Binding Properties of Two Novel Phosphane-Modified Tetrapodants and Their Bimetallic Transition Metal Complexes

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Received June 18, 1998

Keywords: Supramolecular chemistry / Metallamacrocycle / Hydrogen bonding / Phosphane

Two novel phosphane ligands **3** and **4** based on the rigid diphenylglycoluril molecule have been synthesized and characterised. Binding studies with **3** and **4**, using 1,3-dihydroxybenzene derivatives reveal that ligands **3** and **4** behave similarly to clip molecule **5**, which has the same binding site as ligands **3** and **4**. The size of the flexible spacers in the ligands has been varied and the effect of this variation on the association constant of resorcinol derivatives has been determined. These cavity-containing ligands are able to coordinate two transition metal centres, leading to bimetallic macrocycles. The metallamacrocycles formed from **4** containing platinum or rhodium bind the guest, olivetol (5-pentylbenzene-1,3-diol), almost four times as strongly as the free tetrapodant **4**. Complexes of **4** having palladium centres display similar or reduced binding affinities for resorcinol derivatives, when compared to free **4**. Metal complexes of ligand **3** do not form host-guest complexes, probably because of a too small a ring-size of the metallamacrocycle.

Introduction

The use of enzymes as catalysts for organic reactions is a major topic in modern chemistry. Enzyme-catalysed reactions can reach incredibly high rates and selectivities. Man-made catalysts do not reach that level of supremacy yet, but recently some elegant examples of synthetic enzymes (synzymes) have been published. These synzymes consist of the building block diphenylglycoluril (= DPGU),[1−5] a cyclodextrin[6−8] or a cyclophane[9] and a catalytically active centre. Synzymes do not match the natural enzymes in reactivity, but they are interesting molecules to study the fundamental processes taking place in enzyme catalysis. In this way processes like substrate coordination and substrate-metal interactions can be studied in a less complicated environment. The knowledge obtained can then be used in the development of shape-selective catalysts.[3−5,10,11] Non-covalent binding interactions like hydrogen bonding, π-π stacking, electrostatic, and van der Waals interactions induce substrate discrimination in the processes mentioned above.

In this paper two tetrapodant host molecules **3** and **4** based on the rigid building block DPGU are described. The binding affinities of these host molecules towards 5-substituted resorcinol (1,3-dihydroxybenzene) derivatives will be presented. Several transition metal complexes of **3** and **4** were prepared and the effect of metal complexation on the bond strength between host and guest was investigated. These results are of interest for future applications of metal complexes of **3** and **4** as catalysts for e.g. the hydroformylation reaction or cross-coupling reactions.

Results and Discussion

Ligand Synthesis

The tetrapodant starting compounds **1** and **2** were prepared according to literature procedures[12] and subsequently converted into **3** and **4** after reaction with four equivalents of $LiPPh_2$ (see Scheme 1). The two tetradentate ligands **3** and **4** were obtained in 80% and 67% yield, respectively. Also, we tried to synthesize compound **4** from **2** and four equivalents of $HPPh_2$ in the presence of 10 equivalents of *t*BuOK. This reaction afforded only small amounts of the desired product. Under these conditions, the main reaction that occurred was cleavage of the ether moieties.

The two ligands (**3** and **4**) are moderately air-sensitive, but they are stable under an inert atmosphere. When the products were not carefully worked up or stored, ^{31}P-NMR spectra showed signals in the phosphane oxide region (δ = + 30). These oxide contaminations could be removed by

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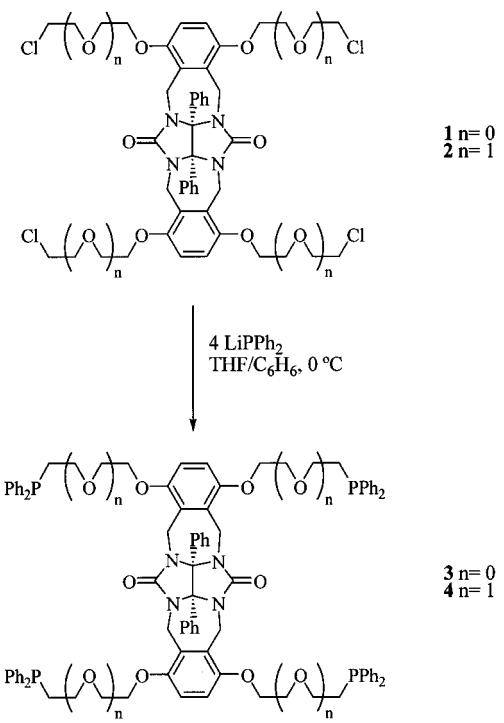
reduction with an excess of $HSiCl_3$ in the presence of 3 equivalents of NEt_3 per $HSiCl_3$ in refluxing benzene.[13]

Scheme 1. Synthesis of ligands **3** and **4**



Metal Complex Synthesis

The starting compounds in the metal complexation reactions and the yields are summarised in Table 1. Most of the complexes of **3** and **4** were synthesized from starting metal complexes containing triphenylphosphane. After addition of the tetradentate ligands **3** or **4** to these PPh_3-containing compounds, the bimetallic complexes of **3** or **4** were formed. The driving force of this reaction is the replacement of a triarylphosphane ligand by an alkyldiphenylphosphane, which is a stronger donor ligand. The reaction is also entropy-driven; a monodentate ligand is always replaced by a bidentate ligand having similar electronic and steric properties.

A phosphane-free precursor compound [e.g. $(COD)PdCl_2$] could also be used, provided that a small amount of PPh_3 was added to the reaction mixture. When the syntheses were performed without PPh_3, large amounts of insoluble compounds were formed in addition to the desired product. The replacement of COD or CH_3CN by a phosphane ligand is fast compared to a phosphane-by-phosphane replacement. Before intramolecular ring closure can occur, intermolecular complexation takes place. The polymeric complexes precipitate and cannot equilibrate to form the desired bimetallic complexes. These reactions were also performed at lower concentrations (3×10^{-4} M), but always some insoluble product was formed. A suspension of precipitated (polymeric) complex could be treated with a small amount of PPh_3 to redissolve the polymeric products. The PPh_3 that remained after the reaction could be removed with the same ease as weakly bound ligands such as COD and CH_3CN. A simple precipitation of the metal complex after the addition of pentane, hexane or diethyl ether, followed by filtration or decantation of the suspension was sufficient to remove PPh_3.

There are two exceptions to the general procedure described above: the formation of **L**$[Pd(BF_4)_2]_2$ and **L**$[Pd(TCNE)]_2$ (**L** = **3** or **4**, TCNE= tetracyanoethylene). For the preparation of the aforementioned ionic palladium compounds, CH_3CN was used as a cosolvent. The products formed still contained two molecules of CH_3CN, which increased the solubility of the products. Hence, polymeric structures did not precipitate and the desired products were obtained. For the formation of the **L**$[Pd(TCNE)]_2$ complexes the reaction of $Pd(DBA)_2$ (DBA= dibenzylideneacetone) with either **3** or **4** was chosen. This resulted in the initial formation of **L**$[Pd(DBA)]_2$ complexes. The replacement of the second DBA molecule is known to be less favourable,[14] but this could be achieved by the addition of TCNE, an extremely electron-poor alkene. Complexes possessing other electron-poor alkenes like maleic anhydride, dimethyl fumarate or fumaronitrile could not be isolated. These alkenes are not as tightly bound to the Pd centre as TCNE and therefore afford less stable compounds.

Table 1. Starting compounds, products, yields and spectroscopic data of the bimetallic macrocycles of **3** and **4**

Entry	Starting compound	Product	Yield [%]	$\delta(^{31}P)$ [ppm] ($^1J_{M\text{-}P}$ [Hz])	$\nu(CX)$[f] [$^{-1}$]
1	$(PPh_3)_2PdCl_2$	**3**$(PdCl_2)_2$	58	12.5[a]	1710[g]
2	$CODPdCl_2/PPh_3$	**4**$(PdCl_2)_2$	75	14.9[a]	1710[g]
3	$(PPh_3)_2PdMeCl$	**3**$(PdMeCl)_2$	84	15.4[b]	1710[g]
4	$CODPdMeCl/PPh_3$	**4**$(PdMeCl)_2$	85	21.9[b]	1710[g]
5	$(CH_3CN)_4Pd(BF_4)_2$	**3**$[Pd(BF_4)_2]_2$	93	38.4[c]	1648[g]
6	$(CH_3CN)_4Pd(BF_4)_2$	**4**$[Pd(BF_4)_2]_2$	79	42.8[c]	1670[g]
7	$Pd(DBA)_2$ + TCNE	**3**$[Pd(TCNE)]_2$	85	24.8[b]	1701[g], 2220[h]
8	$Pd(DBA)_2$ + TCNE	**4**$[Pd(TCNE)]_2$	84	12.8[b]	1707[g], 2213[h]
9	$(PPh_3)_2PtCl_2$	**3**$(PtCl_2)_2$	79	0.4[b] (3550[d])	1707[g]
10	$(PPh_3)_2PtCl_2$	**4**$(PtCl_2)_2$	68	4.8[b] (3610[d])	1708[g]
11	$(PPh_3)_2RhClCO$	**3**$(RhClCO)_2$	96	18.6[b] (124[e])	1710[g], 1972[i]
12	$(PPh_3)_2RhClCO$	**4**$(RhClCO)_2$	96	22.0[b] (123[e])	1708[g], 1970[i]
13	$(PPh_3)_2IrClCO$	**3**$(IrClCO)_2$	89	14.8[a]	1710[g], 1959[j]
14	$(PPh_3)_2IrClCO$	**4**$(IrClCO)_2$	85	17.7[a]	1711[g], 1958[j]

[a] Measured in C_6D_6. – [b] Measured in $CDCl_3$. – [c] Measured in CD_3CN. – [d] $^1J_{Pt\text{-}P}$ (*cis*). – [e] $^1J_{Rh\text{-}P}$ (*trans*). – [f] Measured in KBr. – [g] $\nu(CO)$. – [h] $\nu(CC)$. – [i] $\nu[(CO)_{Rh}]$. – [j] $\nu[(CO)_{Ir}]$.

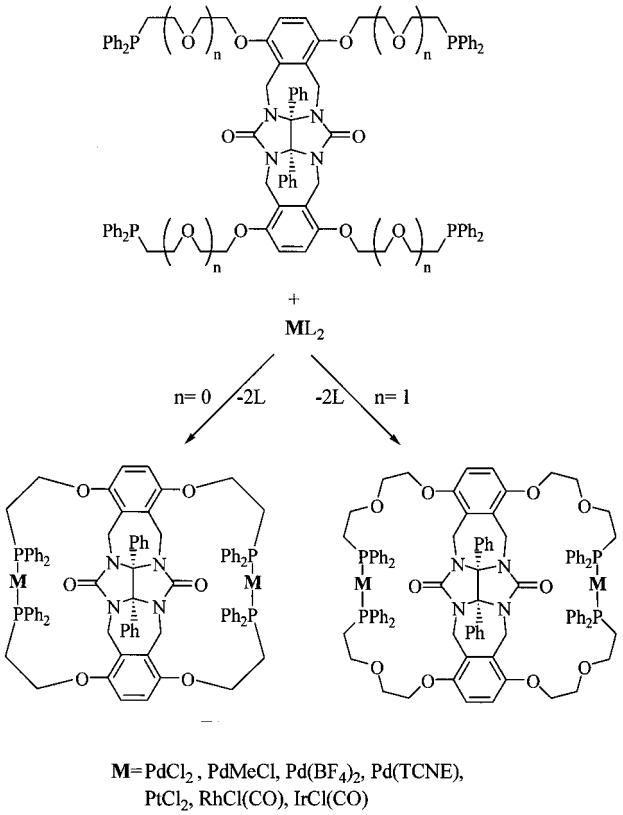
Identification

The ^{1}H-NMR spectra of the metal complexes of **3** and **4** have characteristic signals, viz. a doublet, at $\delta = 5.5-5.7$. This signal is due to one of the inequivalent (CO)NCHH′ protons. The coupling constant of these two protons is in the range of $J = 15-16$ Hz.[4,15−20] The other doublet is generally found at $\delta \approx 3.8$ depending on the solvent. When a large deviation from this ppm value is found, the three-dimensional structure of the building block is distorted. Another characteristic signal in the ^{1}H-NMR spectrum is the singlet arising from the hydroquinone walls at $\delta = 6.5 \pm 0.1$. This signal was used in the determination of the host-guest association constants (see below). The IR spectra of DPGU derivatives always show a strong absorption of the urea carbonyl groups [ν(CO) at 1705 ± 5 cm^{-1} (KBr disk)]. This carbonyl stretching frequency can be used to observe interactions involving the carbonyl group. For example, hydrogen bonding between the carbonyl group and resorcinol derivatives induces a shift of -25 ± 5 cm^{-1}, as has been described in the literature [16,21,22].

The ^{1}H- and ^{13}C-NMR spectra of **3** and **4** indicated that the concave part of the host, i.e. where the binding of substrates occurs, is similar to that of the rigid clip molecule **5** (see Figure 2). The coupling constant of the doublet at $\delta \approx 5.5$ and the chemical shift of the hydroquinone parts were in good agreement with literature values for these type of compounds[4,15,16,18−20]. In the ^{31}P{^{1}H}-NMR spectrum singlets at $\delta = -21.1$ and -21.7 were found for **3** and **4**, respectively, which are values similar to those of other alkyldiphenylphosphanes. The IR spectra of **3** and **4** showed a carbonyl resonance at the expected frequency around 1710 cm^{-1}. The elementary analyses of ligands **3** and **4** showed that two molecules of water are present in the host in the solid state. This could be confirmed by IR and NMR spectroscopy, which both revealed small amounts of water. These water molecules did not seem to disturb any of our further studies and therefore no attempts were made to remove them.

The various transition metal complexes of ligands **3** and **4** have ^{31}P-NMR resonances (see Table 1) at higher ppm values compared to the free tetrapodants. The difference between the chemical shift of the free ligand and that of its transition metal complex ($\Delta\delta_{compl}$) is a suitable tool to determine what type of complex has been formed. The ^{31}P-NMR values of these complexes are similar to phosphanemetal complexes known from literature,[23][24] showing that ligands **3** and **4** are suitable ligands for coordination chemistry studies. A comparison of the change in chemical shift on coordination ($\Delta\delta_{compl}$) with values found in literature leads to the following conclusions about the immediate surroundings of the transition metal centres. All complexes except **L**[Pd(TCNE)]$_2$ have a square planar conformation. Complexes containing the PdMeCl fragment have two equal, *trans*-coordinated phosphane moieties, which can be derived from the singlet in the ^{31}P{^{1}H}-NMR spectrum. Complexes **L**(PdCl$_2$)$_2$ displayed a singlet in the ^{31}P{^{1}H}-NMR spectrum around $\delta = 13$. From literature it

Scheme 2. Schematic representation of the synthesis of the metal complexes (used starting compounds: $(PPh_3)_2PdCl_2$; $(COD)PdCl_2$; $(PPh_3)_2PdMeCl$; (COD)PdMeCl; i) $Pd(DBA)_2$, ii) TCNE; $(CH_3CN)_4Pd(BF_4)_2$; $(PPh_3)_2PtCl_2$; $(PPh_3)_2RhCl(CO)$; $[PPh_3)_2IrCl(CO)]$



M= $PdCl_2$, PdMeCl, $Pd(BF_4)_2$, Pd(TCNE), $PtCl_2$, RhCl(CO), IrCl(CO)

is known that the value of $\Delta\delta_{compl}$ after the formation of a *cis*-$PdCl_2$ complex is 43−47 ppm, whereas 32−36 ppm is found when *trans* complexes are formed.[24] In our case the values are $\Delta\delta_{compl} = 34.2$ for **3**(PdCl$_2$)$_2$ and 36 ppm for **4**(PdCl$_2$)$_2$, which indicates that bimetallic *trans*-coordinated complexes have been formed.

In this series of complexes, **3**(PtCl$_2$)$_2$ and **4**(PtCl$_2$)$_2$ are the only *cis*-coordinated compounds we were able to isolate. The ^{31}P-NMR spectra of these complexes showed coupling constants around $^1J_{Pt-P} = 3500$ Hz (Table 1, entries 9 and 10), which indicates the formation of *cis* complexes.[23] These coupling constants were also observed in the ^{195}Pt-NMR spectrum of **4**(PtCl$_2$)$_2$, which afforded a triplet at $\delta = -4390$. In addition to the magnitude of the coupling constant ($^1J_{Pt-P}$), the ^{195}Pt chemical shift itself is indicative of a *cis*-coordinated complex. The typical chemical shift value of a *trans* complex is found at $\delta = -3950$.[25] For electronic reasons, i.e. the larger *trans* influence of phosphanes compared to chloride, $PtCl_2$ complexes of phosphane ligands with small cone angles prefer *cis* coordination.

The zero-valent palladium complexes (Table 1, entries 7 and 8) are stabilised by the electron-poor alkene TCNE, which reduces the electron density on the Pd^0 centre. The coordination mode around the metal centre is probably pseudo-tetrahedral, as has been found for several crystal structures of related Pd^0 complexes.[26] The IR spectra of

3[Pd(TCNE)]$_2$ and **4**[Pd(TCNE)]$_2$ showed sharp bands of the CN vibration of the TCNE molecule. The values were found at 2213 cm^{-1} and 2220 cm^{-1}, respectively, which are in good agreement with values reported in the literature for TCNE metal complexes.[26] The urea carbonyl groups in the ligands gave rise to strong and sharp bands at 1707 cm^{-1} and 1710 cm^{-1} in **3**[Pd(TCNE)]$_2$ and **4**[Pd(TCNE)]$_2$, respectively.

The two ionic palladium(II) complexes of **3** and **4** are square-planar complexes. The phosphane moieties in these complexes are coordinated in a *trans* fashion as can be seen from the phosphorus chemical shift values[27] (δ = 38.4 and 42.8 for **3**[Pd(BF$_4$)$_2$]$_2$ and **4**[Pd(BF$_4$)$_2$]$_2$, respectively). In the solid state the two Pd^{II} tetrafluoroborate complexes still contain one molecule of CH_3CN per Pd atom, as could be concluded from the elementary analyses of **3**[Pd(BF$_4$)$_2$]$_2$ and **4**[Pd(BF$_4$)$_2$]$_2$. However, their IR spectra did not show a band at 2100−2000 cm^{-1}, the typical region of a coordinated CH_3CN molecule. The IR spectra did show strong carbonyl bands at 1648 cm^{-1} for **3**[Pd(BF$_4$)$_2$]$_2$ and at 1670 cm^{-1} for **4**[Pd(BF$_4$)$_2$]$_2$. The shifts of 60 cm^{-1} and 40 cm^{-1} compared to the **L**(PdCl$_2$)$_2$ complexes, indicate that there is an interaction between the carbonyl group of the ligand and the cationic palladium centre. Electron donation of the urea carbonyl group to the Pd^{II} centre will result in a reduced bond strength, leading to an absorption at a lower frequency. This frequency shift is larger in **3**[Pd(BF$_4$)$_2$]$_2$ than that in **4**[Pd(BF$_4$)$_2$]$_2$, probably because the shorter spacer groups in the latter complex enforce a shorter metal-to-carbonyl distance. The interaction between the carbonyl group and the metal centre could not be detected in solution. The cationic complexes dissolve in polar, coordinating solvents only (e.g. CH_3CN or DMSO), which replace the coordinated carbonyl groups.

The iridium and rhodium complexes in Table 1 are similar in structure to the original Vaska complex[28] that contains two triphenylphosphane ligands coordinated in a *trans* fashion to an iridium centre. The rhodium complex showed a doublet in the $^{31}P\{^1H\}$-NMR spectrum with $^1J_{Rh\text{-}P}$ = 124 Hz, indicative of *trans* coordination.[29] We also determined the ^{103}Rh chemical shift of **4**[RhCl(CO)]$_2$, which was found at δ = −419, close to that of reference compound (PPh$_3$)$_2$RhCl(CO).[25] The IR spectra of **3**[RhCl(CO)]$_2$ and **4**[RhCl(CO)]$_2$ showed bands for the urea carbonyl groups ($\tilde{\nu}$ = 1710 and 1708 cm^{-1}) and for the carbon monoxide ligand [ν(CO)$_{Rh}$]. The latter absorptions were found at 1970 and 1972 cm^{-1}, respectively, which are slightly lower values than those found in (PPh$_3$)$_2$RhCl(CO). Finally, we determined the molecular weight of complex **4**[RhCl(CO)]$_2$ in a dichloromethane solution (by vapour pressure osmometry) and found a value of 1850 ± 100 (calcd. 1919). The molecular weight determination of **3**[RhCl(CO)]$_2$ proved to be difficult due to its poor solubility.

The $^{31}P\{^1H\}$-NMR spectra of the iridium complexes of **3** and **4** showed a singlet for both compounds (see Table 1, entries 13 and 14), proving the formation of a *trans* complex. The peaks of the CO ligand [ν(CO)$_{Ir}$] in the infra red spectra of **3**[IrCl(CO)]$_2$ and **4**[IrCl(CO)]$_2$ were found at a frequency 3 cm^{-1} below that of the original Vaska complex (1962 cm^{-1}). In these iridium complexes the band of the urea carbonyl group was found at 1710 ± 2 cm^{-1} (in KBr).

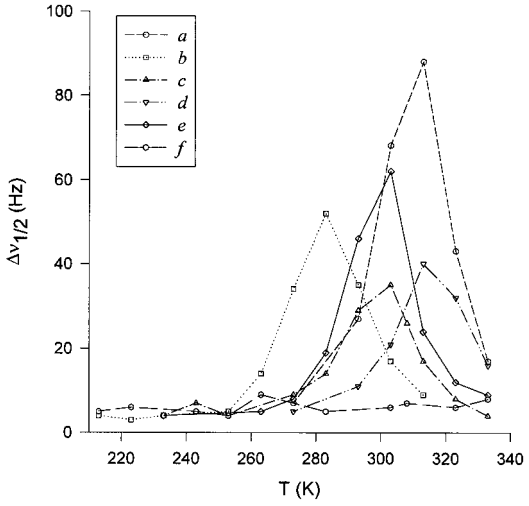
We attempted to isolate the cationic complexes **3**[Rh(CO)$^+$]$_2$ and **4**[Rh(CO)$^+$]$_2$, by the reaction of $AgBF_4$ with the two **L**[RhCl(CO)]$_2$ complexes. Turbid solutions containing a fine precipitate were formed after the addition of $AgBF_4$, but the precipitate could not be removed; centrifugation and subsequent filtration with Celite did not result in the removal of AgCl. IR measurements on the crude complexes showed that the $\nu(CO)_{Rh}$ had shifted to a higher frequency (1990 cm^{-1}). The peaks of the urea carbonyl group shifted approximately 30 cm^{-1} to a lower frequency in both **3**[Rh(CO)$^+$]$_2$ and **4**[Rh(CO)$^+$]$_2$. These frequency shifts for both the urea carbonyl and the coordinated CO molecule strongly indicate the formation of a cationic Rh^I complex in which an interaction exists between the cationic Rh centre and the urea carbonyl group. The positive shift of $\nu(CO)_{Rh}$ indicates a reduced π back donation of the electron-poor cationic rhodium(I) centre to the coordinated CO molecule. The negative shift of the urea carbonyl band indicates that the carbonyl group coordinates to the cationic rhodium(I) centre. This electron donation was also found in the aforementioned cationic palladium(II) complexes, which showed a larger shift of $\Delta\nu$ = −60 cm^{-1} and $\Delta\nu$ = −40 cm^{-1} for **3**[Pd(BF$_4$)$_2$]$_2$ and **4**[Pd(BF$_4$)$_2$]$_2$, respectively.

Variable-Temperature NMR Experiments

To investigate a possible interaction between the phosphane end groups of **4** and guests we recorded the ^{31}P-NMR spectra of **4** and five host-guest complexes of **4** with resorcinol derivatives. Figure 1 shows the temperature dependence of the $^{31}P\{^1H\}$ line width of these complexes. At 333 K all the $^{31}P\{^1H\}$-NMR signals were visible as sharp singlets having a line width of $\Delta\nu_{1/2}$ = 5−7 Hz. These are the normal values in $^{31}P\{^1H\}$-NMR spectra. When **4** was measured without additives, this sharp singlet remained in the temperature range of T = 223−333 K. The metal complex **4**[RhCl(CO)]$_2$ also gave rise to a sharp signal in this temperature range. Experiments using a mixture of **4** and a resorcinol derivative , however, showed a gradual increase in the $\Delta\nu_{1/2}$ of the ^{31}P signal on lowering of the temperature. The $\Delta\nu_{1/2}$ passed through a maximum value at T_{max}, followed by a decrease in $\Delta\nu_{1/2}$ on further lowering of the temperature. The chemical shift of the ^{31}P signal also shifted on variation of the temperature. At high temperatures the signal was found at δ = −20.5, whereas at low temperatures, the signal shifted to δ = −24. The substrate apparently has an influence on both the value of $\Delta\nu_{1/2}$ and the T_{max} at which the maximum broadening is found. T_{max} and $\Delta\nu_{1/2}$ were also affected by the amount of substrate present. When a mixture of one equivalent of **4** and 6.5 equivalents of octyl 3,5-dihydroxybenzoate was measured, the value of T_{max} was found at 313 K having a $\Delta\nu_{1/2}$ of 88 Hz. When the host-guest ratio was lowered to 1:2, the value of T_{max} was found at a lower temperature (283 K) and the maxi-

mum broadening was now 52 Hz. The size of the substituent on resorcinol also had an effect on the value of $\Delta\nu_{1/2}$. 5-Chlororesorcinol, for example, had a smaller effect on $\Delta\nu_{1/2}$ than the aforementioned octyl ester of 3,5-dihydroxybenzoic acid. These measurements indicate that the flexible spacer groups, attached to the concave part of tetrapodant **4**, have an interaction with an incoming substrate. In a reference experiment without addition of a substrate no change in line width was observed. This indicates that the presence of a substrate is required to induce this line broadening. The nature of the interaction between **4** and the substrates, however, cannot be determined from these experiments.

Figure 1. Plot of the line width ($\Delta\nu_{1/2}$) of the ^{31}P-NMR signal of **4** versus temperature (T) in the presence of various resorcinol derivatives (*a:* [**4**]/[octyl 3,5-dihydroxybenzoate] = 1:6.5; *b:* [**4**]/[octyl 3,5-dihydroxybenzoate] = 1:2; *c:* [**4**]/[olivetol] = 1:7.4; *d:* [**4**]/[5-chlororesorcinol] = 1:6.5; *e:* [**4**]/[5-(*p*-tol)resorcinol] = 1:4; *f:* **4** without additives) (conditions: solvent $CDCl_3$, [**4**] = 8×10^{-3} M)



Association Constant Determinations

In order to determine the association constants of host-guest complexes between **1**−**4** and guests the ^{1}H-NMR shifts of the aromatic-wall protons of the tetrapodants were monitored. These signals shift to lower ppm values on association with an aromatic guest molecule and a chemically induced shift (CIS) is observed. Dihydroxybenzenes bind in the cavity of the host molecule via hydrogen bonds between the hydroxy groups of the guest and the urea carbonyl groups of the host molecule[15,16,22]. A second interaction is π-π stacking between the aromatic walls of the host and the aromatic ring of the guest molecule. Thirdly, electrostatic repulsion might occur, which diminishes the total bond strength between the host and its guest.

Resorcinol derivatives containing electron-withdrawing groups at the 5-position bind relatively strongly to **4** (see Table 2). Titration experiments using 5-chlororesorcinol and **4** resulted in an association constant of $K = 4704\ M^{-1}$. Electron-donating groups on the resorcinol ring, like alkyl substituents have a slightly negative influence on the association constant of **4** and a guest, e.g. K is 1676 M^{-1} for olivetol (5-pentylbenzene-1,3-diol). Resorcinol derivatives with an aromatic substituent at the 5-position also give rise to increased association constants ($K > 6200\ M^{-1}$). An additional π-π stacking interaction between the phenyl groups of the diphenylphosphane moieties and the additional aromatic ring of the substrates may be responsible for this increase in binding affinity. These numbers (except those found with aryl-substituted resorcinol derivatives) are in reasonably good agreement with the values recently published by Reek and co-workers.[16] They used compound **5** in their studies of the binding properties of molecular clips based on DPGU and showed that electron-donating groups on the resorcinol guests lead to reduced association constants. Electron-withdrawing groups on the guest increase the acidity of the hydroxy groups and the π-π stacking interactions, which both result in an increase in association constant. Reek and co-workers tested a number of resorcinol derivatives in their study and found a linear Hammet relationship between the free energy of association (ΔG_{ass}) and the σ_m' values of the substituents on the 5-position of resorcinol.

Table 2. Association constants of tetrapodant **4** with several resorcinol derivatives

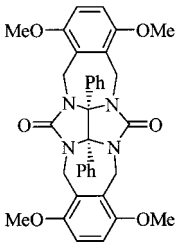
Guest	K [M^{-1}][a]	CIS [ppm]
olivetol	1676 (61)	−0.45
5-chlororesorcinol	4704 (407)	−0.43
5-bromoresorcinol	5360[b] (164)	−0.34
5-iodoresorcinol	3952 (272)	−0.37
5-phenylresorcinol	6537[b] (257)	−0.44
5-(4-chlorophenyl)resorcinol	6228 (132)	−0.44
5-(4-methylphenyl)resorcinol	6437 (556)	−0.48
octyl 3,5-dihydroxybenzoate	7406 (431)	−0.45

[a] Duplo experiments, obtained from NMR titrations using $0.25-0.75 \times 10^{-3}$ M solutions of host and $2.5-7.5 \times 10^{-3}$ M solutions of guest compound in $CDCl_3$, errors are given in parentheses, T = 293 K. − [b] Single experiment; association constants were calculated using the Granot[42] procedure.

A plot of the ΔG_{ass} values calculated from the data collected in Table 2 versus σ_m, did not show a linear relationship. The only difference between our tetrapodants and **5** is that the latter does not contain flexible spacer groups (including the PPh_2 moieties). These spacer groups are probably responsible for the non-linear relationship between σ_m and ΔG_{ass}. They can interact with an incoming substrate, as shown by the lineshape analyses of the $^{31}P\{^1H\}$-NMR spectra (vide supra), and therefore influence the association constant. In the case of **3** and **4** the steric bulk of the end group will also be of great importance and contribute to the magnitude of the association constant. The two resorcinol derivatives substituted with alkyl chains (olivetol and octyl 3,5-dihydroxybenzoate), for example, give rise to relatively low association constants compared to the values that would be expected on the basis of their σ_m values.

The results obtained for tetrapodants **1**−**4** and olivetol (see Table 3), lead to two conclusions: Larger end groups

Figure 2. Molecular clip **5** used in association constant studies by Reek[16] and co-workers



5

on the ethylene glycol chains have a negative effect on the association constant using olivetol as the guest. Replacement of the chlorine groups in **1** by diphenylphosphane moieties giving **3** causes a decrease of the association constant of 20%. A similar decrease of 20% is found when **2** (chloro compound) and **4** (PPh_2 compound) are compared. This is probably the result of a steric interaction between the large PPh_2 groups and the substrate. Another explanation for this drop in binding affinity might be that one of the phenyl groups of the PPh_2 moieties is clammed between the aromatic walls of the cavity, which will compete with binding of the guests. The latter explanation could not be confirmed by low-temperature NMR because of the low solubility of **4** at lower temperatures.

Table 3. Association constants of tetrapodants **1**–**4** with olivetol in $CDCl_3$

Host	K [M^{-1}][a]	CIS [ppm]
1	2769 (148)	−0.56
2	2025 (98)	−0.54
3	2201 (165)	−0.46
4	1676 (61)	−0.45

[a] Duplo experiments, obtained from NMR titrations using 0.5×10^{-3} M solutions of host and 5×10^{-3} M solutions of guest compound, errors are given in parentheses, $T = 293$ K; association constants were calculated using the Granot[42] procedure.

The increase of the number of ethylene glycol units in the spacer arms also has a negative effect on the association constant between host and guest, as can be seen when **1** is compared with **2** and when **3** is compared with **4**. A decrease of the association constant of approximately 20% is found when the flexible arms are extended with one ethylene glycol unit. This decrease of the association constant is probably caused by a difference in entropy loss after the formation of a host-guest complex. Binding of a guest molecule will restrict the rotational and translational movements of the side arms of the host. In particular rotation around the $ArO-CH_2$ bond will be hampered. This can be derived from the ^{1}H-NMR spectra of the host in the presence of guest molecules. The CH_2 groups of the side arms give rise to two signals, which indicates a restricted rotation. It should be noted that the effect becomes less for the distant CH_2 groups in host **4**.

In the absence of a substrate, the "small" tetrapodants **1** and **3** possess less degrees of freedom compared to their "larger" analogues **2** and **4**, because less rotational movements are available. Therefore, after binding of a guest, the ΔS_{ass} value will be less for hosts **1** and **3** than that of **2** and **4**. A less negative ΔS_{ass} value will result in a more negative ΔG_{ass} value and thus higher association constants for **1** and **3**.

Table 4. Association constants of bimetallic complexes of **3** and **4** with olivetol

Metallohost	K [M^{-1}][a]	CIS [ppm]
3$(PdCl_2)_2$	n.d.[b]	n.d.[b]
3$(PdMeCl)_2$	562 (367)	−0.02
3$[Pd(TCNE)]_2$	n.d.[b]	n.d.[b]
3$(PtCl_2)_2$	n.d.[b]	n.d.[b]
3$[RhCl(CO)]_2$	164 (73)	−0.02
4$(PdCl_2)_2$	2346 (499)	−0.44
4$(PdMeCl)_2$	2502 (77.83)	−0.47
4$[Pd(TCNE)]_2$	960 (362)	−0.48
4$(PtCl_2)_2$	4314[c] (338)	−0.47
4$[RhCl(CO)]_2$	4514[c] (835)	−0.51

[a] Single-fold experiments, obtained from NMR titrations using 5×10^{-3} M solutions of host and 50×10^{-3} M solutions of guest compound in $CDCl_3$, errors are given in parentheses, $T = 293$ K. – [b] n.d. = not determined, NMR signals did not change and $K < 100$ M^{-1}. – [c] Duplo experiment; association constants were calculated using the Granot[42] procedure.

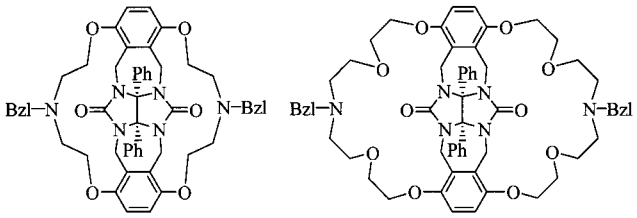
Host-Guest Binding Properties of Metal Complexes

As discussed above the tetrapodant ligands **3** and **4** and appropriate transition metals form basket-shaped bimetallic complexes, which have different cavity sizes. The binding properties of transition metal complexes of **3** were found to be rather poor compared to the free ligand. The complexes **3**$[RhCl(CO)]_2$ and **3**$(PdMeCl)_2$ have binding constants of $K = 164$ M^{-1} and $K = 562$ M^{-1}, respectively, for olivetol (see Table 4). From the small chemically induced shifts (CIS) values of these host-guest complexes it can be concluded that there is hardly any interaction between host and guest. The ^{1}H-NMR signals of complexes **3**$(PtCl_2)_2$, **3**$(PdCl_2)_2$, and **3**$[Pd(TCNE)]_2$ did not change after addition of 10 equivalents of olivetol. These NMR experiments show that, after coordination of **3** to two transition metal centres, a basket is formed that is too small for substrate binding. Coordination of the phosphane moieties to a metal centre should facilitate the binding of a substrate in the cavity because a preshaped cavity is formed and less entropy will be lost during the association process. However, the cavity of complexes of ligand **3** is not large enough to give access to resorcinol derivatives.

A similar effect has been observed for host **6**, which is formed by a ring-closure reaction between **1** and benzylamine.[12,30,31] A crystal structure of **6** showed that, due to the small ring size in **6**, the $ArOCH_2$ groups (see Figure 3) are directed towards the cavity and block the entrance of this cavity[20] for entering guests. Although the transition metal complexes of ligand **3** possess a larger cavity than **6**, i.e. instead of one amine two phosphanes and a transition metal are now incorporated in the macrocycle, the cavity is probably still too small to allow a strong interaction of the host with resorcinol guest molecules.

Host **7** and its derivatives do bind dihydroxybenzene derivatives as was shown in previous studies.[3,15,20,30,32] The cavity of this host is large enough to give access to resorcinol derivatives and 2,7-dihydroxynaphthalene. The metal complexes of ligand **4** have an even larger macrocyclic cavity than **7** and will therefore be accessible for organic substrates. This is confirmed by the experimental data (see Table 4).

Figure 3. Basket-shaped host molecules **6** and **7**



Compared to free **4**, complex **4**Pd(TCNE) has a lower binding affinity to olivetol. All the other complexes of **4** show an increased affinity to this guest. The increase in association constant is partly caused by fixation of the flexible arms of the tetrapodant. The degrees of freedom are reduced compared to the free ligand, resulting in an increase in the ground-state free energy. After complexation of a substrate, a relatively small loss in entropy (ΔS_{ass}) will result in a more negative ΔG_{ass} value, and a higher association constant.

Compounds **4**$(PtCl_2)_2$ and **4**$[RhCl(CO)]_2$ form host-guest complexes with olivetol which display association constants of 4314 M^{-1} (Pt) and 4514 M^{-1} (Rh), respectively. These association constants are nearly three times as high as the value of the free phosphane tetrapodant **4**. Complexes **4**$(PdCl_2)_2$ and **4**$(PdMeCl)_2$ also show an increase in association constant when compared to free **4** and values of K = 2346 M^{-1} and 2505 M^{-1} were found, respectively.

There are several possible explanations for the observed increase in binding affinity of the metal complexes and olivetol: (i) An additional interaction between the substrate and the metal centre, e.g. a dipole-dipole interaction, (ii) a weak interaction between the oxygen atom or the aromatic ring of the substrate with the metal centre, e.g. coordination at the axial position of the metal centre, (iii) extra hydrogen-bonding interactions between the hydroxy groups of olivetol and auxiliary ligands in the complexes, e.g. Cl or CO at the metal centre, (iv) difference in flexibility of the spacer groups, (v) conformational differences between the metal complexes.

To investigate an interaction between olivetol and a transition metal centre, we measured the ^{195}Pt and ^{103}Rh chemical shifts of mixtures of **4**$(PtCl_2)_2$ with olivetol and **4**$[RhCl(CO)]_2$ with olivetol. Changes in the second and outer coordination sphere of the metal centre, as well as steric or electronic variations are known to have a pronounced effect on the chemical shift of the transition metal.[25] Addition of eight equivalents of olivetol to an NMR sample containing **4**$(PtCl_2)_2$ or **4**$[RhCl(CO)]_2$, did not affect the transition metal chemical shift of either the rhodium or the platinum complex. This indicates that, although the metal centre is probably able to come into close proximity of the binding site, it does not have an interaction with the guest.

Infrared spectroscopy was used to investigate the nature of hydrogen-bond formation between host and guest. The experiments indicated that additional hydrogen bonds between the carbon monoxide ligand of the rhodium complex and the hydroxy groups of the guest could be excluded; after the addition eight equivalents of olivetol a shift of +4 cm^{-1} was found in the IR spectrum of **4**$[RhCl(CO)]_2$. This is a too small a difference to be the result of hydrogen bonding and additionally, the shift is in the wrong direction. Hydrogen bonds to the carbon monoxide ligand would shift the carbonyl frequency to a lower value, as described by Kazarian and co-workers for other carbon monoxide containing compounds.[33] Hydrogen bonds to the metal centre itself would induce a positive shift,[33] but the reported shifts are usually larger than 20 cm^{-1}.

One example of a hydrogen bond between a platinum coordinated chloride and a phenolic hydroxy group has been reported in the literature.[34] Evidence for hydrogen bonding between a chloride ligand of our metal complex and a hydroxy group of the substrate, however, could not be found.

Monitoring the carbonyl frequency of the urea carbonyl group, showed that ligand **4** as well as its metal complexes bind olivetol via hydrogen bonds. After addition of eighth equivalents of olivetol to several **4**M_2 complexes the IR spectrum showed a shift of ν(CO) of -30 cm^{-1}. Apparently, unlike Na^+ ions the metal centres do not prevent the formation of hydrogen bonds between host and guest. Hosts of type **7** bind two Na^+ ions to their crown ether parts. In these host-guest complexes the sodium ions are responsible for the binding of olivetol, as hydrogen bonds between the carbonyl groups of the host and hydroxy groups of the guest could not be detected.[21]

Summarising, we can state that a different type of binding is not responsible for the change in binding affinity with the guest. Conformational changes in the metal complexes or restricted flexibility of the spacer groups might therefore be a likely explanation. The difference in flexibility of the spacer groups might be caused by partial ligand dissociation in solution. Perhaps the palladium–phosphorus bond in complex **4**$[Pd(TCNE)]_2$ is more labile compared to the metal–phosphorus bond in the other complexes. This may have an effect on the flexibility of the crown ether fragments, which are not as rigidly oriented as in the other metal complexes. The crown ether fragments may still have an interaction with the incoming substrate, and a compound more similar to the parent ligand **4** is formed. The lower association constant can then be explained by the larger end group on the spacer groups (i.e. PPh_2–Pd instead of PPh_2 only) which will result in a relatively low association constant (K = 960 M^{-1}).

The crown ether fragments of complexes **4**$(PtCl_2)_2$ and **4**$[RhCl(CO)]_2$ may be more hampered in their movements

and form a preshaped cavity for an incoming guest. Since the loss in entropy after complexation of a guest (ΔS_{ass}) will be smaller for these complexes compared to the parent ligand **4**, an increase in binding affinity of a factor of 2.5 is found. The same positive effect on the association constant was found for complexes **4**$(PdCl_2)_2$ and **4**$(PdMeCl)_2$, although the increase in binding affinity is only a factor of 1.5 for these complexes. Finally, a change in conformation, induced by the transition metals, cannot be excluded but the required structural information about these complexes is still lacking.

Conclusions

In this paper we report novel host molecules that possess a cavity in which substrates can be bound in addition to two transition metal centres that are potential catalysts for many reactions. A surprising increase in binding affinity for olivetol was found upon coordination of ligand **4** to various transition metals, whereas the transition metal complexes of ligand **3** are unable to bind substrates.

For host molecules **3** and **4** the association equilibria are influenced by the following factors: (i) the presence of flexible spacers, (ii) the bulk of the spacer, (iii) the size and σ_m value of substituents on the resorcinol derivative, (iv) the ring size of the (metalla)macrocycle after coordination of the phosphane moieties to a metal centre and finally, (v) the metal centre itself. As yet, not all contributing factors can be understood in full detail. These results are promising in view of future catalytic applications with this type of host compounds.

This work was supported by the *Netherlands Foundation for Chemical Research* (SON) with financial aid from the *Netherlands Organisation for Scientific Research* (NWO).

Experimental Section

General: NMR: ^{1}H NMR (300.1 MHz), ^{31}P{^{1}H} NMR (121.5 MHz), ^{13}C{^{1}H} NMR (75.5 MHz), ^{195}Pt NMR (64.3 MHz) and ^{103}Rh NMR (9.48 MHz) were measured with Bruker AMX 300 and DRX 300 machines. The external references were: TMS (^{1}H NMR and ^{13}C NMR), H_3PO_4 (^{31}P NMR) and K_2PtCl_6 (^{195}Pt NMR), Ξ(^{103}Rh NMR) = 3.16 MHz at 100 MHz. ^{195}Pt NMR was measured directly, ^{103}Rh NMR was measured via the ^{31}P-inverse HMQC technique.[35][36] − IR spectra were measured with a Nicolet 510m FT-IR spectrophotometer. − Melting points were determined with a Gallenkamp MFB-595 melting-point apparatus, the values are uncorrected. − Column chromatography was performed with silica gel 60, 70−230 mesh ASTM (Merck). − Analytical TLC was performed on TLC aluminium foil, silica gel 60 F_{254} (Merck). − Microanalyses were carried out in our own laboratory with an Elementar Vario EL apparatus (Foss Electric). − M_w determinations were performed with a Hewlett-Packard vapour-pressure osmometer model 301A, with benzil as the reference compound.

Chemicals: CH_3CN and CH_2Cl_2 were distilled from CaH_2, C_6H_6 was distilled from Na/benzophenone. $CDCl_3$ used in association constant determinations was distilled from P_2O_5 before use. 1,4,8,11-Tetrakis(2-chloroethoxy)-5,7,12,13b,13c,14-hexahydro-13b,13c-diphenyl-6 H,13*H*-5a,6a,12a,13a-tetrabenz[5,6]azuleno-[2,1,8-*ija*]benz[*f*]azulene-6,13-dione[12] (**1**), 1,4,8,11-tetrakis[2-(2-chloroethoxy)ethoxy]-5,7,12,13b,13c,14-hexahydro-13b,13c-diphenyl-6 H,13*H*-5a,6a,12a,13a-tetraazabenz[5,6]azuleno[2,1,8-*ija*]benz[*f*]azulene-6,13-dione[12] (**2**), $(PPh_3)_2RhCl(CO)$,[37] $(PPh_3)_2IrCl(CO)$,[28] $Pd(DBA)_2$,[38] $(CH_3CN)_4Pd(BF_4)_2$,[39] $(COD)PdCl_2$[40] and all the 5-substituted resorcinol derivatives[41] were prepared according to literature procedures. $(PPh_3)_2PdCl_2$ and $(PPh_3)_2PtCl_2$ were obtained after refluxing PPh_3 and $PdCl_2$ or $PtCl_2$ in CH_3CN, followed by evaporation of the solvent.

Ligands

1,4,8,11-Tetrakis[(2-diphenylphosphanyl)ethoxy]-5,7,12,13b,13c,14hexahydro-13b,13c-diphenyl-6H,13H-5a,6a,12a,13a-tetrabenz[5,6]azuleno[2,1,8-ija]benz[f]azulene-6,13-dione (**3**): A solution of 2.5 g of compound **1** (3.1 mmol) in 40 ml of THF and 40 ml of benzene was titrated under N_2 at 0°C with 20 ml of a THF solution of $LiPPh_2$. The $LiPPh_2$ solution was prepared from 2.52 g of $HPPh_2$ (13.6 mmol) and 5.4 ml of 2.5 M *n*BuLi in hexane (13.5 mmol). When the solution remained orange, 40 ml of degassed H_2O was added. The H_2O layer was separated and washed with 20 ml of benzene. The collected organic layers were dried with $MgSO_4$ and concentrated. The product was dissolved in 15 ml of CH_2Cl_2 and precipitated with 100 ml of diethyl ether. After filtration, the remaining solvent was removed in vacuo. The product was purified by column chromatography with silica gel, eluent $MeOH/CH_2Cl_2$ (1:99, v/v). Yield 3.47 g (80%) of a white solid, m.p. > 195°C (dec.). − NMR ($CDCl_3$): δ_H = 7.45−7.29 (m, 40 H, P−*Ar*), 7.08−7.01 (m, 10 H, Ar*H*), 6.47 (s, 4 H, H−Ar side wall), 5.45 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.15 (m, 4 H, OC*H*H), 3.94 (m, 4 H, OCH*H*), 3.76 [d, 4 H, (CO)NC*H*H, ^2J = 15.8 Hz], 2.65−2.59 (m, 8 H, CH_2P); δ_P = −21.7 (s); δ_C = 158.2 (*C*=O), 150.5 (Ar*C*−O), 138.5−138.2, 134.7, 133.12−132.8, 128.8−128.5, 128.3, 113.52, 85.3 [N*C*(Ar)N], 67.59 (d, O−*C*H$_2$, $^2J_{P-C}$ = 24.8 Hz), 37.31 (N*C*H$_2$Ar), 28.61 (d, *C*H$_2$−P, $^1J_{P-C}$ = 12.8 Hz). − IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (w), 2911 (w, OC−H), 1730 (s), 1710 (s, CO), 1482 (m), 1461 (s), 1433 (m), 1255 (m). − M_w (CH_2Cl_2): calcd. 1411; found 1445 ± 100. − $C_{88}H_{78}N_4O_6P_4 \cdot H_2O$ (1414): calcd. C 73.94, H 5.64, N 3.92; found C 73.92, H, 5.51, N 4.05.

1,4,8,11-Tetrakis{2-[2(diphenylphosphanyl)ethoxy]ethoxy}-5,7,12,13b,13c,14-hexahydro-13b,13c-diphenyl-6H,13H-5a,6a,12a,13a-tetrabenz[5,6]azuleno[2,1,8-ija]benz[f]azulene-6,13-dione (**4**): This compound was prepared in a similar way as compound **3**. The following amounts were used: 3.21 g of $HPPh_2$ (17.3 mmol), 6.9 ml of a 2.5 M solution of *n*BuLi (17.25 mmol) and 4.26 g of compound **2** (4.31 mmol). The eluent used for column chromatography was $MeOH/CH_2Cl_2$ (6:94, v/v). Yield 4.7 g (67%) of a white solid, m.p. 91−114°C. − NMR ($CDCl_3$): δ_H = 7.4−7.2 (m, 40 H, Ar*H*−P), 7.03 (m, 10 H, Ar*H*), 6.61 (s, 4 H, *H*−Ar side wall), 5.47 [d, 4 H, (CO)NCH*H*, ^2J = 15.9 Hz], 4.0−3.6 [m, 28 H, (CO)NC*H*H, OCH_2], 2.42 (t, 8 H, CH_2P, ^3J = 8.1 Hz); δ_P = −21.1 (s); δ_C = 158.0 (*C* =O), 151.2 (Ar*C*−O), 138.8−138.4, 134.5, 133.0 (d, Ar*C*−P, $^2J_{P-C}$ = 18.8 Hz), 128.8−128.5, 115.1, 85.41 [N*C*−(Ar)N], 70.5, 69.9, (O−*C*H$_2$), 68.9 (d, O−*C*H$_2$, $^2J_{P-C}$ = 24.0 Hz), 37.37 (N*C*H$_2$Ar), 29.10 (d, *C*H$_2$−P, $^1J_{P-C}$ = 12.8 Hz). − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} (w), 2865 (w, OC−H), 1709 (s, CO), 1482 (m), 1460 (s), 1432 (s), 1264 (m). − M_w (CH_2Cl_2): calcd. 1588; found 1540 ± 100. − $C_{96}H_{94}N_4O_{10}P_4 \cdot 2\ H_2O$ (1586): calcd. C 70.92, H 6.20, N 3.45; found C 70.77, H 5.84, N 3.45.

Metal Complexes

3*(PdCl$_2$)$_2$:* Compound **3** (20.3 mg, 14.3 μmol) was dissolved in 10 ml of benzene and 20.1 mg (28.6 μmol) of $(PPh_3)_2PdCl_2$ was added. The yellow solution was stirred for 2 h and the volume was

reduced to approximately 2 ml. The product was precipitated with 10 ml of pentane, the yellow suspension was decanted and the product was washed twice with 10 ml of pentane. The product was dried in vacuo. Yield 14.5 mg (58%) of a light yellow powder, m.p. > 245°C (dec.). – NMR ([D$_6$]benzene): δ_H = 8.2–6.7 (m, 50 H, Ar*H*), 6.26 (s, 4 H, *H*–Ar side wall), 5.66 (m, 4 H, ArOCH*H*), 5.58 [d, 4 H, (CO)NCH*H*, ^2J = 15.9 Hz], 4.33 (m, 4 H, ArOC*H*H), 3.49 (m, 4 H, C*H*HP), 3.23 [d, 4 H, (CO)NC*H*H, ^2J = 15.9 Hz], 3.20 (m, 4 H, CH*H*P); δ_P = 12.5. – IR (KBr): $\tilde{\nu}$ = 1710 cm^{-1} (s, CO), 1480 (s), 1461 (s), 1435 (s), 1351 (w), 1248 (m). – $C_{88}H_{78}Cl_4N_4O_6P_4Pd_2 \cdot 6\ H_2O$ (1764.8): calcd. C 56.39, H 4.84, N 2.98; found C 56.54, H 5.43, N 2.33.

4*(PdCl$_2$)$_2$:* Compound **4** (22.5 mg, 14.2 μmol) was dissolved in 5 ml of dichloromethane and 8.3 mg of (COD)PdCl$_2$ (28.4 μmol) was added. A small amount of PPh$_3$ was added to the solution and a clear yellow solution was obtained. After 2 h of stirring, the volume was reduced to 2 ml and 10 ml of pentane was added. The yellow suspension was decanted and the product was washed twice with 10 ml of pentane. The product was dried in vacuo. Yield 20.7 mg (75%) of a yellow powder, m.p. > 180°C (dec.). – NMR ([D$_6$]benzene): δ_H = 8.0–6.6 (m, 50 H, Ar*H*), 6.37 (s, 4 H, *H*–Ar side wall), 5.93 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.6–3.7 (m, 24 H, OCH_2), 3.53 [d, 4 H, (CO)NC*H*H, ^2J = 15.8 Hz], 3.08 (m, 4 H, CH$_2$C*H*HP), 2.92 (m, 4 H, CH$_2$CH*H*P); δ_P = 14.9. – IR (KBr): $\tilde{\nu}$ = 1710 cm^{-1} (s, CO), 1480 (m), 1461 (s), 1435 (s), 1248 (m). – $C_{96}H_{94}Cl_4N_4O_{10}P_4Pd_2$ (1940.8): calcd C 59.36, H 4.88, N 2.88; found C 59.08, H 5.35, N 2.70.

3*(PdMeCl)$_2$:* Compound **3** (100 mg, 71 μmol) was dissolved in 5 ml of CH$_2$Cl$_2$ and 97 mg (142 μmol) of (PPh$_3$)$_2$PdMeCl, dissolved in 10 ml of benzene, was added. The colourless solution was stirred for 2 h and the volume was reduced to approximately 2 ml. The product was precipitated with 10 ml of pentane, the suspension was decanted and the product was washed twice with 10 ml of pentane. The product was dried in vacuo. Yield 103 mg (84%) of a white powder, m.p. > 176°C (dec.). – NMR (CDCl$_3$): δ_H = 7.8–6.9 (m, 50 H, Ar*H*), 6.59 (s, 4 H, *H*–Ar side wall), 5.63 [d, 4 H, (CO)NCH*H*, ^2J = 15.9 Hz], 4.96 (m, 4 H, ArOC*H*H), 4.15(m, 4 H, ArOCH*H*), 3.64 [d, 4 H, (CO)NC*H*H, ^2J = 15.9 Hz], 3.22(m, 4 H, C*H*HP), 2.95(m, 4 H, CH*H*P), –0.36(t, 6 H, Pd–CH_3, $^3J_{P\text{-}H}$ = 6.0 Hz); δ_P = 15.4. – IR (KBr): $\tilde{\nu}$ = 1710 cm^{-1} (s), 1482 (m), 1461 (s), 1435 (s), 1253 (m). – Satisfactory analysis could not be obtained due to hygroscopicity of the compound.

4*(PdMeCl)$_2$:* Compound **4** (30 mg, 18.9 μmol) was dissolved in 5 ml of CH$_2$Cl$_2$, followed by addition of 2 ml CH$_2$Cl$_2$, containing 10 mg of (COD)PdMeCl (37.8 μmol) and a small amount of PPh$_3$. The colourless solution was stirred for 2 h, the volume was reduced to 2 ml and 10 ml of pentane was added. The suspension was decanted and the product was washed twice with 10 ml of pentane. The product was dried in vacuo. Yield 30 mg (85%) of a white powder, m.p. > 154°C (dec.). – NMR (CDCl$_3$): δ_H = 7.8–6.9 (m, 50 H, Ar*H*), 6.63 (s, 4 H, *H*–Ar side wall), 5.59 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.5–3.7 (m, 24 H, CH_2O), 3.66 [d, 4 H, (CO)NC*H*H, ^2J = 15.8 Hz], 3.07 (m, 4 H, C*H*HP), 2.92 (m, 4 H, CH*H*P), –0.05 (t, 6 H, Pd-CH_3, $^3J_{P\text{-}H}$ = 6.0 Hz); δ_P = 21.9. – IR (KBr): $\tilde{\nu}$ 1710 cm^{-1} (s, CO), 1483 (m), 1460 (s), 1433 (s), 1248 (m). – $C_{98}H_{100}Cl_2N_4O_{10}P_4Pd_2 \cdot 4\ H_2O$ (1899.8): calcd. C 59.64, H 5.52, N 2.84; found C 59.73, H 5.34, N 2.52.

3*[Pd(BF$_4$)$_2$]$_2$:* A solution of 24.8 mg of compound **3** (17.5 μmol) in 2 ml of CH$_2$Cl$_2$ was added to a solution of 15.5 mg of (CH$_3$CN)$_4$Pd(BF$_4$)$_2$ (35 μmol) in 5 ml of CH$_3$CN. After stirring for 3 h, the solution was concentrated to dryness, yielding 35.5 mg (95%) of a yellow powder, m.p. > 175°C (dec.). – NMR (CD$_3$CN): δ_H = 7.8–7.3 (m, 50 H, Ar*H*), 7.18 (s, 4 H, *H*–Ar side wall), 5.5 [d, 4 H, (CO)NCH*H*, ^2J = 16.1 Hz], 4.62 (m, 4 H, OCH*H*), 4.41 (m, 4 H, OC*H*H), 4.02 [d, 4 H, (CO)NC*H*H, ^2J = 16.1 Hz], 3.53 (m, 4 H, C*H*HP), 3.37 (m, 4 H, CH*H*P); δ_P = 38.4. – IR (KBr): $\tilde{\nu}$ = 3444 cm^{-1} (m, O–H), 3365 (m, O–H), 3062 (w), 2924 (w), 1648 (s, CO), 1586 (m), 1470 (s), 1437 (s), 1400 (s). – $C_{88}H_{78}B_4F_{16}N_4O_6P_4Pd_2 \cdot 2\ H_2O \cdot 2CH_3CN$ (1796.8): calcd. C 52.87, H 4.25, N 4.02; found C 52.46, H 4.45, N 4.36.

4*[Pd(BF$_4$)$_2$]$_2$:* This compound was prepared in a similar way as **3**[Pd(BF$_4$)$_2$]$_2$ with the following amounts: 13 mg of (CH$_3$CN)$_4$Pd(BF$_4$)$_2$ (29.3 μmol) and 23.3 mg of compound **4** (14.7 μmol). Yield 32.1 mg (93%) of a white powder, m.p. > 172°C (dec.). – NMR (CD$_3$CN): δ_H = 8.1–7.0 (m, 50 H, Ar*H*), 6.82 (s, 4 H, *H*–Ar side wall), 5.70 [d, 4 H, (CO)NCH*H*, ^2J = 16.0 Hz], 4.7–3.7 [m, 28 H, (CO)NC*H*H, CH_2O], 3.08 (m, 8 H, CH_2P); δ_P = 42.8. – IR (KBr): $\tilde{\nu}$ = 3381 cm^{-1} (m, O–H), 3060 (m, O–H), 2928 (m), 2883 (w, OC–H), 1670 (s, CO), 1587 (m), 1478 (s), 1437 (s), 1259 (m). – $C_{96}H_{94}B_4F_{16}N_4O_{10}P_4Pd_2 \cdot 2\ CH_3CN$ (1972.8): calcd. C 53.87, H 4.52, N 3.77; found C 53.76, H 4.76, N 3.69.

3*[Pd(TCNE)]$_2$:* Compound **3** (50 mg, 35 μmol) was dissolved in 3 ml of benzene and a solution of 40 mg of Pd(DBA)$_2$ (70 μmol) in 10 ml of benzene was added. The orange-brown solution was stirred for 10 min and 9.1 mg of TCNE (70 μmol) and 2 ml of benzene were added. After 4 h, the solution was reduced to ca. 5 ml and the product was precipitated with 15 ml of Et$_2$O. The suspension was decanted and the product was washed with 10 ml of diethyl ether and 10 ml of pentane. The product was dried in vacuo. Yield 110 mg (85%) of a green solid, m.p. > 211°C (dec.). – NMR (CDCl$_3$): δ_H = 7.6–7.1 (m, 50 H, Ar*H*), 6.46 (s, 4 H, *H*–Ar side wall), 5.59 [d, 4 H, (CO)NCHH, ^2J = 15.8 Hz], 4.45 (m, 4 H, ArOCH*H*), 4.24 (m, 4 H, ArOC*H*H), 3.75 [d, 4 H, (CO)NCHH, ^2J = 15.8 Hz], 3.17 (m, 4 H, C*H*HP), 2.80 (m, 4 H, CH*H*P); δ_P = 24.8. – IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 2922 (w), 2220 (m, CN), 1701 (s, CO), 1465 (s), 1435 (s), 1252 (m). – $C_{100}H_{78}N_{12}O_6P_4Pd_2 \cdot 2\ H_2O$ (1878.8): calcd. C 63.22, H 4.25, N 8.85; found C 63.19, H 4.34, N 8.83.

4*[Pd(TCNE)]$_2$:* This compound was prepared in a similar way as **3**[Pd(TCNE)]$_2$ with the following amounts: 40.7 mg of Pd(DBA)$_2$ (71 μmol), 62.6 mg of compound **4** (39.5 μmol) and 9.2 mg of TCNE (71 μmol). Yield 61 mg (84%) of a green powder, m.p. > 275°C (dec.). – NMR (CDCl$_3$): δ_H = 7.5–7.35 (m, 40 H, Ar*H*), 7.12 (m, 10 H, Ar*H*), 6.67 (s, 4 H, *H*–Ar side wall), 5.65 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.0–3.8 [m, 28 H, OCH_2, (CO)NC*H*H, ^2J = 15.8 Hz], 2.69 (m, 4 H, CH$_2$CH*H*P), 2.59 (m, 4 H, CH$_2$C*H*HP); δ_P = 12.8. – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}(w), 2871 (w), 2213 (m, CN), 1707 (s, CO), 1458 (s), 1436 (s), 1258 (m). – $C_{108}H_{94}N_{12}O_{10}P_4Pd_2$ (2054.8): calcd. C 63.07, H 4.64, N 8.17; found C 63.05, H 4.74, N 7.94.

3*(PtCl$_2$)$_2$:* (PPh$_3$)$_2$PtCl$_2$ (28.8 mg, 36.4 μmol) and 25.7 mg of compound **3** (18.2 μmol) were dissolved in 5 ml of CH$_2$Cl$_2$ and the solution was stirred for 2 h. The volume was reduced to ± 2 ml followed by addition of 15 ml of pentane. The suspension was decanted and the white solid was washed three times with 10 ml of pentane. The product was dried in vacuo. Yield 27.9 mg (79%) of a white solid, m.p. > 290°C (dec.). – NMR (CDCl$_3$): δ_H = 8.0–7.0 (m, 50 H, Ar*H*), 6.76 (s, 4 H, *H*–Ar side wall), 5.69 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.99 (m, 4 H, ArOCH*H*), 4.70 (m, 4 H, ArOC*H*H), 3.80 [d, 4 H, (CO)NC*H*H, ^2J = 15.8 Hz], 3.12 (m, 4 H, C*H*HP), 2.94(m, 4 H, CH*H*P); δ_P = 0.4 ($^1J_{Pt\text{-}P}$ = 3550 Hz). – IR (KBr): $\tilde{\nu}$ = 1707 cm^{-1}(s, CO), 1464 (s), 1436 (s), 1247 (m). – $C_{88}H_{78}Cl_4N_4O_6P_4Pt_2$ (1678): calcd. C 54.38, H 4.05, N 2.88; found C 54.15, H 4.33, N 2.62.

4*(PtCl$_2$)$_2$:* (COD)PtCl$_2$ (12.7 mg, 34 μmol) was dissolved in 5 ml of CH_2Cl_2 and after addition of 27.0 mg of compound **4** (17 μmol), the solution was stirred for 2 h. The volume was reduced to ± 2 ml followed by addition of 15 ml of pentane. The suspension was decanted and the white solid was washed three times with 10 ml of pentane. The product was dried in vacuo. Yield 24.6 mg (68%) white powder, m.p. > 255°C (dec.). − NMR ($CDCl_3$): δ_H = 7.9−7.0 (m, 50 H, Ar*H*), 6.73 (s, 4 H, *H*−Ar side wall), 5.63 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.2−3.5 [m, 28 H, OCH_2, (CO)NC*H*H], 2.66 (m, 4 H, CH_2CHHP), 2.53 (m, 4 H, CH_2CH*H*P); δ_P = 4.8 ($^1J_{Pt\text{-}P}$ = 3610 Hz); δ_{Pt} (CD_2Cl_2) = −4390 (t, $^1J_{Pt\text{-}P}$ = 3610 Hz). − IR (KBr): $\tilde{\nu}$ = 1708 cm^{-1} (s, CO), 1481 (m), 1458 (s), 1435 (s), 1256 (m). − $C_{96}H_{94}Cl_4N_4O_{10}P_4Pt_2 \cdot H_2O$ (2118): calcd. C 53.94, H 4.53, N 2.62; found C 53.94, H 4.40, N 2.62.

3*[RhCl(CO)]$_2$:* To a solution of 100 mg of compound **3** (71 μmol) in 3 ml of CH_2Cl_2 93 mg of $(PPh_3)_2$RhCl(CO) (135 μmol), dissolved in 6 ml of CH_2Cl_2 and 14 ml of C_6H_6, was added and the solution was stirred for 3 h. The volume was reduced to ca. 5 ml followed by addition of 25 ml of pentane. The suspension was decanted and the white solid was washed three times with 20 ml of pentane. The product was dried in vacuo. Yield 119 mg (96%) of a yellow solid, m.p. > 195°C (dec.). − NMR ($CDCl_3$): δ_H = 7.9−7.0 (m, 50 H, Ar*H*), 6.55 (s, 4 H, *H*−Ar side wall), 5.57 [d, 4 H, (CO)NCHH, ^2J = 15.6 Hz], 5.1 (m, 4 H, ArOCH*H*), 4.1 (m, 4 H, ArOC*H*H), 3.64 [d, 4 H, (CO)NCHH, ^2J = 15.6 Hz], 3.0(m, 4 H, C*H*HP), 2.7 (m, 4 H); δ_P = 18.6 (d, $^1J_{Rh\text{-}P}$ = 124 Hz). − IR (KBr): $\tilde{\nu}$ = 1972 cm^{-1} (s, CO_{Rh}), 1710 (s, CO), 1482 (m), 1462 (s), 1435 (s), 1385 (m), 1354 (w), 1307 (w), 1253 (m). − $C_{90}H_{78}Cl_2N_4O_8P_4Rh_2 \cdot 3\ H_2O$ (1743): calcd. C 60.11, H 4.71, N 3.12; found C 59.98, H 4.45, N 3.06.

4*[RhCl(CO)]$_2$:* This compound was prepared in a similar way as **3** [RhCl(CO)]$_2$ with the following amounts: 230 mg of $(PPh_3)_2$RhCl(CO) (333 μmol) and 240 mg of compound **4** (170 μmol). Yield 285 mg (96%) of a yellow powder, m.p. > 149°C (dec.). − NMR ($CDCl_3$): δ_H = 7.9−7.0 (m, 50 H, Ar*H*), 6.55 (s, 4 H, *H*−Ar side wall), 5.57 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 4.5−3.8 (m, 24 H, OCH_2), 3.68 [d, 4 H, (CO)NC*H*H, ^2J = 15.8 Hz], 3.12(m, 4 H, CH_2CHHP), 2.91 (m, 4 H, CH_2CH*H*P); δ_P = 22.0 (d, $^1J_{Rh\text{-}P}$ = 123 Hz); δ_{Rh} = −418. − IR (KBr): $\tilde{\nu}$ = 1970 cm^{-1} (s, CO_{Rh}), 1708 (s, CO), 1481 (m), 1458 (s), 1435 (s), 1256 (m) − M_w (CH_2Cl_2): calcd. 1919, found 1850. − $C_{98}H_{94}Cl_2N_4O_{12}P_4Rh_2 \cdot 3\ H_2O$ (1919): calcd. C 59.61, H 5.10, N 2.84; found C 59.47, H 4.98, N 2.80.

3*[IrCl(CO)]$_2$:* A mixture of 44.4 mg of compound **3** (31.5 μmol) and 49 mg of $(PPh_3)_2$IrCl(CO) (63 μmol) in 10 ml of C_6H_6 was stirred overnight. The volume was reduced to ca. 2 ml and 15 ml of pentane was added. The solvent was decanted and the residue washed twice with 10 ml of pentane. The product was dried in vacuo. Yield 54 mg (89%) of a yellow solid, m.p. > 180°C (dec.). − NMR ([D$_6$]benzene): δ_H = 7.96 (m, 16 H, Ar*H*), 7.2−6.8 (m, 34 H, Ar*H*), 6.34 (s, 4 H, *H*−Ar side wall), 5.90 [d, 4 H, (CO)NCH*H*, ^2J = 15.8 Hz], 5.8 (m, 4 H, ArOCH*H*), 4.5 (m, 4 H, ArOC*H*H), 4.1 (m, 4 H, C*H*HP), 3.43 [d, 4 H, (CO)NC*H*H, ^2J = 15.8 Hz], 3.3 (m, 4 H, CH*H*P); δ_P = 14.8. − IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} (w), 2922 (w), 1959 (s, CO_{Ir}), 1710 (s, CO), 1480 (s), 1462 (s), 1435 (s), 1248 (m). − $C_{90}H_{78}Cl_2N_4O_8P_4Ir_2 \cdot 2\ H_2O$ (1921.4): calcd. C 55.18, H 4.22, N 2.86; found C 55.20, H 4.63, N 2.62.

4*[IrCl(CO)]$_2$:* This compound was prepared in a similar way as **3**[IrCl(CO)]$_2$ with the following amounts: 49 mg of $(PPh_3)_2$IrCl(CO) (63 μmol) and 50 mg of compound **4** (31.5 μmol). Yield 56 mg (85%) of a yellow powder, m.p. > 165°C (dec.). − NMR ([D$_6$]benzene): δ_H = 8.1−7.9 (dm, 16 H, Ar*H*), 7.2−6.8 (m, 34 H, Ar*H*), 6.34 (s, 4 H, *H*−Ar side wall), 5.95 [d, 4 H, (CO)NCH*H*, ^2J = 15.9 Hz], 4.68 (m, 4 H, OCH_2), 4.48 (m, 4 H, OCH_2), 4.31 (m, 4 H, OCH_2), 4.13 (m, 12 H, OCH_2), 3.54 [d, 4 H, (CO)NC*H*H, ^2J = 15.9 Hz], 3.40 (m, 4 H, CH_2CHHP), 3.27 (m, 4 H, CH_2CH*H*P); δ_P = 17.7. − IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 2922 (w), 1958 (s, CO_{Ir}), 1711 (s, CO), 1482 (m), 1458 (s), 1435 (s), 1258 (m). − $C_{98}H_{94}Cl_2N_4O_{12}P_4Ir_2 \cdot 2\ H_2O$ (2097.4): calcd. C 55.13, H 4.63, N 2.62; found C 55.08, H 4.42, N 2.58.

[1] M. Bonchio, T. Carofiglio, F. Di Furia, R. Fornassier, *J. Org. Chem.* **1995**, *60*, 5986−5988.
[2] J. Rebek Jr., *Pure Appl. Chem.* **1996**, *68*, 1261−1266.
[3] H. K. A. C. Coolen, J. A. M. Meeuwis, P. W. N. M. van Leeuwen, R. J. M. Nolte, *J. Am. Chem. Soc.* **1995**, *117*, 11906−11913.
[4] C. F. Martens, R. J. M. Klein Gebbink, M. C. Feiters, R. J. M. Nolte, *J. Am. Chem. Soc.* **1994, 116**, 5667−5670.
[5] H. K. A. C. Coolen, P. W. N. M. van Leeuwen, R. J. M. Nolte, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 905−907.
[6] M. T. Reetz, S. R. Waldvogel, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 865−867.
[7] O. S. Tee, B. C. Javed, *J. Chem. Soc., Perkin Trans 2* **1994**, 23−29.
[8] H. J. Schneider, F. XIao, *J. Chem. Soc., Perkin Trans 2* **1992**, 387−391.
[9] F. Diederich, H.-D. Lutter, *J. Am. Chem. Soc.* **1989**, *111*, 8438−8446.
[10] Y. Murakami, J.-I. Kukuchi, Y. Hisaeda, O. Hayashida, *Chem. Rev.* **1996**, *96*, 721.
[11] G. Wulff, T. Gross, R. Schönfeld, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1962−1964.
[12] R. P. Sijbesma, R. J. M. Nolte, *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 643−647.
[13] K. Tani, M. Yabuta, S. Nakamura, T. Yamagata, *J. Chem. Soc., Dalton Trans.* **1993**, 2781−2789.
[14] C. Amatore, G. Broeker, A. Jutand, F. Khalil, *J. Am. Chem. Soc.* **1997**, *119*, 5176−5185.
[15] R. P. Sijbesma, R. J. M. Nolte, *J. Org. Chem.* **1991**, *56*, 3199.
[16] J. N. H. Reek, A. H. Priem, H. Engelkamp, A. E. Rowan, J. A. A. W. Elemans, R. J. M. Nolte, *J. Am. Chem. Soc.* **1997**, *119*, 9956−9964.
[17] J. W. H. Smeets, R. P. Sijbesma, L. van Dalen, A. L. Spek, W. J. J. Smeets, R. J. M. Nolte, *J. Org. Chem.* **1989**, *54*, 3710.
[18] J. W. H. Smeets, R. P. Sijbesma, F. G. M. Niele, A. L. Spek, W. J. J. Smeets, R. J. M. Nolte, *J. Am. Chem. Soc.* **1987**, *109*, 928.
[19] H. K. A. C. Coolen, P. W. N. M. van Leeuwen, R. J. M. Nolte, *J. Org. Chem.* **1996**, *61*, 4739.
[20] C. F. Martens, R. P. Sijbesma, R. J. M. Klein Gebbink, R. J. M. Nolte, *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 400.
[21] G. C. Dol, F. Hartl, P. C. J. Kamer, P. W. N. M. van Leeuwen, R. J. M. Nolte, *J. Chem. Soc., Dalton Trans.*, accepted.
[22] R. P. Sijbesma, A. P. M. Kentgens, E. T. G. Lutz, J. H. van der Maas, R. J. M. Nolte, *J. Am. Chem. Soc.* **1993**, *115*, 8999−9005.
[23] C. J. Cobley, P. G. Pringle, *Inorg. Chim. Acta* **1997**, *265*, 107−115.
[24] S. O. Grim, R. L. Keiter, *Inorg. Chem. Acta* **1970**, *4*, 56.
[25] P. S. Pregosin, *Studies in Inorganic Chemistry 13*, Elsevier, Amsterdam, Oxford, New York, Tokyo, **1991**.
[26] M. Kranenburg, J. P. G. Delis, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Vrieze, N. Veldman, A. L. Spek, K. Goubitz, J. Fraanje, *J. Chem. Soc., Dalton Trans.* **1997**, 1839−1849.
[27] S. Murata, Y. Ido, *Bull. Chem. Soc. Jpn.* **1994**, *67*,1746−1748.
[28] J. P. Collman, C. T. Sears Jr., M. Kubota, *Inorg. Synth.* **1990,** *28*, 92−94.
[29] T. H. Brown, P. J. Green, *J. Am. Chem. Soc.* **1970**, *92*, 2359−2362.
[30] R. P. Sijbesma, A. M. Kentgens, R. J. M. Nolte, *J. Org. Chem.* **1991**, *56*, 3122.
[31] R. P. Sijbesma, W. P. Bosman, R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.* **1991**, 885.
[32] R. P. Sijbesma, R. J. M. Nolte, *Top. Curr. Chem.* **1995**, *175*, 26−56.
[33] S. G. Kazarian, P. A. Hamley, M. Poliakoff, *J. Am. Chem. Soc.* **1993**, *115*, 9069−9079.
[34] P. J. Davies, N. Veldman, D. M. Grove, A. L. Spek, B. T. G.

Lutz, G. van Koten, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1959–1961.
[35] C. J. Elsevier, J. M. Ernsting, d. L. W.G.J., *J. Chem. Soc., Chem. Commun.* **1989**, 585–586.
[36] A. Bax, R. H. Griffey, B. L. Hawkins, *J. Magn. Reson.* **1983**, *55*, 301.
[37] J. A. Osborn, G. Wilkinson, *Inorg. Synth.* **1990,** *28*, 79–80.
[38] M. F. Rettig, P. M. Maitlis, *Inorg. Synth.* **1977**, *17*, 134.
[39] B. J. Hathaway, A. E. Underhill, *J. Chem. Soc.* **1962**, 2257, 2444.
[40] J. Chatt, L. M. Vallarino, L. M. Venanzi, *J. Chem. Soc.* **1957**, 3413.
[41] G. C. Dol, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Org. Chem.* **1998**, 359–364.
[42] J. Granot, *J. Magn. Reson.* **1983**, *55*, 216.

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