60 × 0.60 × 0.15 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 13.2138(1), b = 19.6378(1), c = 22.6813(2) Å, α = 65.8298(3), β = 77.0409(3), γ = 76.6873(3)°, V = 5169.01(7) Å^3, Z = 4, D_x = 1.160 g/cm^3[*], μ = 0.20 mm^{-1}[*]. 102943 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 110 K. 23594 reflections were unique (R_{int} = 0.0416). The crystal structure contains large voids (603.0 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program[42] resulting in 168 electrons/unit cell. Two ^{t}butyl groups were rotationally disordered. 1207 parameters were refined with 204 restraints concerning the disordered ^{t}butyl groups. R1/wR2 [I > 2σ(I)]: 0.0415/0.1049. R1/wR2 [all refl.]: 0.0511/0.1090. S = 1.072. Residual electron density between −0.59 and 0.42 e/Å^3.

[*] Derived values do not contain the contribution of the disordered solvent molecules.

X-ray crystal structure determination of 4. $C_{55}H_{63}ClNO_4PPd\cdot 2C_4H_{10}O$ + disordered solvent, Fw = 1123.12 [*], colourless plate, 0.30 × 0.24 × 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 26.1478(2), b = 12.9326(1), c = 18.9151(1) Å, β = 94.6368(3)°, V = 6375.38(8) Å^3, Z = 4, D_x = 1.170 g/cm^3[*], μ = 0.40 mm^{-1}[*]. 99310 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 110 K. 14575 reflections were unique (R_{int} = 0.0560). The crystal structure contains large voids (740.4 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program[42] resulting in 97 electrons/unit cell. One ^{t}butyl group was rotationally disordered. 706 parameters were refined with 105 restraints concerning the disordered ^{t}butyl group and the diethylether molecules. R1/wR2 [I > 2σ(I)]: 0.0401/0.1027. R1/wR2 [all refl.]: 0.0596/0.1105. S = 1.101. Residual electron density between −1.05 and 1.25 e/Å^3.

[*] Derived values do not contain the contribution of the disordered solvent molecules.

X-ray crystal structure determination of 6. $C_{108}H_{120}Cl_2N_2O_8P_2Pt\cdot 5CH_3CN$ + disordered solvent, Fw = 2107.26 [*], colourless block, 0.20 × 0.20 × 0.20 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 16.7427(6), b = 20.2761(8), c = 22.7693(10) Å, α = 67.813(2), β = 83.508(2), γ = 75.362(1)°, V = 6923.7(5) Å^3, Z = 2, D_x = 1.011 g/cm^3[*], μ = 1.12 mm^{-1}[*]. X-ray intensities were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.61 Å^{-1} at a temperature of 150 K. The crystal appeared to be cracked into two fragments. Only 61712 non-overlapping reflections of the major fragment were integrated. An absorption correction was not considered necessary. 22534

reflections were unique (R_{int} = 0.0871). Pt, P, Cl, and O atoms were refined with anisotropic displacement parameters; C and N atoms were refined isotropically. The crystal structure contains large voids (2009.7 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program[42] resulting in 387 electrons/unit cell. Three ^{t}butyl groups were rotationally disordered. 661 parameters were refined with 1008 restraints concerning the disordered ^{t}butyl groups, the acetonitrile molecules. Additionally, chemically equivalent parts of the molecule were restrained to obtain similar bond distances and angles. R1/wR2 [$I > 2\sigma(I)$]: 0.0832/0.1987. R1/wR2 [all refl.]: 0.0978/0.2063. S = 1.052. Residual electron density between −1.52 and 3.83 e/Å^3.

[*] Derived values do not contain the contribution of the disordered solvent molecules.

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