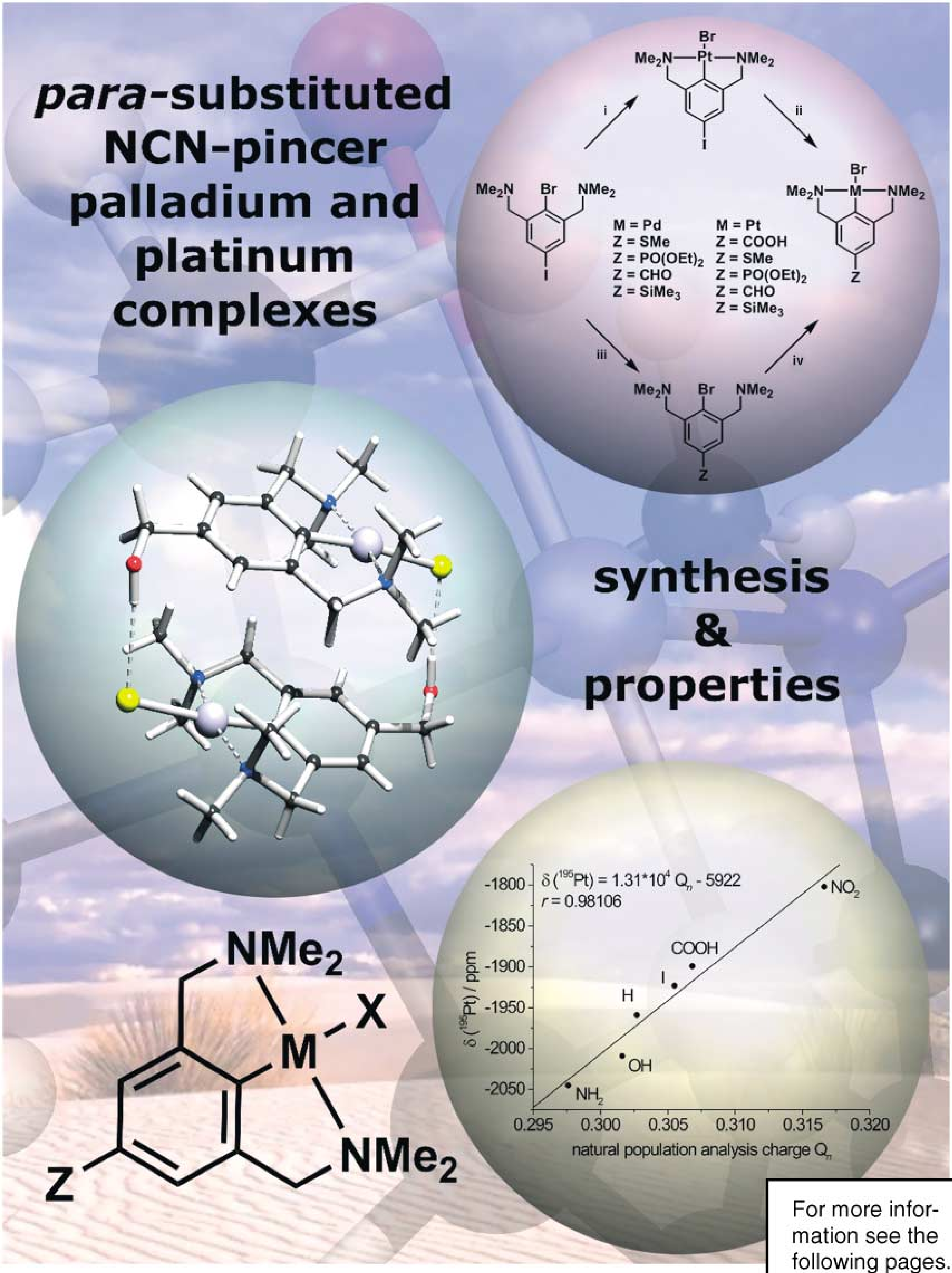


For more information see the following pages.

DOI: 10.1002/chem.200305336

Synthesis and Properties of *para*-Substituted NCN-Pincer Palladium and Platinum Complexes

**Martijn Q. Slagt,[a] Gema Rodríguez,[a] Michiel M. P. Grutters,[a]
Robertus J. M. Klein Gebbink,[a] Wim Klopper,[b] Leonardus W. Jenneskens,[c]
Martin Lutz,[d] Anthony L. Spek,[d] and Gerard van Koten*[a]**

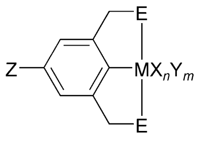
Dedicated to Professor D. C. Koningsberger on the occasion of his 65th birthday

Abstract: A variety of *para*-substituted NCN-pincer palladium(II) and platinum(II) complexes [MX(NCN-Z)] (M = Pd^{II}, Pt^{II}; X = Cl, Br, I; NCN-Z = [2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_2$-4-Z]$^-$; Z = NO$_2$, COOH, SO$_3$H, PO(OEt)$_2$, PO(OH)(OEt), PO(OH)$_2$, CH$_2$OH, SMe, NH$_2$) were synthesised by routes involving substitution reactions, either prior to or, notably, after metalation of the ligand. The solubility of the pincer complexes is dominated by the nature of the *para* substituent Z, which renders several complexes water-soluble. The influence of the *para* substituent on the electronic properties of the metal centre was studied by ^{195}Pt NMR spectroscopy and DFT calculations. Both the ^{195}Pt chemical shift and the calculated natural population charge on platinum correlate linearly with the σ_p Hammett substituent constants, and thus the electronic properties of predesigned pincer complexes can be predicted. The σ_p value for the *para*-PtI group itself was determined to be −1.18 in methanol and −0.72 in water/methanol (1/1). Complexes substituted with protic functional groups (CH$_2$OH, COOH) exist as dimers in the solid state due to intermolecular hydrogen-bonding interactions.

Keywords: aromatic substitution · chelates · density functional calculations · N ligands · substituent effects

Introduction

Organometallic complexes based on the potentially terdentate, monoanionic NCN-pincer ligand[1] (NCN = 2,6-bis[(dimethylamino)methyl]phenyl anion) have been prepared for a wide range of (transition) metals, and are therefore found in numerous applications, such as catalysis, catalyst immobilisation, optical devices and sensor materials.[2,3] The aryl pincer ligand in complexes of type **1** contains two *meta*-positioned substituents bearing N-, O-, P- or S-donor groups that allow chelation to the metal centre, thereby enhancing stability due to the formation of metallacycles. Among the most stable pincer complexes are the square-planar complexes of metals of the nickel triad (Ni, Pd, Pt).[4]



1

Z = functional group, H
E = NR$_2$, PR$_2$, OR, SR
M = (transition)metal
X,Y = halogen, ancillary ligand

Variations in the *para* substituent Z of these ligands have drawn our particular interest for several reasons. The electronic properties, and consequently the catalytic, spectroscopic, and diagnostic properties, of pincer complexes can be fine-tuned by choosing the appropriate *para* substituent. A striking example of electronic tuning of the metal centre in NCN-Z nickel(II) complexes by the *para* substituent was published earlier by us.[5] The Hammett parameters of the

---

[a] Dr. M. Q. Slagt, Dr. G. Rodríguez, Drs. M. M. P. Grutters,
Dr. R. J. M. Klein Gebbink, Prof. Dr. G. van Koten
Debye Institute, Department of Metal-Mediated Synthesis
Utrecht University, Padualaan 8, 3584 CH Utrecht (The Netherlands)
Fax: (+31) 30-2523615
E-mail: g.vankoten@chem.uu.nl

[b] Dr. W. Klopper
Debye Institute, Department of Theoretical Chemistry
Utrecht University, Padualaan 14, 3584 CH Utrecht (The Netherlands)

[c] Prof. Dr. L. W. Jenneskens
Debye Institute, Department of Physical Organic Chemistry
Utrecht University, Padualaan 8, 3584 CH Utrecht (The Netherlands)

[d] Dr. M. Lutz, Prof. Dr. A. L. Spek
Bijvoet Centre for Biomolecular Research, Department of Crystal and Structural Chemistry
Utrecht University, Padualaan 8, 3584 CH Utrecht (The Netherlands)

DOI: 10.1002/chem.200305336

para substituents showed a linear relationship with the Ni^{II}/Ni^{III} oxidation potential, and consequently with its catalytic activity in atom-transfer radical additions.[5c] Recently, Reinhoudt et al. published a linear Hammett relationship for the complex stability of an array of *para*-substituted pyridines complexed to cationic SCS-pincer palladium complexes.[6] The NCN- and SCS-pincer complexes have been supported via a *para* substituent on poly(ethylene glycol),[7] poly-(*N*-octadecylacrylamide),[8] polysiloxanes,[9] benzene rings,[10] hyperbranched polytriallylsilanes and polyglycerols,[11] carbosilane[12,13] and Fréchet-type[14] dendrimers and dendronised polymers,[14e] buckminsterfullerene,[15] and silica.[16] Substitution in the *para* position also allows the buildup of supramolecular assemblies,[17,18] the placement of an additional metal centre,[19,20] or the introduction of functional groups such as α-amino acid residues[21,22] or other auxiliaries[23] to give new materials.[24] The major potential of the pincer system motivated us to develop synthetic routes towards new *para*-functionalised NCN-pincer complexes. Several steps in this study involve substitutions directly on metalated NCN-ligands. While ample reports have been published on ligand functionalisation of π-aryl organometallic complexes such as ferrocenes, similar reactions of σ-aryl organometallic complexes are scarce. Furthermore, the latter mainly involve organometallic σ-aryl complexes in which the metal centre is sterically shielded from the environment by bulky ligands.[25] The approach in which metalated ligands are functionalised is of great interest, since it allows the creation of compact multifunctional building blocks with catalytic or sensor properties on one side, and functional substituents for (non)covalent bonding to create nanosize structures on the other. The pronounced influence of the *para* substituent on the properties of these NCN-pincer building blocks is discussed with respect to ^{195}Pt NMR spectroscopy, solid-state structures, and DFT calculations. Some of the resulting complexes have intriguing solid-state and physicochemical properties. Some of the unexpected results of the synthetic work were published earlier in a communication.[26]

Abstract in Dutch: *Een verscheidenheid aan para-gesubstitueerde NCN-pincer-palladium(II) en -platina(II) complexen [MX(NCN-Z)] (M = Pd^{II}, Pt^{II}; X = Cl, Br, I; NCN-Z = [2,6-(CH_2NMe_2)C_6H_2-4-Z]$^-$; Z = NO_2, COOH, SO_3H, $PO(OEt)_2$, PO(OH)(OEt), $PO(OH)_2$, CH_2OH, SMe, NH_2) is gesynthetiseerd via substitutiereacties zowel voor, en hoogst opmerkelijk, ook na de metallering van het ligand. De oplosbaarheid van de pincer-complexen wordt gedomineerd door de aard van de* para-*substituent Z, waardoor enkele van de complexen wateroplosbaar zijn. De invloed van de* para-*substituent op de elektronische eigenschappen van het metaalcentrum is bestudeerd met behulp van ^{195}Pt-NMR en DFT-berekeningen. Zowel de chemische verschuiving van de ^{195}Pt-kern, als de berekende 'natural population' lading op platina vertonen een lineaire correlatie met de σ_p Hammett-substituentconstante, hetgeen het voorspellen van de elektronische eigenschappen van nieuwe pincercomplexen mogelijk maakt. De σ_p-waarde van de para-PtI eenheid blijkt respectievelijk −1.18 in methanol en −0.72 in waterige methanol (1/1, v/v) te zijn. Door de aanwezigheid van intermoleculaire waterstofbruggen komen de complexen met protische functionele groepen (CH_2OH, COOH) in de vaste stof voor als dimeren.*

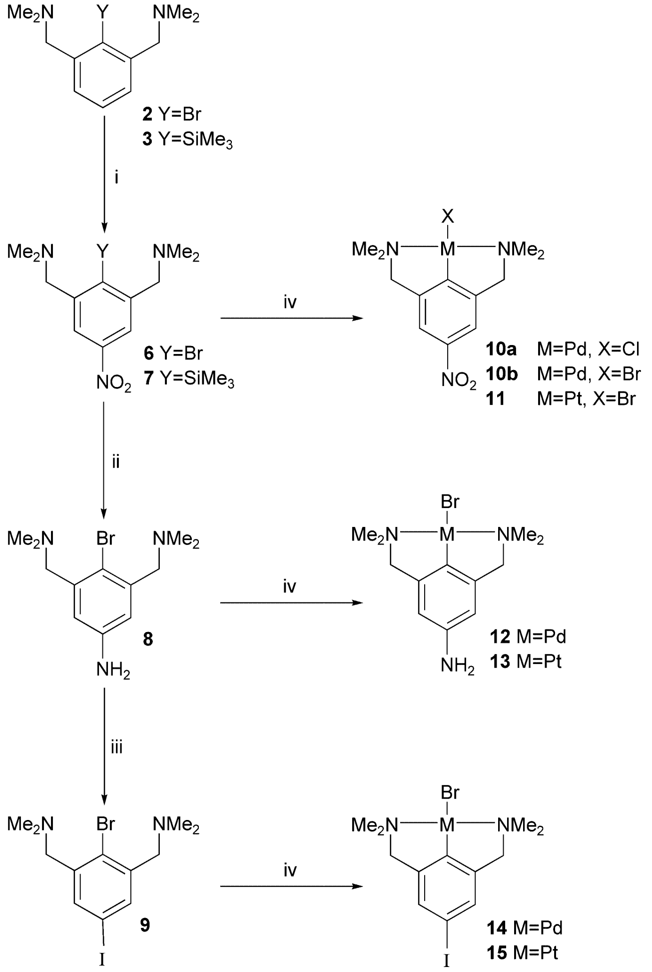
Results

Two main synthetic strategies were followed for the synthesis of *para*-substituted pincer metal complexes, denoted as [MX(NCN-Z)] (**1**). Apart from selective metalation of prefunctionalised *meta*-bis-aminoarene (NCN-pincer) ligands (approach I), selective *para* substitution of bis-*ortho*-aminoaryl pincer complexes offers an alternative strategy (approach II).

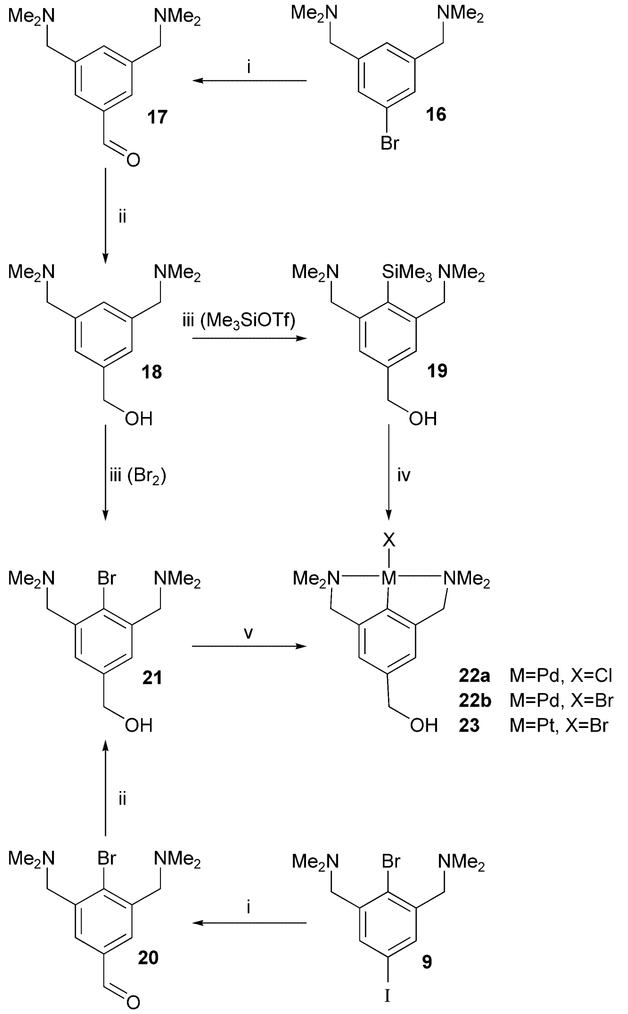
Approach I is commonly the method of choice because the metal–carbon bond is often the most reactive part of the complex. However, recently we observed that the metal–carbon bond in palladium(II) and, in particular, platinum(II) NCN-pincer complexes, has remarkable stability under a wide variety of reaction conditions. For example, the platinated complexes [PtX(NCN-Z)] are stable in refluxing acetone/HCl, as well as under the highly basic and nucleophilic conditions encountered in lithiation reactions.[21] This remarkable stability allows the exploration of unconventional strategies (approach II) for *para* functionalisation of pincer complexes. The availability of various metalation procedures is an essential part of their syntheses. Oxidative addition and lithiation *trans*-metalation procedures are available for both palladium and platinum.[21] Obviously, the latter procedure is not suitable when *para* substituents are used which are incompatible with lithium alkyls. In addition, direct palladation is possible by electrophilic aromatic substitution of a trimethylsilyl-substituted pincer ligand with $Pd(OAc)_2$.[27]

Approach I: selective metalation of prefunctionalised NCN-pincer ligands: The nitro-, amino-, and iodo-*para*-substituted platinum and palladium pincers were essentially obtained from *ortho*-bromo compound **2** (Scheme 1). The nitro substituent at the *para* position could also be introduced into *ortho*-trimethylsilyl compound **3**, albeit in a much lower yield and with poorer selectivity. Metalation of *para*-nitro ligand **7** with $Pd(OAc)_2$ and subsequent treatment with LiCl afforded *para*-nitro complex **10a** in 97% yield. Ligands **6**, **8** and **9** were all metalated by mild oxidative addition with $[Pd_2(dba)_3]\cdot CHCl_3$ or $[Pt(p\text{-tol})_2(SEt_2)]_2$.

Nitration of **2** in H_2SO_4 with HNO_3 afforded exclusively the *para*-nitro ligand **6**.[5b] Metalation of **6** led to clean formation of palladium(II) complex **10b** and platinum(II) complex **11** in yields of 97 and 95%, respectively. The *para*-amino-substituted ligand **8** was obtained by reduction of **6** with hydrazine monohydrate in the presence of 5% Ru/C catalyst.[5b] Metalation of **8** to afford *para*-amino complexes **12** and **13** led to concomitant formation of Pd^0 and Pt^0 particles, respectively, which resulted in an overall lower yield (ca. 80%). *para*-Iodo-substituted pincer ligand **9** was obtained by diazotation of **8** with $NaNO_2$ and subsequent treatment with KI. Platination of **9** with $[Pt(p\text{-tol})_2(SEt_2)]_2$ in refluxing benzene afforded complex **15** in quantitative



Scheme 1. Substitution of the NCN-pincer ligands prior to metalation. i) HNO_3/H_2SO_4; ii) $N_2H_4\cdot H_2O$, 5 mol% Ru/C; iii) H_2SO_4, H_2O, $NaNO_2$, NaI; iv) Y = Br: $[Pd_2(dba)_3]\cdot CHCl_3$ (**10b**, **12**, **14**) or $[Pt_2(p\text{-tol})_2(SEt_2)_2]_2$ (**11**, **13**, **15**); Y = $SiMe_3$: $Pd(OAc)_2$/LiCl (**10a**). dba = *trans,trans*-dibenzylideneacetone.



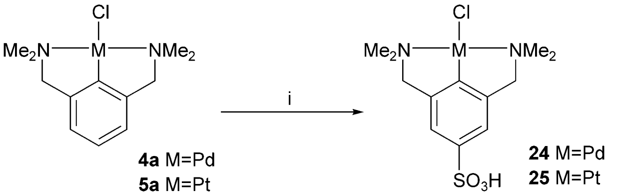
Scheme 2. Synthesis of *para*-hydroxymethyl complexes **22** and **23** by two different approaches. i) *t*BuLi, DMF; ii) $NaBH_4$; iii) a) $t\text{BuMe}_2\text{SiCl}$/imidazole; b) *n*BuLi, Me_3SiOTf, or Br_2; c) $Et_3N\cdot 3HF$; iv) $Pd(OAc)_2$, LiCl; v) M = Pd: $[Pd_2(dba)_3]\cdot CHCl_3$, M = Pt: $[\{Pt(p\text{-tol})_2SEt_2\}_2]$.

yield. The high selectivity of this reaction is attributed to the coordinating properties of the N-donor groups, which enable site-selective platination. The synthesis of palladium analogue **14** was less straightforward. Palladation with $[Pd_2(dba)_3]\cdot CHCl_3$ at −78 °C followed by slow warming to room temperature ultimately afforded **14** in moderate yield.[21]

The synthesis of hydroxymethyl-substituted palladium pincer compound **22** was possible by two different routes (Scheme 2). The first approach starts from the *para*-bromo ligand **16**. Lithiation of **16** with two equivalents of *t*BuLi in diethyl ether followed by addition of DMF afforded aldehyde **17** quantitatively. Reduction of **17** to its corresponding benzylic alcohol **18** proceeded rapidly and in a yield of 95% with $NaBH_4$ in methanol. Protection of **18** with a *tert*-butyldimethylsilyl group allowed lithiation of C_{ipso} with *n*BuLi in hexanes followed by quenching with trimethylsilyl triflate. Deprotection with $Et_3N\cdot 3HF$ afforded hydroxymethyl ligand **19** in 78% yield. Subsequent treatment of **19** with $Pd(OAc)_2$ and LiCl in methanol resulted in the formation of **22a** in 87% yield. Instead of an $SiMe_3$ substituent, a bromo-substituent could be introduced into **18** by using Br_2 instead of $SiMe_3OTf$ for quenching the lithio intermediate, to afford *para*-hydroxymethyl compound **21**, which allowed both palladation and platination to give complexes **22b** and **23**, respectively.

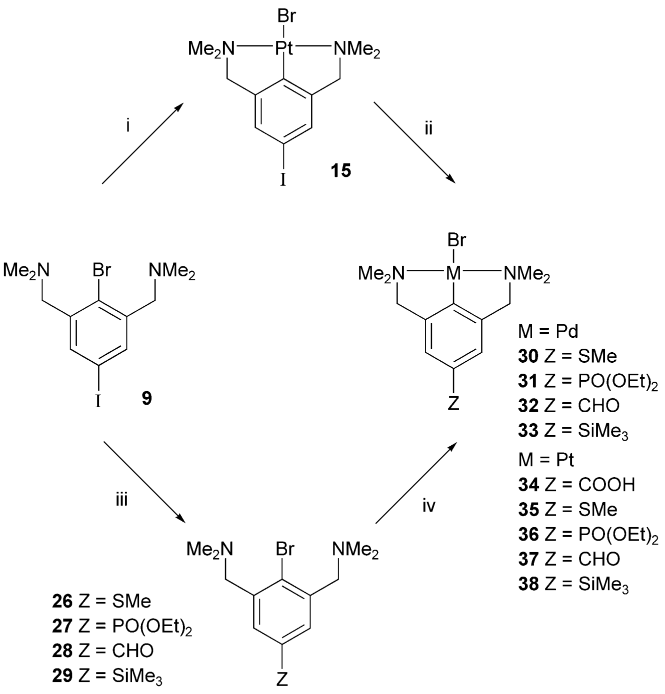
An alternative route, which allowed the synthesis of both the platinum and palladium *para*-hydroxymethyl NCN-pincer complexes, started from bifunctional bromoiodo pincer ligand **9**. Due to the higher reactivity of *t*BuLi towards the aryl iodide bond compared to the aryl bromide bond, selective substitution reactions can be performed.[21] Lithiation of **9** at −100 °C in diethyl ether with two equivalents of *t*BuLi, selectively afforded the *para*-lithio pincer in situ. This lithio intermediate could be treated with electrophiles to produce novel *para*-substituted pincer ligands. For instance, quenching of the lithio intermediate with DMF afforded aldehyde **20**, which was easily reduced to benzylic alcohol **21** and subsequently metalated as described above to afford palladium and platinum complexes **22b** and **23**, respectively.[21]

Approach II: selective *para* substitution of bis-*ortho*-aminoaryl metal complexes: Direct treatment of the unsubstituted palladium and platinum complexes **4a** and **5a** with chlorosulfonic acid in dichloromethane afforded a mixture containing predominantly (ca. 50%) the *para*-substituted sulfonated complexes **24** and **25**, together with the *meta* isomer and several unidentified (decomposition) products (Scheme 3).



Scheme 3. Direct sulfonation of NCN palladium and platinum complexes. i) $HOSO_2Cl$.

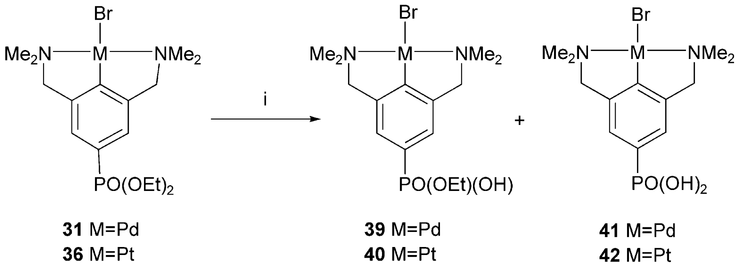
Decomposition pathways starting with protonation of the amine donor arms can be envisaged. Purification of **24** was achieved by several extractions with acetonitrile followed by careful precipitation, while **25** could be purified by fractional precipitations from methanol. Complexes **24** and **25** were obtained in respective yields of 18 and 25%. Due to the presence of the polar sulfonic acid functional group, **24** and **25** are only soluble in THF or in highly polar (protic) solvents such as water, DMSO, and acetonitrile.



Scheme 4. Substitutions of metalated NCN platinum complexes, and an alternative route for their palladium analogues. i) $[\{Pt(p\text{-}tol)_2SEt_2\}_2]$; ii) a) *t*BuLi, b) CO_2 (**34**), Me_2S_2 (**35**), $ClPO(OEt)_2$ (**36**), DMF (**37**), Me_3SiCl (**38**); iii) a) *t*BuLi; b) Me_2S_2 (**26**), $ClPO(OEt)_2$ (**27**), DMF (**28**), Me_3SiCl (**29**); iv) $[Pd_2(dba)_3]\cdot CHCl_3$ (**30–33**), $[\{Pt(p\text{-}tol)_2SEt_2\}_2]$ (**35–38**).

The *para*-iodo-substituted NCN-pincer complex **15** is a convenient starting material for further modifications (Scheme 4). Due to the lower stability of the *para*-iodo NCN palladium(II) complexes compared to the corresponding NCN platinum(II) analogues, we were unable to perform successful transformations on *para*-iodo palladium(II) complex **14**. Remarkably, platinum(II) complex **15** could be lithiated at the *para* position with *t*BuLi at −100 °C in THF to produce $[PtBr(NCN\text{-}Li)]_n$ in situ. Temperature control is a crucial factor in this lithiation reaction, since the lithio intermediate can polymerise to produce $[Pt(NCN)]_n$-type linear chains.[28] After lithiation, the reaction mixture was quenched at −100 °C with several electrophiles, that is, CO_2, MeSSMe, $ClPO(OEt)_2$, DMF, and Me_3SiCl, to produce in high to excellent yields *para*-substituted pincer platinum(II) complexes functionalised with a carboxy (**34**, 89%), methylthio ether (**35**, 95%), diethylphosphonato (**36**, 95%), aldehyde (**37**, 74%), and trimethylsilyl (**38**, 75%) group, respectively (Scheme 4). Although the analogous NCN palladium(II) complexes **30–33** were not accessible by selective functionalisation of *para*-iodo NCN-pincer palladium(II) complex **14**, they could be synthesised via the methylthio (**26**), diethylphosphonato (**27**), aldehyde (**28**), and trimethylsilyl (**29**) *para*-substituted NCN-pincer ligands. These precursors were obtained in nearly quantitative yields by selective lithiation at the *para* position (iodo substituent) of **9** with *t*BuLi in diethyl ether and subsequent treatment with dimethyl disulfide, diethyl chlorophosphate, DMF, or trimethylsilyl chloride. Palladation of ligands **26–29** with $[Pd_2(dba)_3]\cdot CHCl_3$ afforded the metalated methylthio (**30**, 85%), diethylphosphonato (**31**, 92%), aldehyde (**32**, 74%) and trimethylsilyl (**33**, 78%) derivatives. Platinum(II) complexes **35–38** were also accessible via this route by treatment of **26–29** with $[Pt(p\text{-}tol)_2(SEt_2)]_2$.

The diethylphosphonato-substituted NCN-palladium and -platinum complexes **31** and **36** were subsequently (partially) hydrolysed to obtain their respective phosphonic acid derivatives. Scheme 5 illustrates this saponification to the monoethylphosphonic acid (**39** and **40**), and phosphonic acid derivatives (**41** and **42**) on treatment with trimethylsilyl bromide and methanol. Repeated extractions of the crude product with dichloromethane afforded the monoethylphosphonic acid palladium and platinum pincer complexes **39** and **40** as pure materials in yields of 15 and 23%, respectively. The unfavourable solubility properties of **41** and **42** hampered their complete purification.



Scheme 5. (Partial) saponification of phosphonate esters on metalated ligands. i) a) Me_3SiBr; b) MeOH.

Solubility: During the synthesis and workup of this series of *para*-substituted pincer palladium and platinum complexes, we observed that the nature of the *para* substituent has a crucial influence on their solubility. A much smaller effect, as compared to the influence of the *para* substituent, is exerted by the halo ligand on the metal atom. Larger halide ions have a more diffuse charge, and the more covalent character of their bonds to the metal atom results in slightly enhanced solubility in apolar solvents. The *para*-H-, -*t*Bu-, and -$SiMe_3$-substituted palladium and platinum complexes are soluble in dichloromethane, chloroform and THF, but to a lesser extent in benzene and diethyl ether. The introduction of protic *para* substituents such as COOH, PO(OH)(OEt), SO_3H and NH_2, markedly lowers their solubility in aprotic solvents. Water-soluble and -stable NCN-pincer complexes are obtained by introduction of a sulfonato, a monoalkylphosphonato, and, to a lesser extent, a carboxyl substituent.

^{195}Pt NMR studies: The chemical shift of the ^{195}Pt nucleus proved to be a valuable tool for probing the electron density on the metal centre of the various *para*-substituted pincer complexes. The ^{195}Pt chemical shift is highly sensitive towards subtle changes in geometry, oxidation state, and nature of the coordination sphere.[29] The magnetic shielding of the heavier nuclei contains contributions from both a paramagnetic and a diamagnetic shielding term. Both shielding terms are, to a different extent, sensitive towards σ and π contributions to the electronic charge on the metal centre. In general, an increase in electron density on the metal atom leads to an increase in shielding of the nucleus. In 1976, a broad, but dated survey of the ^{195}Pt chemical shifts for a wide variety of platinum complexes showed that no linear Hammett correlation is observed for several *para*-substituted diaryl platinum(II) complexes.[30] In contrast, Wu et al. later reported the synthesis and ^{195}Pt NMR analysis of ferrocenyl-based platinum complexes, for which a linear relation between the ^{195}Pt chemical shift and the σ_p Hammett substituent constants was found.[31]

To study the influence of the *para* substituent on the electron density of the pincer complexes by ^{195}Pt NMR spectroscopy, all other structural features in the complex, that is, halide and coordination geometry, were kept constant. ^{195}Pt chemical shifts were recorded for various *para*-substituted pincer complexes in $CDCl_3$ (0.1 M) and referenced to H_2PtCl_6. The chemical shift data are collected in Table 1 and fit reasonably well ($r = 0.974$) to the σ_p Hammett substituent constants reported by Taft (Figure 1).[32]

Table 1. ^{195}Pt chemical shifts of the NCN-pincer platinum(II) complexes [PtCl(NCN-Z)] and their corresponding Hammett substituent constants σ_p.

Z	σ_p[a]	$\delta(^{195}Pt)$ [ppm][b]
NO_2	0.78	−1802
CHO	0.42	−1843
COOH	0.45	−1899
I	0.18	−1923
H	0.0	−1959
$SiMe_3$	−0.07	−1963
*t*Bu	−0.20	−1988
OH	−0.37	−2009
NH_2	−0.66	−2045

[a] Taken from reference [32]; [b] 0.1 M in $CDCl_3$, referenced to $H_2[PtCl_6]$.

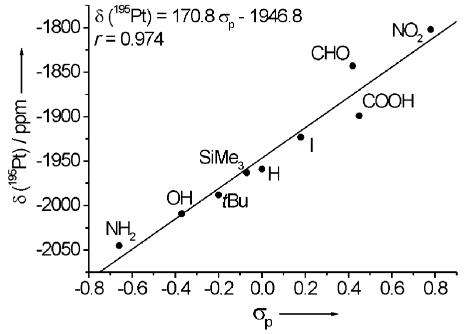


Figure 1. Correlation between the ^{195}Pt chemical shift of [PtCl(NCN-Z)] and the σ_p Hammett substituent constant.

DFT calculations: The general increase in chemical shielding resulting from an increase in negative charge has been correlated in many studies with the charge densities described by Mulliken population analysis (MPA).[29] However, a recent study showed that natural population analysis (NPA) charges on carboxylate groups had the strongest correlation with the corresponding pK_a values in a series of *para*-functionalised aromatic carboxylic acids.[33] To gain more insight into the influence of the substituent on the properties of the metal centre, several *para*-substituted NCN-pincer platinum(II) chloride complexes [PtCl(NCN-Z)] were investigated by the DFT method B3LYP/LANL2DZ[34] and natural bond order population analysis as implemented in Gaussian 98.[35] Of specific interest in our calculations was the influence of the *para* substituent on the calculated charges of the platinum centres and the calculated structural features in comparison with single-crystal X-ray structures.

Starting from structures calculated by MM2, further optimisation was performed with the DFT method B3LYP/LANL2MB (minimal basis set). These molecular structures were in turn used as starting geometries for calculations with the double-ζ basis set. The coordination environment, that is, bond lengths and angles, of the platinum centre were hardly affected by variations in the *para* substituent. The calculated bond lengths and angles of selected pincer complexes [PtCl(NCN-Z)] (Z = NMe_2, H, NO_2) covering the whole Hammett range, together with earlier reported crystallographic data[17c] are given in Table 2.

The Mulliken and natural population analysis charges on the platinum centre are given in Table 3. The calculated Mulliken charges show only a very modest correlation with the σ_p Hammett constants for the *para* substituents ($Q_{Mulliken} = 0.022\sigma_p + 0.233$; $r = 0.78648$), whereby especially the substituents NH_2, NMe_2 and OH deviate from the linear fit. In contrast, the NPA charges perform well in this correlation ($Q_{NPA} = 0.010\sigma_p + 0.3045$; $r = 0.93589$), as is visualised in Figure 2. Correlation of the experimental ^{195}Pt chemical shift with the calculated NPA charges afforded an even better fit

Table 2. Selected bond lengths [Å] and angles [°] for the experimental structure of [PtCl(NCN-H)][17c] (X-ray) and calculated (DFT-B3LYP/LANL2DZ) geometries of [PtCl(NCN-Z)].

	[PtCl(NCN-H)] (X-ray)	[PtClNCN-NMe_2]	[PtCl(NCN-H)]	[PtClNCN-NO_2]
Pt–C_{ipso}	1.907(5)	1.944	1.944	1.933
Pt–Cl	2.407(1)	2.540	2.533	2.514
Pt–N	2.083(3)	2.131	2.129	2.130
N-Pt-N	164.26(13)	164.4	165.0	165.4
Cl-Pt-C_{ipso}	177.05(12)	180.0	180.0	180.0

Table 3. Calculated Mulliken charges $Q_{Mulliken}$ and natural population analysis charges Q_{NPA} on platinum (DFT-B3LYP/LANL2DZ) in [PtCl(NCN-Z)] and their corresponding Hammett substituent constants σ_p.

Z	σ_p[a]	$Q_{Mulliken}$	Q_{NPA}
NO_2	0.78	0.2646	0.3167
COOH	0.45	0.2434	0.3068
I	0.18	0.2309	0.3055
SMe	0.00	0.2243	0.3033
H	0.00	0.2190	0.3027
OH	−0.37	0.2281	0.3016
NH_2	−0.66	0.2249	0.2976
NMe_2	−0.83	0.2213	0.2979

[a] Taken from ref. [32].

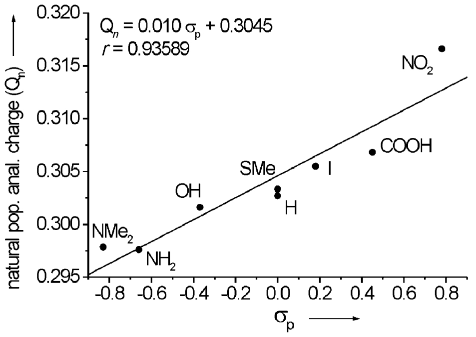


Figure 2. Correlation between the calculated natural population analysis (NPA) charges (DFT-B3LYP/LANL2DZ) of [PtCl(NCN-Z)] and the σ_p Hammett substituent constant.

($\delta(^{195}Pt) = 1.31 \times 10^4 Q_{NPA} - 5922$; $r = 0.98106$). This correlation is graphically presented in Figure 3.

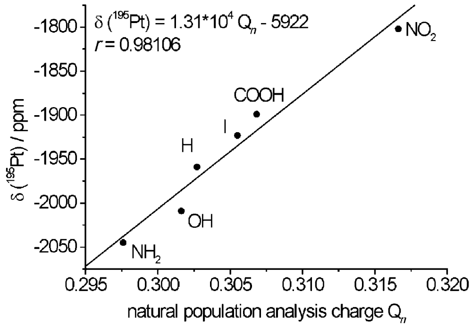


Figure 3. Correlation between the calculated natural population analysis (NPA) charges (DFT-B3LYP/LANL2DZ) of [PtCl(NCN-Z)] and their corresponding ^{195}Pt chemical shifts.

Table 4. pK_a for **34** in MeOH and H_2O/MeOH (1/1) and resulting σ_p values for the *para*-PtI group.

Solvent	pK_a	ρ[a]	σ_p[b]
MeOH	8.3	1.537	−1.18
H_2O/MeOH (1/1)	6.0	1.085	−0.72

[a] Reaction constant, taken from reference [51]. [b] The tabulated σ_m value of the $CH_2(NMe_2)$ group is 0.00 (see reference [32]).

Hammett σ_p values for the *para*-PtI group: The influence of the *para* substituent of the NCN-pincer complexes on the properties of the metal centre can be rationalized by Hammett relations, as described above. However, it is of physical-inorganic interest to determine a substituent constant for the organometallic *para*-PtX group itself, as was done earlier for cobaloxime complexes by Brown et al.[36] For this purpose the pK_a value of [PtI(NCN-COOH)] (**34**) was determined in methanol and in a H_2O/MeOH (1/1). The experimentally determined pK_a values and the derived σ_p values of the *para*-PtX group are listed in Table 4.

Structures in the solid state: Crystal structures of various (*para*-functionalised) NCN-pincer palladium and platinum halide complexes were determined earlier.[26,37] Crystals suitable for X-ray crystallographic structure determination of [PtI(NCN-COOH)] (**34**) were grown by vapour diffusion of pentane into a saturated solution in toluene/diethyl ether (1/1). From these apolar solvents, **34** crystallises as the hydrogen-bonded dimer. This is in contrast with an earlier reported crystal structure of **34** obtained from DMSO solution,[26] and with a structurally related carboxyl-functionalised CNN-pincer palladium complex.[38] Figure 4 shows the molecular structure of **34** in the crystal, together with a

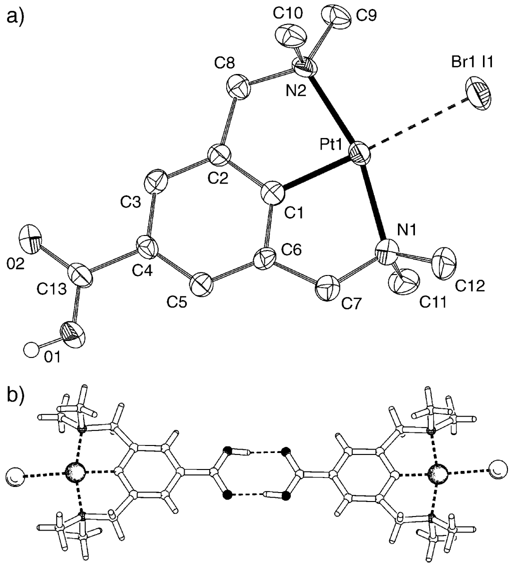


Figure 4. a) Displacement ellipsoid plot (50% probability level) of [PtI(NCN-COOH)] (**34**). The halogen position is occupied by 19% Br and 81% I, which were constrained to the same position and displacement parameters. Hydrogen atoms, except that of the carboxyl group, have been omitted for clarity. b) Packing graph of **34** showing the dimeric structure formed by hydrogen bonding.

packing graph. Selected bond lengths, angles, and dihedral angles are collected in Table 5. The crystals contain disordered molecules of co-crystallised toluene solvent.

Table 5. Selected bond lengths [Å], angles [°], and torsion angles [°] of **22a** and **34**.

[PdCl(NCN-CH$_2$OH)] (**22a**)		[PtI(NCN-COOH)] (**34**)	
Pd1–C1	1.9174(18)	Pt1-C1	1.921(5)
Pd1–N1	2.1083(15)	Pt1-N1	2.088(5)
Pd1–N2	2.1066(15)	Pt1-N2	2.098(5)
Pd1–Cl1	2.4392(5)	Pt1-Br1/I1	2.7020(5)
C1-Pd1-N1	81.33(7)	C1-Pt1-N1	81.5(2)
C1-Pd1-N2	80.85(7)	C1-Pt1-N2	81.9(2)
C1-Pd1-Cl1	173.08(5)	C1-Pt1-Br1/I1	175.29(14)
N1-Pd1-N2	161.93(6)	N1-Pt1-N2	163.38(18)
Pd1-N1-C7-C2	−32.76(15)	Pt1-N1-C7-C6	31.5(5)
Pd1-N2-C10-C6	−32.64(15)	Pt1-N2-C8-C2	30.0(5)

Because of halide scrambling due to incomplete exchange of bromide for iodide on the platinum centre in this sample, the crystal contained about 19 % bromide and about 81 % iodide on the metal centre, as determined by refinement of the occupancies. The Br1/I1 atoms were constrained on the same positions and to the same displacement parameters. Therefore, the observed Pt1–Br1/I1 distance is a weighted average of both contributions. The metal centre adopts a distorted square-planar geometry, and the coordination plane of platinum is almost coplanar with the plane of the aryl ring. The two five-membered metallacycles are puckered in the same direction with Pt1-N1-C7-C6 and Pt1-N2-C8-C2 torsion angles of 31.5(5) and 30.0(5)°, respectively. The hydrogen bonds between the carboxyl groups have H10–O1, H10···O2, and O1–O2 bond lengths of 0.89(8), 1.71(9), and 2.595(6) Å, respectively, and an almost linear O1-H10-O2 angle of 173(8)°.

Crystals suitable for X-ray crystallographic structure determination of [PdCl(NCN-CH$_2$OH)] (**22a**) were grown by slow vapour diffusion of diethyl ether into a concentrated solution of **22a** in dichloromethane. Figure 5 shows the molecular structure and a packing graph. In the solid state, **22a** is self-assembled into dimers by hydrogen bonding. Preliminary NMR studies indicate that dimeric (or oligomeric) structures persist in CDCl$_3$ solution at room temperature.

The geometry around the palladium(II) centre is distorted square-planar, and the metal is bound to the chloro and the η^3-*mer* NCN ligand. The bond lengths and angles are similar to those generally encountered in NCN-pincer palladium(II) complexes. The five-membered metallacycles are puckered in the same direction, with Pd1-N1-C7-C2 and Pd1-N2-C10-C6 torsion angles of −32.76(15) and −32.64(15)°, respectively. Selected bond lengths, angles, and dihedral angles for **22a** are given in Table 5.

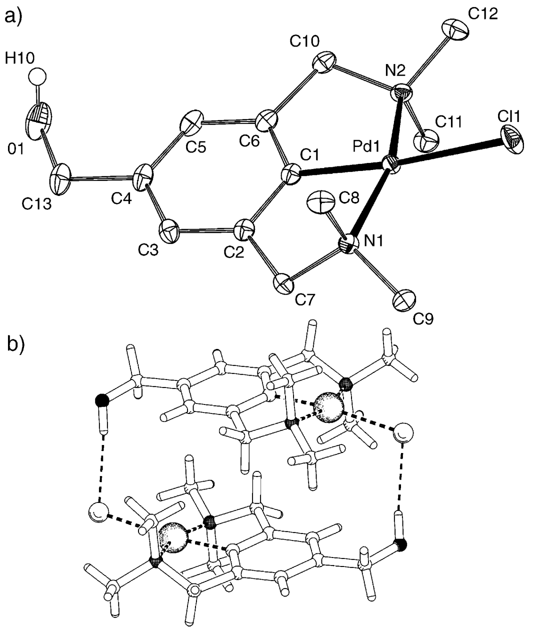


Figure 5. a) Displacement ellipsoid plot (50 % probability level) of [PdCl(NCN-CH$_2$OH)] (**22a**). Hydrogen atoms, except that of the hydroxyl group, have been omitted for clarity. b) Packing graph of **22a** showing the hydrogen bonding in the dimeric substructure.

Discussion

In general, direct modification of ligands in organometallic or coordination complexes is hampered by two major features. First, the complex is often kinetically not stable enough to allow organic transformations directly on a ligand bound to the metal center. Second, metalation procedures may be incompatible with a functional group required for further (organic) modification. This especially applies to the synthesis of organometallic complexes in which a covalent metal–carbon bond is to be formed. Apparently these drawbacks are not encountered in the synthesis of *para*-functionalised NCN palladium and platinum complexes. Due to the exceptional stability of these complexes and the availability of various metalation procedures, we were able to synthesise a wide range of *para*-substituted NCN-pincer palladium and platinum complexes. The present organic transformations carried out directly on the pincer-metal complexes (approach II) can be considered to be unconventional in organometallic synthesis and unexpected on the basis of their open structures, that is, steric accessibility of the square-planar arylpalladium or -platinum starting materials. The preparation and isolation of pincer sulfonate complexes **24** (Pd) and **25** (Pt) illustrates the kinetic inertness of both the C$_{ipso}$–metal and N–metal bonds in the starting NCN-pincer complexes under the highly acidic and electrophilic reaction conditions employed in aromatic sulfonation. Moreover, the possibility to selectively lithiate NCN-pincer platinum complex **15** at the *para* position shows the resistance of the NCN-pincer platinum complexes towards highly basic and nucleophilic reaction conditions. Although the per gramme value of the material is increased upon metalation of the ligand, exploration of approach II can be advantageous to open up a multitude of synthetic routes towards new ranges of ECE-Z pincer platinum derivatives, which would be inaccessible by approach I.

The synthesis of [PdX(NCN-CH$_2$OH)] (**22**, X = Cl, Br) serves to illustrate the synthetic flexibility offered by the

NCN-pincer ligand framework. A straightforward route starts from *para*-bromo NCN-pincer ligand **16**, which can be synthesised in two steps from commercially available materials.[5b] However, because this route involves lithiation of C_{ipso} its scope is limited to *para* substituents which are inert or can be protected during the lithiation step. After introduction of the inert $SiMe_3$ substituent on C_{ipso} by lithiation, selective palladation can be performed directly or after further transformations of the *para* substituent. A second route starts from the bifunctional ligand **9**, which is available from a multistep synthesis but allows a broader range of substituents due to the mild oxidative addition procedures used for metalation. In fact, it is the method of choice for protic or electrophilic *para* substituents.

While in this study only selected *para*-substituted pincer complexes have been prepared, their syntheses represent the basic strategies available. This broadens the scope of possible *para* substituents to virtually any organic functional group.[21,22,23,39] Extension of the presented synthetic routes to PCP- and SCS-pincer complexes can be envisaged, broadening the potential even more.

We found that several prerequisites should be taken into account when performing reactions on metalated pincer ligands. The palladium, and to a lesser extent the platinum pincer complexes, can decompose by reductive elimination on prolonged heating or in highly concentrated solutions, which leads to formation of palladium or platinum black. The cationic platinum complexes $[Pt(OH_2)(NCN)]X$ can, in addition, add to activated alkyl halides (benzyl bromide, methyl iodide), and in certain cases this leads to the formation of stable Wheland arenium intermediates or decomposition products.[40] Furthermore, halide scrambling on the metal centre is a side reaction encountered in the synthesis. Facile halide abstraction followed by addition of an appropriate halide source affords a single product.

Properties of the NCN-pincer complexes: The influence of the *para* substituent on the stability of the metal–carbon bond can be rationalised by considering substituent effects in Hammett relations. The nitro substituent of NCN-pincer complexes **10** and **11** withdraws electron density from the aromatic ring and thus polarizes the C_{ipso}–metal bond in the direction of C_{ipso} and consequently makes the metal centre more positively charged. The lowered electron density on the metal centre can be expected to make it less prone to reductive elimination, which would lead to the formation of zero-valent metal particles. The amino-substituent in complexes **12** and **13** donates electron density to the aromatic ring and leads to a less polarised C_{ipso}–metal bond compared to **10** and **11**. A complex with a more electron rich metal centre is expected to decompose more readily by reductive processes. Indeed, this behaviour is observed in the synthesis and handling of the metalated pincer systems. While a black precipitate, presumably palladium or platinum black, is formed during the synthesis of **12** and **13** and on prolonged standing of their concentrated solutions, these reductive elimination processes have not been observed for the nitro-substituted pincers **10** and **11**. The palladium and platinum pincers bearing highly acidic groups, for example, sulfonic acids **24** and **25**, are highly hygroscopic and decompose slowly in moist air with formation of palladium and platinum black, possibly via pathways involving protonation of the donor arms, followed by cleavage of the metal–carbon bond. Interestingly, these decomposition reactions were not observed in dilute aqueous solutions.

The solubility of the *para*-functionalised pincer complexes is dominated by the *para* substituent. The formation of intermolecular hydrogen bonds between protic *para* substituents and suitable Lewis bases such as the halo ligand on the metal centre, can give rise to the formation of oligomeric or polymeric structures and hence lower solubilities in common organic solvents. The formation of intermolecular hydrogen bonds is most pronounced in the solid state. Supramolecular assemblies of NCN-pincer complexes, formed by $M-Cl\cdots H$ hydrogen bonds, were earlier observed for the *para*-hydroxyl-[17b] and *para*-ethynyl-functionalised [20] platinum(II) complexes. These types of *para* substituents induced the formation of infinite linear α-type networks. Despite the lower acidity of a benzylic hydroxyl functional group compared to an aromatic one, it can still act as hydrogen-bonding donor towards the chloro ligand on the metal center. The flexibility of the hydroxymethyl substituent in palladium(II) complex **22a** makes dimerisation, instead of formation of linear polymers, possible. Since the relative position of the aryl rings in the crystal lattice is not optimal for attractive π-stacking interactions, the origin of the dimerisation can be completely attributed to the formation of the hydrogen bonds. Interestingly, similar $M-Cl\cdots HO$ dimerisation was observed for the structurally related hydroxyl-functionalised NCN-palladium complex $[PdCl(NCN\text{-}SiMe_2\text{-}(CH_2)_6OH]$. This complex has an extended spacer between the aryl ring and the hydroxyl group, which results in the formation of large hydrogen-bonded squares.[41] Another hydrogen-bonding motif is observed in the X-ray structure of **34**. The crystal structure of a DMSO solvate of **34** was published earlier.[26] While in this crystal structure the carboxyl group forms a hydrogen bond to a co-crystallised DMSO molecule, crystallisation from apolar solvents resulted in a molecular structure with the familiar hydrogen-bonding motif for carboxylic acids. This hydrogen bonding motif is favoured over others, such as hydrogen bonding to the halo ligand, as can be expected on the basis of the poor hydrogen-bond acceptor properties of the iodo ligand compared to the more pronounced acceptor properties of the "harder" chloride anions (structure of **22a**). Infrared analysis (DRIFT) of powderous **34** in KBr confirmed that this dimeric structure is the predominant one in the solid state (broad absorption at 2750–2270 cm^{-1}).

Hammett relations: The linear correlation of the ^{195}Pt chemical shift with the σ_p Hammett substituent constants allows the use of NMR spectroscopy as a sensitive probe for the electron density on the metal centre. Since all other structural features of the platinum complexes were found to remain constant (X-ray structures, DFT calculations), changes in shielding can be attributed solely to the *para* substituent. The calculated molecular structures of the pincer platinum complexes resemble the experimental X-ray structures quite well. The calculated parameters are only slightly overestimated (by $<2\%$) with respect to the X-ray structure. The calculated Pt–Cl bond length deviates significantly from the experimental value and is overestimated by 5%. These results allow the use of DFT calculations to study pincer complexes in more detail.[42] The linear Hammett correlation found in the ^{195}Pt NMR studies is well reproduced for the NPA charges obtained from DFT calculations, and thus natural bond order analysis is a powerful tool for probing the electron density on the platinum nucleus. An even better correlation was obtained between these calculated charges and the experimental ^{195}Pt chemical shifts. In contrast, calculated Mulliken charges did not correlate linearly with the σ_p values. Especially the Mulliken charges on platinum for complexes with the substituents NH_2, NMe_2, and OH deviate markedly from the other values in the DFT calculations. Ample evidence is available that natural population analysis (NPA), in contrast to Mulliken population analysis (MPA), is less sensitive to the basis set.[43] In addition, NPA also considers the spatial extent of the atom.

When considering the *para*-PtX group as a *para* substituent, its σ_p value can be determined from the pK_a values in different solvents. The thus-determined values (Table 4) place this group in the realm of strongly electron donating substituents such as NH_2 and NR_2, which donate electron density to the *para*-position of the aromatic ring. This is in line with the observed facile electrophilic substitution of pincer complexes with chlorosulfo substituents.

Conclusion

The present synthetic routes for the synthesis of *para*-functionalised NCN-palladium(II) and -platinum(II) complexes are highly versatile and allow functionalisation with substituents covering the complete range of Hammett constants. The possibility to perform organic transformations on the metalated NCN-ligands makes their application as building blocks in the construction of new (macromolecular) organometallic materials facile. Additionally, both the transition metal(halide) and selected substituents are able to participate in supramolecular assemblies by interactions such as hydrogen bonding, ligand coordination and π–π stacking. This is of special interest for the application of NCN-pincer complexes as multifunctional building blocks for crystal-engineering purposes. The direct and linear influence of the *para* substituent on the platinum centre, as indicated by ^{195}Pt NMR studies and DFT calculations, can be extended to *para*-substituted pincer complexes of other metals. The catalytic and/or optical properties of these complexes can thus be optimised by choosing the appropriate *para* substituent on the basis of its σ_p Hammett substituent constant.

Experimental Section

General: All reactions involving air- or moisture-sensitive reagents were performed by standard Schlenk techniques unless stated otherwise. Benzene, pentane, hexane, THF and Et_2O were distilled from Na/benzophenone and CH_2Cl_2 from CaH_2 prior to use. $[Pd_2(dba)_3]\cdot CHCl_3$,[44] and $[\{Pt(p\text{-tol})_2SEt_2\}_2]$[45] were synthesised according to literature procedures. All other reagents were obtained commercially and were used without further purification. Elemental analyses were performed by Kolbe Mikroanalytisches Laboratorium (Müllheim, Germany). ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Inova 300 spectrometer (operating at 300 and 75 MHz, respectively) or a Varian Mercury 200 spectrometer (operating at 200 and 50 MHz, respectively). Spectra were recorded in $CDCl_3$ or C_6D_6 at room temperature, unless stated otherwise, and were referenced to TMS ($\delta = 0.00$ ppm). The syntheses of **2** and **8**,[5b] **4**,[46] **5**,[46b] **16**,[47] **23**,[23] **6**, **9** (alternative method), **14**, **15**, **20**, **21**, **28**, **29**, **32**, **33**, **37**, and **38**[21] were reported earlier.

1-Trimethylsilyl-2,6-bis[(dimethylamino)methyl]benzene (3): 1,3-Bis[(dimethylamino)methyl]benzene (15.25 g, 79.4 mmol) was dissolved in hexane (100 mL) and cooled to −80 °C. *n*-Butyllithium (50 mL, 1.6 M in hexane, 79.4 mmol) was added dropwise to this solution over 10 min. The reaction mixture was allowed to reach ambient temperature and stirred overnight. A freshly prepared solution of trimethylsilyl trifluoromethyl sulfonate (15.4 mL, 87.4 mmol) in THF (50 mL) was added at 0 °C. After stirring for an additional hour at room temperature all volatile substances were evaporated in vacuo. Extraction with hexane (3 × 100 mL) afforded after evaporation of the solvent a yellow-brown oil. This was further purified by flash vacuum distillation to give **3** as a colourless oil (16.12 g, 60 mmol, 77%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 7.36$ (d, $^3J(H,H) = 7.3$ Hz, 2H; ArH), 7.20 (t, $^3J(H,H) = 7.3$ Hz, 1H; ArH), 3.53 (s, 4H; CH_2N), 2.06 (s, 12H; NMe_2), 0.52 ppm (s, 9H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 146.8$, 138.6, 129.7, 128.6, 66.0, 45.0, 3.4 ppm; elemental analysis (%) calcd for $C_{15}H_{28}N_2Si$: C 68.12, H 10.67, N 10.95; found: C 68.20, H 10.58, N 10.83.

4-Nitro-1-trimethylsilyl-2,6-bis[(dimethylamino)methyl]benzene (7): Compound **3** (3.88 g, 14.6 mmol) was added slowly over 1 h to concentrated H_2SO_4 (10 mL) at 0 °C. Concentrated HNO_3 (2 mL) was added while maintaining the temperature below 10 °C. The mixture was allowed to reach ambient temperature and was stirred for 3 h, after which it was poured onto 100 g of crushed ice. The acidic mixture was neutralised with KOH and subsequently extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and isolated after removal of the solvent in vacuo as a 20/80 mixture of **7** and 4-nitro-2,6-bis[(dimethylamino)methyl]benzene. Purification by column chromatography (Et_2O/hexanes 1/1, 3% TEA, basic alumina) yielded 0.64 g (2.1 mmol, 14%) of **7** as colourless crystals. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 8.17$ (s, 2H; ArH), 3.28 (s, 4H; CH_2N), 1.86 (s, 12H; NMe_2), 0.34 ppm (s, 9H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 149.1$, 148.5, 147.8, 122.5 (Ar), 65.0 (CH_2N), 44.8 (NMe_2), 2.8 ppm ($SiMe_3$); elemental analysis (%) calcd for $C_{15}H_{27}N_3O_2Si$: C 58.21, H 8.79, N 13.58, Si 9.08; found: C 58.15, H 8.71, N 13.62, Si 8.94.

4-Nitro-NCN-palladium(II) chloride (10a): $Pd(OAc)_2$ (85.0 mg, 0.38 mmol) was added at once to a solution of **7** (111.7 mg, 0.36 mmol) in freshly distilled methanol (10 mL). The mixture was stirred for 2 h followed by addition of LiCl (0.15 g, 3.6 mmol), which resulted in the immediate formation of a white precipitate. The reaction mixture was stirred for 1 h, all volatile substances were evaporated in vacuo, and the residue was dissolved in CH_2Cl_2 (60 mL) and washed with water. The dried ($MgSO_4$) organic phase was filtered over Celite, and subsequent evaporation of the solvent in vacuo afforded pure **10** (132.8 mg, 0.35 mmol, 97%) as a yellowish solid. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.61$ (s, 2H; ArH), 4.02 (s, 4H; CH_2N), 2.88 ppm (s, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 167.5$, 145.6, 145.4, 115.0 (Ar), 74.0 (CH_2N), 52.9 ppm (NMe_2); elemental analysis (%) calcd for $C_{12}H_{18}ClN_3O_2Pd$: C 38.11, H 4.80, N 11.11; found: C 38.19, H 4.91, N 11.02.

4-Nitro-NCN-platinum(II) bromide (11): 1-Bromo-4-nitro-2,6-bis[(dimethylamino)methyl]benzene (**6**) (0.57 g, 1.80 mmol) was dissolved in benzene (10 mL) and added dropwise to a suspension of $[\{Pt(p\text{-tol})_2(SEt)_2\}_2]$ (0.84 g, 0.90 mmol) in benzene (15 mL). The mixture was refluxed for 3 h, and on cooling a yellow precipitate formed. Et_2O (75 mL) was added and the precipitate was isolated by centrifugation. The product was washed with Et_2O (2 × 90 mL) to yield pure **11** as a yellow solid (0.89 g, 1.73 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.74$ (s, 2H; ArH), 4.09 (s, $^3J(H,Pt) = 45.6$ Hz, 4H; CH_2N), 3.13 ppm (s, $^3J(H,Pt) = 38.4$ Hz, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 157.5$ (C_{para}), 144.7 (C_{ipso}), 143.9 ($^2J(C,Pt) = 81.1$ Hz, C_{ortho}), 115.5 ($^3J(C,Pt) = 37.2$ Hz, C_{meta}), 76.6 ($^2J(C,Pt) = 59.8$ Hz, CH_2N), 55.0 ppm ($^2J(C,Pt) = 13.4$ Hz, NMe_2); elemental analysis (%) calcd for $C_{12}H_{18}BrN_3O_2Pt$: C 28.19, H 3.55, N 8.22; found: C 28.29, H 3.51, N 8.16.

4-Amino-NCN-palladium(II) bromide (12): A solution of **8** (2.00 g, 7.0 mmol) in benzene (20 mL) was added to a solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (5.66 g, 7.0 mmol) in benzene (50 mL). The mixture was stirred overnight and THF (5 mL) was added. After stirring for an additional hour all volatile substances were removed in vacuo, and the residue was redissolved in CH_2Cl_2 (10 mL). The dark brown solution was filtered over Celite, and **12** precipitated upon addition of Et_2O (80 mL). The solid was washed four times with Et_2O (90 mL) and dried in vacuo to afford **12** as a brown solid (2.09 g, 5.3 mmol, 76 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.20$ (s, 2H; ArH), 3.89 (s, 4H; CH_2N), 2.94 ppm (s, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 149.4$, 145.8, 129.2, 107.4 (Ar), 74.7 (CH_2N), 54.0 ppm (NMe_2); elemental analysis (%) calcd for $C_{12}H_{20}BrN_3Pd$: C 36.71, H 5.13, N 10.70; found: C 36.58, H 5.10, N 10.64.

4-Amino-NCN-platinum(II) bromide (13): $[\{Pt(p\text{-tol})_2SEt_2\}_2]$ was added at once to a solution of **8** (0.80 g, 2.8 mmol) in benzene (1.31 g, 1.4 mmol). The mixture was refluxed until a clear solution was obtained, which was kept at reflux temperature for an additional 15 min followed by evaporation of all volatile substances. The residue was dissolved in CH_2Cl_2 (10 mL) and filtered over Celite. Precipitation with Et_2O (80 mL) and decantation afforded a brownish powder. This powder was washed twice with Et_2O (90 mL) and dried in vacuo to afford **13** as a light brown solid (1.10 g, 2.3 mmol, 82 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.26$ (s, 2H; ArH), 3.10 (s, $^3J(H,Pt) = 45.8$ Hz, 4H; CH_2N), 3.13 ppm (s, $^3J(H,Pt) = 38.2$ Hz, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 144.0$, 143.1, 132.4, 107.0 (Ar), 77.4 (CH_2N), 55.1 ppm (NMe_2); elemental analysis (%) calcd for $C_{12}H_{20}BrN_3Pt$: C 29.95, H 4.19, N 8.73; found: C 29.78, H 4.23, N 8.56.

3,5-Bis[(dimethylamino)methyl]benzaldehyde (17): *t*BuLi (1.5 M in hexanes, 40 mL, 58 mmol) was added dropwise to a solution of **16** (7.82 g, 29 mmol) in Et_2O (250 mL) at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, and DMF (4.5 mL, 58 mmol) was added at once. The mixture was allowed to reach room temperature, stirred for an additional hour and carefully quenched with water (50 mL). The organic phase was washed with 1 M NaOH and brine. Subsequent drying over $MgSO_4$ and removal of all volatile substances afforded **17** as a yellow oil (6.40 g, 29 mmol, 99 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.02$ (s, 1H; CHO), 7.72 (s, 2H; ArH), 7.55 (s, 1H; ArH), 3.47 (s, 4H; CH_2N), 2.23 ppm (s, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 191.1$ (CHO), 140.6, 136.9, 134.6, 128.4 (Ar), 63.3 (CH_2N), 44.8 ppm (NMe_2); elemental analysis (%) calcd for $C_{13}H_{20}N_2O$: C 70.87, H 9.15, N 12.72; found: C 70.81, H 9.22, N 12.85.

1-Hydroxymethyl-3,5-bis[(dimethylamino)methyl]benzene (18): $NaBH_4$ (1.21 g, 31.9 mmol) was added in portions to a solution of **17** (6.40 g, 29 mmol) in MeOH (100 mL). After addition, the mixture was stirred for 3 h at room temperature, all volatile substances were removed and the residue was redissolved in Et_2O (100 mL). The organic layer was washed with water (2 × 50 mL) and brine and dried over $MgSO_4$. Removal of all volatile substances in vacuo afforded **18** as a colourless oil (6.12 g, 27.6 mmol, 95 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.23$ (s, 2H; ArH), 7.13 (s, 1H; ArH), 4.64 (s, 2H; CH_2O), 3.41 (s, 4H; CH_2N), 2.22 ppm (s, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 142.8$, 135.7, 130.0, 128.1 (Ar), 63.9 (CH_2O), 62.9 (CH_2N), 44.8 ppm (NMe_2); elemental analysis (%) calcd for $C_{13}H_{22}N_2O$: C 70.23, H 9.97, N 12.60; found: C 70.36, H 10.08, N 12.69.

1-Hydroxymethyl-4-trimethylsilyl-3,5-bis[(dimethylamino)-methyl]benzene (19): a) A mixture of *tert*-butyldimethylsilyl chloride (1.91 g, 12.7 mmol) and imidazole (1.44 g, 21.1 mmol) in THF (50 mL) was stirred for 30 min at room temperature. Benzyl alcohol **18** (2.35 g, 10.6 mmol) in THF (20 mL) was added at once. The mixture was refluxed overnight and treated with freshly distilled MeOH (2 mL). All volatile substances were evaporated in vacuo, and the residue was redissolved in hexane (150 mL), washed with water (2 × 50 mL) and dried over $MgSO_4$. Removal of the solvent in vacuo afforded 3,5-bis[(dimethylamino)methyl]benzyl *tert*-butyldimethylsilyl ether as a yellow oil (2.64 g, 74 %). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.16$ (s, 3H; ArH), 4.72 (s, 2H; CH_2O), 3.43 (s, 4H; CH_2N), 2.42 (s, 12H; NMe_2), 0.92 (s, 9H; *t*Bu), 0.09 ppm (s, 6H; $SiMe_2$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 141.6$, 138.1, 128.8, 126.2 (Ar), 64.9 (CH_2O), 64.0 (CH_2N), 45.1 (NMe_2), 26.0 (CMe_3), 18.4 (CMe_3), −5.2 ppm ($SiMe_2$); elemental analysis (%) calcd for $C_{19}H_{36}N_2OSi$: C 67.80, H 10.78, N 8.32, Si 8.34; found: C 67.94, H 10.70, N 8.19, Si 8.46.

b) *n*BuLi (4.9 mL, 1.6 M in hexanes, 7.8 mmol) was added dropwise to a solution of 3,5-bis[(dimethylamino)methyl]benzyl *tert*-butyldimethylsilyl ether (2.64 g, 7.8 mmol) in hexane (50 mL) at −78 °C. The mixture was allowed to reach room temperature and was stirred for 6 h. A solution of trimethylsilyl trifluoromethanesulfonate (2.27 mL, 11.8 mmol) in THF (25 mL) was added dropwise at 0 °C, and the mixture stirred for an additional hour. All volatile substances were removed in vacuo and the product was extracted with hexane (3 × 50 mL). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over $MgSO_4$. Removal of the solvent afforded 4-trimethylsilyl-3,5-bis[(dimethylamino)-methyl]benzyl *tert*-butyldimethylsilyl ether as a yellow oil (2.48 g, 77 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.27$ (s, 2H; ArH), 4.72 (s, 2H; CH_2O), 3.53 (s, 4H; CH_2N), 2.13 (s, 12H; NMe_2), 0.95 (s, 9H; *t*Bu), 0.38 (s, 9H; $SiMe_3$), 0.10 ppm (s, 6H; $SiMe_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 146.4$, 141.4, 136.9, 126.2 (Ar), 65.4 (CH_2O), 64.8 (CH_2N), 45.0 (NMe_2), 25.9 (CMe_3), 18.4 (CMe_3), 3.2 ($SiMe_3$), −5.2 ppm ($SiMe_2$); elemental analysis (%) calcd for $C_{22}H_{44}N_2OSi_2$: C 64.64, H 10.85, N 6.85, Si 13.74; found: C 64.54, H 10.92, N 6.78, Si 13.65.

c) $NEt_3\cdot 3HF$ (2.97 mL, 18.2 mmol) was added to a solution of 4-trimethylsilyl-3,5-bis[(dimethylamino)methyl]benzyl *tert*-butyldimethylsilyl ether (2.48 g, 6.1 mmol) in THF (50 mL). The solution was stirred overnight at room temperature, after which all volatile substances were removed in vacuo. The residue was redissolved in CH_2Cl_2 (250 mL) and washed twice with aqueous NaOH (1 M, 50 mL) and once with brine. Removal of the solvent after treatment with $MgSO_4$ afforded **19** as a colourless oil (1.40 g, 4.8 mmol, 78 %). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.34$ (s, 2H; ArH), 4.66 (s, 2H; CH_2O), 3.56 (s, 4H; CH_2N), 2.14 (s, 12H; NMe_2), 0.36 ppm (s, 9H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 146.4$, 141.6, 130.4, 127.1 (Ar), 65.3 (CH_2O), 65.2 (CH_2N), 45.2 (NMe_2), 3.6 ppm ($SiMe_3$); elemental analysis (%) calcd for $C_{16}H_{30}N_2OSi$: C 65.25, H 10.27, N 9.51; found: C 65.15, H 10.21, N 9.46.

4-Hydroxymethyl-NCN-palladium(II) chloride (22a): $[Pd(OAc)_2]$ (0.47 g, 2.1 mmol) was added to a stirred solution of **19** (0.59 g, 2.0 mmol) in MeOH (20 mL). The solution was stirred for 4 h, and an excess of LiCl (0.85 g, 20 mmol) was added, resulting in a yellow suspension. The volatile substances were removed in vacuo, and the residue was redissolved in CH_2Cl_2 (20 mL) and carefully filtered over Celite. Addition of hexane (80 mL) to the filtrate resulted in precipitation of **22a** as a yellow solid (0.63 g, 1.7 mmol, 87 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.82$ (s, 2H; ArH), 4.58 (s, 2H; CH_2O), 3.99 (s, 4H; CH_2N), 2.96 ppm (s, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 156.1$, 145.3, 137.9, 119.2 (Ar), 74.8 (CH_2N), 65.6 (CH_2N), 53.3 ppm (NMe_2); elemental analysis (%) calcd for $C_{13}H_{21}ClN_2OPd$: C 42.99, H 5.83, N 7.71; found: C 42.95, H 5.75, N 7.61.

4-SO_3H-NCN-palladium(II) chloride (24): Chlorosulfonic acid (0.37 g, 3.14 mmol) was added to a cooled (0 °C) solution of **4a** (0.95 g, 2.86 mmol) in CH_2Cl_2 (10 mL), and the mixture stirred at ambient temperature overnight. After evaporation of all volatile substances in vacuo, the crude product was extracted with boiling acetonitrile. Slow precipitation on cooling to room temperature afforded **24** as a brown solid (0.21 g, 0.51 mmol, 18 %). ^1H NMR (300 MHz, $[D_6]DMSO$, 25 °C, TMS): $\delta = 9.77$ (brs, 1H; SO_3H), 7.61 (s, 2H; ArH), 4.36 (s, 4H; CH_2N), 2.77 ppm (s, 12H; NMe_2); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]DMSO$, 25 °C, TMS): $\delta = 150.3$, 134.6, 131.4, 129.9 (Ar), 59.9 (CH_2N), 42.6 ppm (NMe_2); elemental analysis (%) calcd for $C_{12}H_{19}ClN_2O_3PdS$: C 34.88, H 4.63, N 6.78; found: C 34.71, H 4.57, N 6.68.

4-SO_3H-NCN-platinum(II) chloride (25): Chlorosulfonic acid (0.55 g, 4,74 mmol) was added to a cooled (0 °C) solution of **5a** (1.01 g, 2.37 mmol) in CH_2Cl_2 (10 mL), and the mixture stirred at ambient temperature overnight. Evaporation of all volatile substances in vacuo afforded a red solid, which analysed as a mixture of isomers. The *para* isomer selectively precipitated from a boiling saturated solution of the crude product in methanol. Pure **25** was obtained after recrystallisation from methanol as a yellow solid (0.30 g, 0.59 mmol, 25 %). ^1H NMR

(300 MHz, [D$_6$]DMSO 25 °C, TMS): $\delta = 7.52$ (s, 2H; ArH), 4.39 (s, ^3J(H,Pt) = 28.8 Hz, 4H; CH$_2$N), 2.91 ppm (s, ^3J(H,Pt) = 28.8 Hz, 12H; NMe$_2$); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 144.9$, 140.9, 127.6, 123.1 (Ar), 76.2 (CH$_2$N), 56.5 ppm (NMe$_2$); elemental analysis (%) calcd for $C_{12}H_{19}ClN_2O_3PtS$: C 28.72, H 3.82, N 5.58; found: C 28.79, H 3.90, N 5.49.

1-Bromo-2,6-bis[(dimethylamino)methyl]phenyl methyl sulfide (26): A solution of **9** (1.00 g, 2.5 mmol) in Et$_2$O was treated with *t*BuLi (3.3 mL, 1.5 M in pentane, 5 mmol) at −100 °C. The solution was stirred for 10 min at −100 °C, and dimethyldisulfide (0.4 g, 3.8 mmol) was added at once. The mixture was allowed to reach room temperature, and all volatile substances were removed in vacuo. The residue was redissolved in pentane (50 mL), washed with water (2 × 25 mL) and dried over MgSO$_4$. Removal of the volatile substances afforded **26** as a colourless oil (0.65 g, 2.1 mmol, 82 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.51$ (s, 2H; ArH), 3.48 (s, 4H; CH$_2$N), 2.10 (s, 12H; NMe$_2$), 2.06 ppm (s, 3H; SMe); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 139.8$, 138.3, 127.2, 122.9 (Ar), 63.8 (CH$_2$N), 45.5 (NMe$_2$), 15.4 ppm (SMe); elemental analysis (%) calcd for $C_{13}H_{21}BrN_2S$: C 49.21, H 6.67, N 8.83; found: C 49.32, H 6.56, N 8.87.

1-Bromo-2,6-bis[(dimethylamino)methyl]phenyl diethylphosphonate (27): *t*BuLi (4.0 mL, 1.5 M in pentane, 6.0 mmol) was added dropwise to a solution of **9** (1.2 g, 3.0 mmol) in Et$_2$O (25 mL) at −100 °C. After 10 min. at −100 °C, diethyl chlorophosphate (0.6 g, 3.5 mmol) was added at once. The solution was allowed to reach room temperature and stirred for 2 h. All volatile substances were removed in vacuo, and the residue was redissolved in hexane (50 mL), washed with water (2 × 25 mL) and dried over MgSO$_4$. Removal of the solvent in vacuo afforded **27** as a colourless oil (0.85 g, 2.1 mmol, 69 %). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 8.16$ (d, ^3J(H,P) = 13.2 Hz, 2H; ArH), 3.94 (m, 4H; O*CH$_2$*CH$_3$), 3.42 (s, 4H; CH$_2$N), 2.04 (s, 12H; NMe$_2$), 1.00 ppm (t, ^3J(H,H) = 7.2 Hz, 6H; OCH$_2$*CH$_3$*); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 140.1$, 132.4, 131.2, 129.6 (Ar), 63.6 (CH$_2$N), 61.8 (OCH$_2$), 45.2 (NMe$_2$), 15.4 ppm (OCH$_2$*CH$_3$*); elemental analysis (%) calcd for $C_{16}H_{28}N_2BrO_3P$: C 47.18, H 6.93, N 6.88, P 7.60; found: C 46.96, H 7.14, N 6.95, P 7.38.

4-Methylthio-NCN-palladium(II) bromide (30): [Pd$_2$(dba)$_3$]·CHCl$_3$ (0.77 g, 0.95 mmol) was added to a solution of **26** (0.30 g, 0.95 mmol) in benzene (25 mL). The mixture was stirred overnight and then for an additional hour after addition of 1 mL of THF. The solution was filtered over Celite and concentrated to 5 mL, after which **30** precipitated on addition of hexane (25 mL). The resulting solid was washed with hexane (2 × 25 mL) and dried in vacuo to afford **30** as a yellowish solid (0.34 g, 0.80 mmol, 85 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 6.73$ (s, 2H; ArH), 3.95 (s, 4H; CH$_2$N), 2.95 (s, 12H; NMe$_2$), 2.41 ppm (s, 3H; SMe); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 155.1$, 145.8, 134.2, 119.6 (Ar), 74.6 (CH$_2$N), 54.0 (NMe$_2$), 17.4 ppm (SMe); elemental analysis (%) calcd for $C_{13}H_{21}BrN_2PdS$: C 36.85, H 5.00, N 6.61; found: C 36.78, H 5.10, N 6.47.

4-PO(OEt)$_2$-NCN-palladium(II) bromide (31): [Pd$_2$(dba)$_3$]·CHCl$_3$ (2.58 g, 3.2 mmol) was added at once to a solution of **27** (1.30 g, 3.2 mmol) in benzene (25 mL). The mixture was stirred overnight, and THF (5 mL) was subsequently added. After filtration over Celite, the solution was concentrated to 10 mL, after which hexane (90 mL) was added to induce precipitation of **31**. The solid was washed with hexane (3 × 100 mL) to afford pure **31** as an off-white solid (1.51 g, 2.94 mmol, 92 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.18$ (d, ^3J(H,P) = 20.1 Hz, 2H; ArH), 4.06 (m, 4H; O*CH$_2$*CH$_3$), 3.98 (s, 4H; CH$_2$N), 2.94 (s, 12H; NMe$_2$), 1.29 ppm (t, ^3J(H,H) = 10.6 Hz, 6H; OCH$_2$*CH$_3$*); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 164.3$, 145.5, 125.4, 123.1 (Ar), 74.4 (CH$_2$N), 62.1 (O*CH$_2$*CH$_3$), 53.8 (NMe$_2$), 16.5 ppm (OCH$_2$*CH$_3$*); elemental analysis (%) calcd for $C_{16}H_{28}BrN_2O_3PPd$: C 37.41, H 5.49, N 5.45, P 6.03; found: C 37.48, H 5.53, N 5.52, P 6.11.

4-COOH-NCN-platinum(II) iodide (34): *t*BuLi (2.4 mL, 1.5 M in pentane, 3.6 mmol) was added dropwise to a cooled (−100 °C) solution of **15** (1.06 g, 1.79 mmol) in THF (20 mL),. The reaction was quenched after 2 min by bubbling dry CO$_2$ gas through the mixture. On reaching ambient temperature the CO$_2$ supply was stopped, and the product was treated with a saturated aqueous NH$_4$Cl solution (1 mL). All volatile substances were evaporated in vacuo and the crude mixture was redissolved in CHCl$_3$ (50 mL), washed with saturated NH$_4$Cl solution (2 × 5 mL) and dried over MgSO$_4$. After removal of the volatile substances in vacuo, the product was redissolved in acetone (20 mL), treated with NaI (0.28 g, 1.85 mmol) for 30 min and filtered over Celite. Final traces of Na salts were extracted with water from a CHCl$_3$ solution of the product. Pure **34** precipitated as an off-white solid (0.89 g, 1.59 mmol, 89 %) on slow addition of diethyl ether (90 mL) to 10 mL of a solution in CHCl$_3$. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.41$ (s, 2H; ArH), 4.13 (s, ^3J(H,Pt) = 39.0 Hz, 4H; CH$_2$N), 3.07 ppm (s, ^3J(H,Pt) = 28.8 Hz, 12H; N(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 168.2$ (COOH), 156.0, 144.1, 125.6, 120.6, 75.4 (CH$_2$N), 55.6 ppm (NMe$_2$); FTIR (DRIFT, KBr): $\tilde{\nu}$ (intensity in Kubelka–Munk units): 3100–2750 (0.18), 3211.6 (0.17), 2979.8 (0.20), 2922.3 (0.26), 2750–2300 (0.17), 1668.5 (0.59), 1587.7 (0.50), 1465.5 (0.26), 1452.5 (0.33), 1412.1 (0.25), 1345.3 (0.29), 1326.1 (0.37), 1308.0 (0.52), 1274.1 (0.34), 1231.1 cm^{-1} (0.40); elemental analysis (%) calcd for $C_{13}H_{19}N_2IO_2Pt$: C 28.02, H 3.44, N 5.03; found: C 27.88, H 3.40, N 4.91.

4-Methylthio-NCN-platinum(II) bromide (35): Method a: *t*BuLi (2.65 mL, 1.5 M in pentane, 4.0 mmol) was added to a solution of **15** (1.2 g, 2.0 mmol) in THF (40 mL) at −100 °C. After stirring for 5 min at −100 °C, dimethyl disulfide (0.30 g, 3 mmol) was added at once, and the mixture was allowed to reach room temperature. All volatile substances were removed in vacuo, and the residue was redissolved in CH$_2$Cl$_2$ (25 mL). The solution was washed with water (2 × 25 mL and brine (25 mL), dried over MgSO$_4$ and concentrated to 10 mL. Compound **35** precipitated on careful addition of hexane (50 mL). The solid was washed with hexane (2 × 50 mL) and dried in vacuo to afford **35** as an off-white solid (0.61 g, 1.2 mmol, 60 %).

Method b: [Pt(*p*-tol)$_2$(SEt$_2$)]$_2$ (0.44 g, 0.48 mmol) was added at once to a solution of **26** (0.30 g, 0.95 mmol) in benzene (10 mL). The mixture was heated at reflux temperature until a clear solution was obtained. After cooling to room temperature, the solvent was evaporated in vacuo and the resulting residue was redissolved in CH$_2$Cl$_2$ (5 mL). Compound **35** precipitated on addition of hexane (25 mL). The solid was washed with hexane (2 × 25 mL) and dried in vacuo to afford **35** as an off-white solid (0.46 g, 0.90 mmol, 95 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 6.81$ (s, 2H; ArH), 3.99 (s, ^3J(H,Pt) = 45.4 Hz, 4H; CH$_2$N), 3.11 (s, ^3J(H,Pt) = 38.5 Hz, 12H; NMe$_2$), 2.44 ppm (s, 3H; SMe); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 156.2$, 144.3, 132.1, 120.1 (Ar), 77.4 (CH$_2$N), 55.3 (NMe$_2$), 18.0 ppm (SMe); elemental analysis (%) calcd for $C_{13}H_{21}BrN_2PtS$: C 30.47, 4.13, 5.47; found C 30.59, H 4.26, N 5.36.

4-PO(OEt)$_2$-NCN-platinum(II) bromide (36): Method a: *t*BuLi (2.4 mL, 1.5 M in pentane, 3.6 mmol) was added dropwise to a cooled (−100 °C) solution of **15** (1.06 g, 1.79 mmol) in THF (25 mL). After 2 min, the reaction mixture was quenched with diethyl chlorophosphate (0.50 g, 2.70 mmol). The mixture was allowed to reach room temperature and all volatile substances were evaporated in vacuo. The reaction mixture was redissolved in CH$_2$Cl$_2$ (50 mL) and washed with water (50 mL), 1 M NaOH (50 mL) and brine. The CH$_2$Cl$_2$ solution was dried over MgSO$_4$ and evaporated to dryness. Pure **36** (0.86 g, 1.43 mmol, 80 %) precipitated from a CH$_2$Cl$_2$ solution (10 mL) on slow addition of hexane (90 mL).

Method b: [{Pt(*p*-tol)$_2$SEt$_2$}$_2$] (0.56 g, 0.60 mmol) was added at once to a solution of **27** (0.50 g, 1.2 mmol) in benzene (10 mL). The mixture was brought to reflux until a clear solution was obtained. After removal of the volatile substances, the residue was redissolved in CH$_2$Cl$_2$ and precipitated with hexane (50 mL). The solid was washed with hexane (2 × 50 mL) to afford **36** as an off-white solid (0.69 g, 1.1 mmol, 95 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.23$ (d, ^3J(H,P) = 13.5 Hz, 2H; ArH), 4.08 (m, 4H; OCH$_2$), 4.02 (s, ^3J(H,Pt) = 45.1 Hz, 4H; CH$_2$N), 3.16 (s, ^3J(H,Pt) = 38.4 Hz, 12H; NMe$_2$), 1.31 ppm (t, ^3J(H,H) = 7.2 Hz, 6H; CH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 156.2$, 144.0, 123.0, 121.4 (Ar), 77.5 (CH$_2$N), 62.1 (OCH$_2$), 56.6 (NMe$_2$), 16.6 ppm (OCH$_2$*CH$_3$*); elemental analysis (%) calcd for $C_{16}H_{28}IN_2O_3PPt$: C 29.59, H 4.35, N 4.31, P 4.77; found: C 29.75, 4.28, 4.26, 4.59.

4-PO(OEt)(OH)-NCN-palladium(II) bromide (39) and 4-PO(OEt)(OH)-NCN-platinum(II) bromide (40): Both hydrolyses were performed under similar conditions. Trimethylsilyl bromide (3 equiv) was added to a solution of the pincer diethylphosphonate (**31** or **36**) in CH$_2$Cl$_2$ (ca 0.1 M). The mixture was stirred overnight, MeOH (5 mL) was added, and all volatile substances were removed in vacuo. The monoethylphosphonates **39** and **40** were isolated together with remaining **31** or **36** by extraction with

CH_2Cl_2. Careful precipitations with Et_2O from concentrated CH_2Cl_2 solutions afforded **39** and **40** as pure solids in yields of 15 and 23%, respectively. **39** (Pd): ^1H NMR (200 MHz, $[D_6]$DMSO/$CDCl_3$ ca. 1/5, 25 °C, TMS): $\delta = 6.87$ (d, $^3J(H,P) = 13.2$ Hz, 2H; ArH), 3.70 (s, 4H; CH_2N), 3.64 (m, 2H; CH_2O), 2.61 (s, 12H; NMe_2), 0.93 ppm (t, $^3J(H,H) = 7.0$ Hz, 3H; CH_3); $^{13}C\{^1H\}$ NMR (50 MHz, $[D_6]$DMSO/$CDCl_3$ ca. 1/5, 25 °C, TMS): $\delta = 163.0$, 145.5 (d), 125.5, 122.4 (d) (Ar), 74.1 (CH_2N), 61.1 (OCH_2), 53.6 (NMe_2), 16.5 ppm ($OCH_2\mathit{CH_3}$); elemental analysis (%) calcd for $C_{14}H_{24}BrN_2O_3PPd$: C 34.62, H 4.98, N 5.77; found: C 34.53, H 5.03, N 5.71. **40** (Pt): ^1H NMR (200 MHz, $[D_6]$DMSO/$CDCl_3$ ca.1/5, 25 °C, TMS): $\delta = 6.85$ (d, $^3J(H,P) = 13.2$ Hz, 2H; ArH), 3.68 (s, 4H; CH_2N), 3.61 (m, 2H; CH_2O), 2.72 (s, 12H; NMe_2), 0.90 ppm (t, $^3J(H,H) = 6.9$ Hz, 3H; CH_3); elemental analysis (%) calcd for $C_{14}H_{24}BrN_2O_3PPt$: C 29.28, H 4.21, N, 4.88; found: C 29.72, H 4.52, N 4.80.

4-$PO(OH)_2$-NCN-palladium(II) bromide (**41**) and 4-$PO(OH)_2$-NCN-platinum(II) bromide (**42**) were not isolated as pure products, but were present in the crude hydrolysis products, as indicated by $^{31}P\{^1H\}$ NMR analysis.

Crystal structure determinations: Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. The structures were solved with Patterson methods (program DIRDIF97[48]) and refined with the program SHELXL97[49] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were located in the difference Fourier map and refined as rigid groups. The hydrogen atom of the hydroxyl group in **22a** and the hydrogen atom of the carboxyl group in **34** were refined freely with isotropic displacement parameters. The drawings, structure calculations and checking for higher symmetry were performed with the program PLATON.[50]

Crystal data for 22a: $C_{13}H_{21}ClN_2OPd$, $M_r = 363.17$, yellow plate, $0.30 \times 0.30 \times 0.09$ mm, $T = 125(2)$ K, monoclinic, $P2_1/c$ (No. 14), $a = 9.1935(1)$, $b = 10.5160(1)$, $c = 15.9377(2)$ Å, $\beta = 111.3489(7)°$, $V = 1435.11(3)$ Å^3, $Z = 4$, $F(000) = 736$, $\rho_{calcd} = 1.681$ g cm^{-3}, 29867 measured reflections, 3287 unique reflections ($R_{int} = 0.066$). Analytical absorption correction (PLATON[50], routine ABST, $\mu = 1.470$ mm^{-1}, 0.62–0.86 transmission). 171 refined parameters, no restraints. R values $[I > 2\sigma(I)]$: $R1 = 0.0205$, $wR2 = 0.0512$. R values (all data): $R1 = 0.0226$, $wR2 = 0.0522$. $S = 1.033$. Residual electron density (min./max.): $-0.72/0.62$ e Å^{-3}.

Crystal data for 34: Crystals were obtained from a different batch than used in the elemental analysis of **34**. The scrambled product was obtained from incomplete conversion of the platinum bromide/iodide mixture to the platinum iodide complex. $C_{13}H_{19}Br_{0.19}I_{0.81}N_2O_2Pt \cdot 0.5\,C_7H_8$, $M_r = 594.43$, pale yellow plate, $0.06 \times 0.06 \times 0.02$ mm, $T = 150(2)$ K, monoclinic, $P2_1/c$ (No. 14), $a = 21.0837(5)$, $b = 6.0838(1)$, $c = 14.7525(3)$ Å, $\beta = 94.3916(6)°$, $V = 1886.73(7)$ Å^3, $Z = 4$, $F(000) = 1118$, $\rho_{calcd} = 2.093$ g cm^{-3}, 26659 measured reflections, 4316 unique reflections ($R_{int} = 0.064$). An absorption correction was applied (PLATON,[50] routine DELABS, $\mu = 9.173$ mm^{-1}, 0.40–0.80 transmission). 216 refined parameters, 27 restraints. The atoms Br1 and I1 were constrained on the same position with the same displacement parameters. R values $[I > 2\sigma(I)]$: $R1 = 0.0327$, $wR2 = 0.0648$. R values (all data): $R1 = 0.0554$, $wR2 = 0.0704$. $S = 1.043$. Residual electron density (min./max.): $-1.17/0.86$ e Å^{-3}. CCDC-212445 (**22a**) and CCDC-212446 (**34**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Acknowledgement

This work was supported by the Council for Chemical Sciences of The Netherlands Organisation for Scientific Research (CW/NWO), the Dutch Technology Foundation (STW) and the Netherlands Research School Combination Catalysis (NRSC-C).

[1] G. van Koten, *Pure Appl. Chem.* **1989**, *61*, 1681–1694.

[2] M. P. H. Rietveld, D. M. Grove, G. van Koten, *New J. Chem.* **1997**, *21*, 751–771.

[3] M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 5000–5031.

[4] Complexation with these d^8 metals (Ni^{II}, Pd^{II}, Pt^{II}) affords pincer complexes with terdentate meridional η^3-N,C,N bonding to the metal, which affords two five-membered metallacycles. The ligand acts as a monoanionic six-electron donor with the two N-donor atoms *trans* to each other. The d^8 metal ions Ni^{II}, Pd^{II} and Pt^{II} adopt a square-planar geometry with the coordination plane of the metal almost coplanar with the phenyl ring of the pincer ligand (C_2-symmetric). The remaining coordination site can be filled by a halo ligand or a Lewis basic ancillary ligand.

[5] a) R. A. Gossage, L. A. van de Kuil, G. van Koten, *Acc. Chem. Res.* **1998**, 31, 423–431; b) L. A. van de Kuil, H. Luitjes, D. M. Grove, J. W. Zwikker, J. G. M. van der Linden, A. M. Roelofsen, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics* **1994**, *13*, 468–477; c) L. A. van de Kuil, D. M. Grove, R. A. Gossage, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics* **1997**, *16*, 4985–4994.

[6] H-.J. van Manen, K. Nakashima, S. Shinkai, H. Kooijman, A. L. Spek, F. C. J. M. van Veggel, D. N. Reinhoudt, *Eur. J. Inorg. Chem.* **2000**, 2553–2540.

[7] D. E. Bergbreiter, P. L. Osburn, Y. -S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531–9538.

[8] D. E. Bergbreiter, P. L. Osburn, J. D. Frels, *J. Am. Chem. Soc.* **2001**, *123*, 11105–11106.

[9] L. A. van de Kuil, D. M. Grove, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Chem. Mater.* **1994**, *6*, 1675–1683.

[10] a) H. P. Dijkstra, M. D. Meijer, J. Patel, R. Kreiter, G. P. M. van-Klink, M. Lutz, A. L. Spek, A. J. Canty, G. van Koten, *Organometallics* **2001**, *20*, 3159–3168; b) H. P. Dijkstra, P. Steenwinkel, D. M. Grove, M. Lutz, A. L. Spek, G. van Koten, *Angew. Chem.* **1999**, *111*, 2322–2324; *Angew. Chem. Int. Ed.* **1999**, *38*, 2186–2188; c) I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. M. van Klink, G. van Koten, *Tetrahedron Lett.* **2000**, *41*, 1075–1079; d) I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. M. van Klink, G. van Koten, *Tetrahedron Lett.* **2000**, *41*, 1081–1085.

[11] a) C. Schlenk, A. W. Kleij, H. Frey, G. van Koten, *Angew. Chem.* **2000**, *112*, 3587–3589; *Angew. Chem. Int. Ed.* **2000**, *39*, 3445–3447; b) M. Q. Slagt, S.-E. Stiriba, R. J. M. Klein Gebbink, H. Kautz, H. Frey, G. van Koten, *Macromolecules* **2002**, *35*, 5734–5737.

[12] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, P. D. Grove, G. van Koten, *Nature* **1994**, *372*, 659–663.

[13] a) A. W. Kleij, R. A. Gossage, J. T. B. H. Jastrzebski, J. Boersma, G. van Koten, *Angew. Chem.* **2000**, *112*, 179–181; *Angew. Chem. Int. Ed.* **2000**, *39*, 176–178; b) A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 277–285; c) A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 268–276; d) A. W. Kleij, R. A. Gossage, R. J. M. Klein Gebbink, N. Brinkmann, E. J. Reijerse, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2000**, *122*, 12112–12124.

[14] a) M. Albrecht, N. J. Hovestad, J. Boersma, G. van Koten, *Chem. Eur. J.* **2001**, *7*, 1289–1294; b) M. Albrecht, R. A. Gossage, M. Lutz, A. L. Spek, G. van Koten, *Chem. Eur. J.* **2000**, *6*, 1431–1445; c) M. Albrecht, G. van Koten, G. *Adv. Mater.* **1999**, *11*, 171–174; d) M. Albrecht, R. A. Gossage, A. L. Spek, G. van Koten, *Chem. Commun.* **1998**, 1003–1004; e) B. M. J. M. Suijkerbuijk, L. Shu, R. J. M. Klein Gebbink, A. D. Schlüter, G. van Koten, *Organometallics* **2003**, *22*, 4175—4177.

[15] a) M. D. Meijer, G. P. M. van Klink B. de Bruin, G. van Koten, *Inorg. Chim. Acta* **2002**, *327*, 31–40; b) M. D. Meijer, N. Ronde, D. Vogt, G. P. M. van Klink, G. van Koten, *Organometallics* **2001**, *20*, 3993–4000.

[16] a) R. Giminez, T. M. Swager, *J. Mol. Catal. A.* **2001**, *166*, 265–273; b) H. Alper, *J. Mol. Cat. A. Chem.* **2003**, *201*, 23–31.

[17] a) R. van de Coevering, M. Kuil, R. J. M. Klein Gebbink, G. van Koten, *Chem. Commun.* **2002**, 1636–1637; b) M. Albrecht, M. Lutz, A. L. Spek, G. van Koten, *Nature* **2000**, *406*, 970–974; c) M. Al-

brecht, M. Lutz, A. M. M. Schreurs, E. T. H. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **2000**, 3797–3804; d) P. J. Davies, N. Veldman, D. M. Grove, A. L. Spek, B. T. G. Lutz, G. van Koten, *Angew. Chem.* **1996**, *108*, 2078–2081; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1959–1961.

[18] For example: a) B.-H. Huisman, H. Schönherr, W. T. S. Huck, A. Friggeri, H. W. J. van Manen, E. Menozzi, G. J. Vancso, F. C. J. M. Van Veggel, D. N. Reinhoudt, *Angew. Chem.* **1999**, *111*, 2385–2389; *Angew. Chem. Int. Ed.* **1999**, *38*, 2248–2251; b) W. T. S. Huck, L. J. Prins, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1998**, *120*, 6240–6246; c) W. T. S. Huck, F. C. J. M. van Veggel, D. N. Reinhoudt, *Angew. Chem.* **1996**, *108*, 1304–1306; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1213–1215.

[19] P. Steenwinkel, H. Kooijman, W. J. J. Smeets, A. L. Spek, D. M. Grove, G. van Koten, *Organometallics* **1998**, *17*, 5411–5426.

[20] a) S. Back, R. A. Gossage, M. Lutz, I. de Rio, A. L. Spek, H. Lang, G. van Koten, *Organometallics* **2000**, *19*, 3296–3304; b) S. Back, R. A. Gossage, H. Lang, G. van Koten, *Eur. J. Inorg. Chem.* **2000**, 1457–1464; c) S. Back, W. Frosch, I. de Rio, G. van Koten, H. Lang, *Inorg. Chem. Commun. 2* **1999**, 584–586; d) S. Back, R. A. Gossage, G. Rheinwald, H. Lang, G. van Koten, *J. Organomet. Chem.* **1999**, *582*, 126–138.

[21] G. Rodríguez, M. Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2002**, *124*, 5127–5138.

[22] a) G. Guillena, G. Rodríguez, M. Albrecht, G. van Koten, *Chem. Eur. J.* **2002**, *8*, 5368–5376; b) G. Guillena, G. Rodríguez, G. van Koten, *Tetrahedron Lett.* **2002**, *43*, 3895–3898.

[23] a) B. M. J. M. Suijkerbuijk, M. Q. Slagt, R. J. M. Klein Gebbink, M. Lutz, A. L. Spek, G. van Koten, *Tetrahedron Lett.* **2002**, *43*, 6565–6568; b) M. Albrecht, G. Rodríguez, J. Schoenmaker, G. van Koten, G. *Org. Lett.* **2000**, *22*, 3461–3464.

[24] For recent reviews on *para*-substituted PCP ligands, see a) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2002**, *102*, 1759–1792; b) A. Vigalok, D. Milstein, *Acc. Chem. Res.* **2001**, *34*, 798–807.

[25] a) M.-K. Lau, Q.-F. Zhang, J. L. C. Chim, W.-T. Wong, W.-A. Leung, *Chem. Commun.* **2001**, 1478–1479; b) A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *J. Organomet. Chem.* **2000**, *598*, 262–275; c) A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1999**, *18*, 2813–2820; d) C. Coudret, S. Fraysse, J.-P. Launay, *Chem. Commun.* **1998**, 663–664; e) A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1998**, *17*, 4535–4537; f) G. R. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, P. D. Yap, *Inorg. Chim. Acta* **1996**, *251*, 65–74; g) G. R. Clark, C. E. L. Headford, W. R. Roper, L. J. Wright, *Inorg. Chim. Acta* **1994**, *220*, 261–272.

[26] M. Q. Slagt, R. J. M. Klein Gebbink, M. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **2002**, 2591–2592.

[27] a) P. Steenwinkel, R. A. Gossage, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 759–762; b) P. Steenwinkel, J. T. B. H. Jastrzebski, B.-J. Deelman, D. M. Grove, H. Kooijman, N. Veldman, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1997**, *16*, 5486–5498; c) J.-M. Valk, R. van Belzen, J. Boersma, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **1994**, 2293–2302; d) J.-M. Valk, J. Boersma, G. van Koten, *J. Organomet. Chem.* **1994**, *483*, 213–216.

[28] G. Rodríguez, G. van Koten, unpublished results.

[29] C. J. Jameson, J. Mason, *Multinuclear NMR* (Ed.: J. Mason), Plenum Press, New York, London, **1987**, Chaps. 3, 20, and references therein.

[30] J. D. Kennedy, W. McFarlane, R. J. Puddephat, P. J. Thompson, *J. Chem. Soc. Dalton Trans.* **1976**, 874–879, and references therein.

[31] L. Ding, Y. J. Wu, D. P. Zhou, *Polyhedron* **1998**, *17*, 1725–1728.

[32] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.

[33] C. A. Hollingsworth, P. G. Seybold, C. M. Hadad, *Int. J. Quantum. Chem.* **2002**, *90*, 1396–1403.

[34] The DFT-B3LYP/LANL2DZ method uses density functional theory combined with effective core potentials. The basis sets used for chlorine and platinum were the Los Alamos National Laboratory sets (LANL) for effective core potentials (ECP) of the double-ζ type, consisting of a small-core ECP with 3s and 3p orbitals in the valence space. The functional used was B3LYP, and the relativistic correlations for heavy atoms were considered in ECP.

[35] Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; Natural atomic orbital and natural bond orbital analyses by Gaussian NBO, Version 3.1.

[36] K. L. Brown, A. W. Awtrey, R. LeGates, *J. Am. Chem. Soc.* **1978**, *100*, 823–828.

[37] Examples of crystal structures of *para*-functionalised NCN-pincer palladium and platinum complexes: a) H. P. Dijkstra, M. D. Meijer, J. Patel, R. Kreiter, G. P. M. van Klink, M. Lutz, A. L. Spek, A. J. Canty, G. van Koten, G. *Organometallics* **2001**, *20*, 3159–3168; b) M. Albrecht, R. A. Gossage, A. L. Spek, G. van Koten, *Chem. Commun.* **1998**, 1003–1004; c) M.-C. Lagunas, R. A. Gossage, A. L. Spek, G. van Koten, *Organometallics* **1998**, *17*, 731–741; d) S. I. James, G. Verspui, A. L. Spek, G. van Koten, *Chem. Commun.* **1996**, 1309–1310.

[38] F. Neve, A. Crispini, C. Di Pietro, S. Campagna, *Organometallics* **2002**, *21*, 3511–3518.

[39] M. D. Meijer, E. W. de Wolf, M. Lutz, A. L. Spek, G. P. M. van - Klink, G. van Koten, *Organometallics* **2001**, *20*, 4198–4206

[40] a) M. Albrecht, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2001**, *123*, 7233–7246; b) M. Albrecht, R. A. Gossage, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1999**, *121*, 11898–11899.

[41] R. van de Coevering, R. J. M. Klein Gebbink, G. van Koten, unpublished results.

[42] For DFT calculations on NCN- and PCP-pincer complexes, see: a) C. Stadler, L. de Lacey, B. Hernández, H. Fernández, J. C. Conesa, *Inorg. Chem.* **2002**, *41*, 4417–4423; b) H.-J. Fan, M. B. Hall, *J. Mol. Cat. A: Chem.* **2002**, *189*, 111–118.

[43] a) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746; b) R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833–1840.

[44] S. Komiya, *Synthesis of Organometallic Compounds*, Wiley, Winchester, **1997**.

[45] a) A. J. Canty, J. Patel, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *599*, 195–199; b) B. R. Steele, K. Vrieze, *Transition Met. Chem.* **1977**, *2*, 140–144.

[46] a) P. Steenwinkel, R. A. Gossage, T. Maunula, D. M. Grove, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 763–768; b) J. Terheijden, G. van Koten, D. M. Grove, K. Vrieze, A. L. Spek, *J. Chem. Soc. Dalton Trans.* **1987**, *6*, 1359–1366; c) P. L. Alsters, P. J. Baesjou, M. D. Janssen, H. Kooijman, A. Sicherer-Roetman, A. L. Spek, G. van Koten, *Organometallics* **1992**, *11*, 4124–4135.

[47] P. Steenwinkel, S. L. James, D. M. Grove, N. Veldman, A. L. Spek, G. van Koten, *Chem. Eur. J.* **1996**, *2*, 1440–1445.

[48] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. J. M. Smits, C. Smykalla, The DIRDIF97 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1997**.

[49] G. M. Sheldrick, SHELXL97, Program for crystal structure refinement, University of Göttingen, Germany, **1997**.

[50] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[51] H. H. Jaffé *Chem. Rev.* **1953**, *53*, 191–261.

Received: July 15, 2003
Revised: November 17, 2003 [F5336]