DALTON
COMMUNICATION

Synthetic strategies towards new *para*-functionalised NCN-pincer palladium(II) and platinum(II) complexes †

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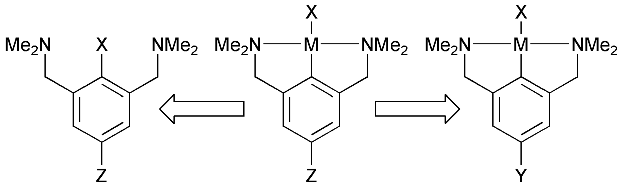
New *para*-functionalised NCN-pincer palladium(II) and platinum(II) complexes were synthesised, giving access to tuneable organometallic catalysts and sensor materials.

Transition metal complexes with NCN-pincer ligands (NCN = $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$) have been prepared for numerous applications in the fields of catalysis, catalyst immobilisation, supramolecular assembly, and sensor materials.[1] An important tool to construct larger structures and to tune the metal centre electronically, has been the introduction of substituents at the *para*-position of the pincer ligand. This functionalisation has been most successful with pincer complexes from the nickel triad (Ni, Pd, Pt), due to their exceptional stability. ‡

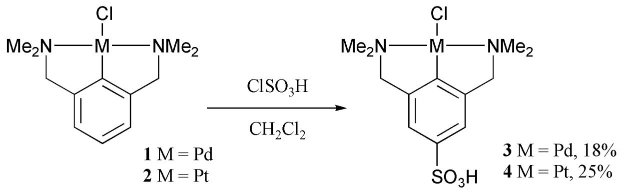
In this communication we report the synthesis of new *para*-functionalised NCN-pincer palladium(II) and platinum(II) complexes with new properties and potential applications. These complexes were prepared using two distinct synthetic strategies (Scheme 1).



Scheme 1 *Para*-functionalisation of pincer complexes.

One strategy involves regular organometallic synthesis, *i.e.* selective metalation of pre-functionalised pincer ligands. Surprisingly, we were also able to selectively *para*-functionalise bis-orthocyclometalated pincer complexes. This second synthetic strategy is, apart from functionalisations on highly stable ferrocene-type complexes, very rare. These transformations on the *para*-substituent allow the construction of a library of pincer palladium(II) and platinum(II) complexes, using common methods in organic synthesis. Chemical transformations on metalated pincer complexes should, however, be compatible with the stability of the metal-to-carbon bond. The palladium(II) and platinum(II) pincer complexes exhibit exceptional stabilities towards a variety of reaction conditions.[2]

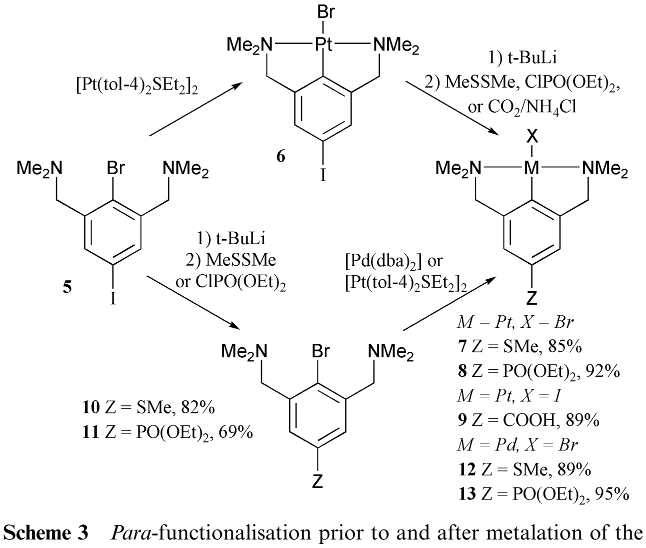
Direct substitution reactions on the aromatic ring of the metalated pincer ligand forms a straightforward route to introduce *para*-substituents. Treatment with chlorosulfonic acid is a generally accepted method to introduce a SO_3H-substituent on an aromatic ring. Similarly, treatment of either [PdCl(NCN)] (**1**) or [PtCl(NCN)] (**2**) with chlorosulfonic acid afforded the *para*-SO_3H substituted palladium(II) (**3**) and platinum(II) (**4**) pincers, respectively (Scheme 2).



Scheme 2 *Para*-functionalisation of metalated pincer complexes.

The crude reaction mixture contained, apart from the desired *para*-substituted complexes, the *meta*-isomers, several unidentified side-products, and palladium or platinum black. However, the feasibility of this electrophilic aromatic substitution, and the isolation of the desired products, emphasises the stability of the palladium(II) and platinum(II) pincer complexes towards highly acidic and electrophilic media. The sulfonated pincer complexes are readily soluble in aqueous and other highly polar (protic) media, and form zwitterionic aqua complexes upon treatment with base.

Starting from the earlier reported[3] bifunctional ligand 1-bromo-4-iodo-2,6-bis[(dimethylamino)methyl]benzene (**5**), we could introduce several new substituents using the two methodologies. Platination of **5** with $[Pt(tol\text{-}4)_2SEt_2]_2$[4] affords the bis-orthocyclometalated complex **6** solely (Scheme 3).[3]



Scheme 3 *Para*-functionalisation prior to and after metalation of the NCN-pincer ligand.

The remaining iodo-substitutent of **6** is available for further modifications, and allows selective lithiation, with t-BuLi at −100 °C in THF. The platinum centre remains unaffected under these conditions. A quench of the lithio intermediate $[PtBr(NCN)Li]_n$ with the electrophiles dimethyl disulfide, chloro diethylphosphate, and carbon dioxide afforded the *para*-methyl

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† Electronic supplementary information (ESI) available: spectroscopic data for **3**, **4**, **8**–**13** and **17**–**20**. See http://www.rsc.org/suppdata/dt/b2/b204239h/

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sulfide (**7**), *para*-diethylphosphonate (**8**), and the *para*-carboxylate (**9**) platinum(II) NCN-pincers, respectively.§ The high selectivity of this lithiation reaction, combined with the inertness of the platinum(II) co-ordination environment, shows the high stability of the pincer complex towards basic and nucleophilic conditions. Complex **9** formed suitable crystals for X-ray diffraction¶, Fig. 1 shows its molecular structure. The carboxylic acid does not form a dimer, but is hydrogen-bonded to a co-crystallised DMSO molecule.

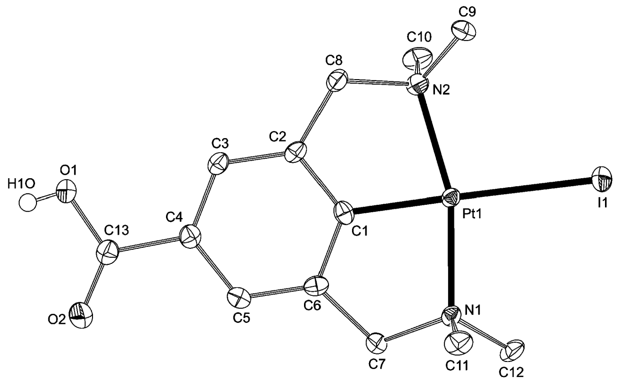
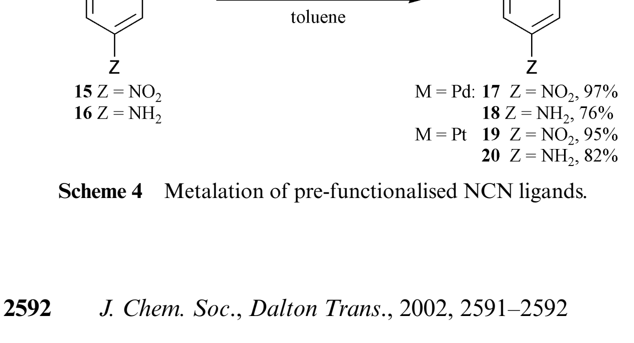


Fig. 1 Displacement ellipsoid plot (50% probability level) of **9**. C–H hydrogen atoms and the DMSO solvent molecule have been omitted for clarity. Pertinent bond lengths (Å), angles and torsion angles (°): Pt1–I1 2.7150(2), Pt1–C1 1.920(3), Pt1–N1 2.090(3), Pt1–N2 2.095(3); I1–Pt1–C1 176.58(10), N1–Pt1–N2 163.67(10); N1–Pt1–C1–C6 −7.5(3), N2–Pt1–C1–C2 −13.9(3), C5–C4–C13–O2 0.4(5).

The *para*-methyl sulfide (**12**) and the *para*-diethylphosphonate (**13**) palladium(II) complexes were not accessible *via* lithiation of [PdBr(NCN-I)]. However, lithiation of ligand **5** could be performed selectively at the iodo-position, leaving the bromo-substituent untouched. A quench with either dimethyl disulfide or chloro diethylphosphate afforded the *para*-substituted ligands **10** and **11**, respectively. Selective palladation by oxidative addition of [Pd(dba)$_2$][5] afforded their corresponding metal complexes **12** and **13**. The platinum(II) complexes **7** and **8** were also accessible *via* this route (Scheme 3). Hydrolysis of the diethylphosphonate-substituted complexes **8** and **13** to their corresponding monoethylphosphonates and phosphonates, renders the NCN-pincer complexes water-soluble.

With respect to electronic tuning, the two extreme cases encountered in Hammett-relationships are the nitro and amino substituents. The mild oxidative addition procedure used in the metalation reactions allows the presence of these substituents on the *para*-position. The *para*-nitro (**15**) and *para*-amino (**16**) substituted NCN-pincer ligands were obtained by nitration of 1-bromo-2,6-bis[(dimethylamino)methyl]benzene (**14**) and subsequent reduction of the nitro substituent.[6] Both ligands were treated with [Pd(dba)$_2$] to obtain the respective palladium(II) complexes **17** and **18**, and with [Pt(tol-4)$_2$SEt$_2$]$_2$ to obtain the platinum(II) analogues **19** and **20**, respectively (Scheme 4).



15 Z = NO$_2$
16 Z = NH$_2$

M = Pd: **17** Z = NO$_2$, 97%
18 Z = NH$_2$, 76%
M = Pt **19** Z = NO$_2$, 95%
20 Z = NH$_2$, 82%

Scheme 4 Metalation of pre-functionalised NCN ligands.

The influence of the introduced *para*-substituents on their structure, spectroscopic properties and catalytic activity is currently under investigation.

In conclusion, various new NCN-pincer palladium(II) and platinum(II) complexes have been synthesised. Due to the high stability of the pincer metal complexes, harsh reaction conditions can be used in the substitution reactions, ranging from basic and nucleophilic to acidic and electrophilic. The new small size organometallic molecules combine several functions. NCN-pincer palladium(II) complexes are applicable as catalysts in various C–C coupling reactions, and NCN-pincer platinum(II) complexes can be used as (bio)markers and switchable SO$_2$-detectors. Furthermore, the *para*-functionalised pincer complexes are available as starting materials for further modifications, opening new fields in (bio)organometallic chemistry. Finally, the large influence of the *para*-substituent on the solubility of the pincer complexes in various solvents, allows their application in biphasic systems.

Acknowledgements

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Notes and references

‡ Metalation of NCN-pincer ligands with the d^8 metals Ni(II), Pd(II), and Pt(II), affords complexes with terdentate meridional η^3-NCN bonding to the metal, affording two stabilising five-membered metallacycles. The ligand acts as a monoanionic six-electron donor with both N-donor atoms positioned *trans* with respect to one another. The metal adopts a square planar geometry. The remaining co-ordination site can be filled with either a halogen ion or a Lewis basic ancillary ligand.

§ Halide scrambling on the metal centre is a side-reaction encountered in these syntheses. Facile halide abstraction, followed by the addition of an appropriate halide source affords a single product.

¶ Crystal data for **9**: $C_{13}H_{19}IN_2O_2Pt\cdot C_2H_6OS$, M = 635.42, yellow needle, 0.45 × 0.15 × 0.09 mm^3, T = 125(2) K, monoclinic, space group $P2_1/c$ (no. 14), a = 5.9677(1), b = 24.5133(14), c = 14.0288(2) Å, β = 108.9673(7)°, V = 1940.82(12) Å^3, Z = 4, D_{calc} = 2.175 g cm^{-3}. Analytical absorption correction (μ = 8.94 mm^{-1}, 0.12–0.63 transmission). Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å). 28006 measured reflections, 4451 unique reflections (R_{int} = 0.060). 218 refined parameters. R-values [$I > 2\sigma(I)$]: $R1$ = 0.0230, $wR2$ = 0.0543. R-values [all reflections]: $R1$ = 0.0262, $wR2$ = 0.0555. S = 1.056. Residual electron density between −1.48 and 1.03 e Å^{-3}. CCDC reference number 178313. See http://www.rsc.org/suppdata/dt/b2/b204239h/ for crystallographic data in CIF or other electronic format.

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