Synthesis and structure of thienyl Fischer carbene complexes of Pt\textsuperscript{II} for application in alkyne hydrosilylation\textsuperscript{†}

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Transmetallation of group 6 thienylne Fischer carbene complexes to Pt\textsuperscript{II} precursors yielded new examples of neutral platinum(II) bisethoxycarbene complexes with either 2-thienyl (T) or 5-thieno[2,3-b]thienylene (TT) carbene substituents. The use of analogous aminocar bene group 6 precursors proceeded to give isomeric platinum(II) product mixtures where the resultant bisaminocarbene ligands displayed different orientations due to restricted rotation around the Pt–aminocarbene bond caused by the sterically demanding TT substituents. The well-defined Pt\textsuperscript{II} ethoxycarbene complexes were screened as catalyst precursors in the benchmark hydrosilylation reaction employing phenylacetylene and triethylsilane substrates. Marked selectivity for the $\beta$-E isomer ($E$)-triethyl(styryl)silane was observed, and the (pre)catalysts proved recyclable, active in solvent-free reactions, and displaying a high alkyne functional group tolerance.

Introduction

Acyclic heteroatom-stabilized carbene complexes of platinum(a) have been known since 1915,\textsuperscript{1–3} and yet the number of isolated examples are limited. In general, there are four methods available to prepare Pt\textsuperscript{II} Fischer carbene complexes (FCCs). Firstly, ligand modification of Pt\textsuperscript{II} isocyanide precursors with alcohols or primary amines produces the corresponding acyclic aminoxy- or diamino-carbene Pt\textsuperscript{II} complexes, respectively (Fig. 1a).\textsuperscript{4} Cationic alkoxycarbene complexes can be prepared by reacting the Pt\textsuperscript{II} precursors with alkynes (Fig. 1b), to yield the $\pi$-bonded intermediates that lead to carbene formation after alkyn modification,\textsuperscript{5} while neutral bisalkoxycarbene complexes are obtained from the reaction of SiMe\textsubscript{3}-substituted alkynes and H\textsubscript{2}PtCl\textsubscript{6}/C\textsubscript{6}H\textsubscript{2}O (Fig. 1c).\textsuperscript{6} The first transmetallation reactions from group 6 transition metal FCCs to produce mononuclear Pt-bis carbene complexes employed [PtCl\textsubscript{2}(MeCN)\textsubscript{2}] or PtCl\textsubscript{2} precursors (Fig. 1d) and the products were stabilized by amine-chelate formation.\textsuperscript{7}

We have recently prepared Pt\textsuperscript{II} multicarbene complexes (Fig. 1e) by carbene transfer reactions of the ethoxy- and aminocar bene ligands of W(0) FCCs to a Pt\textsuperscript{II} centre.\textsuperscript{8} The major products obtained from the reactions with group 6 carbene precursors are neutral bisethoxycarbene complexes of Pt\textsuperscript{II} and cationic mononuclear trisaminocarbene complexes (Fig. 1e). In this study, Pt\textsuperscript{II} Fischer carbene complexes with (annulated) thiophene substituents, are synthesized for the first time employing the methodology of carbene transfer, and their use as catalysts for the alkyne hydrosilylation reaction is investigated. Hydrosilylation of terminal alkyne is one of the leading methods to produce organosilanes, and is catalysed by many transition metals including platinum.\textsuperscript{9–18}

Although Pt\textsuperscript{II} complexes containing N-heterocyclic carbene (NHC)
ligands are commonly employed as catalysts for this reaction, no Fischer carbene catalysts have been reported.

Results and discussion

Synthesis of platinum(II) FCCs

PtII multicarbene complexes were synthesized by transmetallation reactions of the chromium or tungsten carbonyl FCC precursors P1–P4, containing either a 2-thienyl (T) or a 5-thieno[2,3-b]thiophenylene (TT) substituent (see Experimental section and ESI† for the preparation of P1–P4), via a modified procedure of that reported by Sierra and co-workers (Scheme 1).† Transmetallation occurred by stirring a group 6 FCC with a platinum precursor for 24–30 h in refluxing dichloromethane (DCM). The syntheses of PtII FCCs are facile, but purification of the compounds proved challenging. The complexes are light sensitive, insoluble in most solvents (e.g. dichloromethane, chloroform, acetonitrile) and chromatographic purification processes are compromised. Four PtII biscarbene complexes were successfully isolated, namely cis-[PtCl2(C(OEt)-5-C6H3S2)2] (3a), cis-[PtCl2(C(NMe2)-5-C6H3S2)2] (3a-b) and cis-[PtCl2(C(NH2)-5-C6H3S2)2] (4a-b) (Fig. 2). The transmetallation reactions do not run to completion, even with prolonged reaction times, and starting material is recovered from all reactions.

The cis-biscarbene complexes of 3 and 4 have three isomeric possibilities where the TT spacers and amino fragments have various orientations to yield different geometric stereoisomers (Fig. 2) due to restricted rotation enforced by the sterically demanding thieno[2,3-b]thiophene carbene substituent and the amino group with increased C carbene–N bond order. Evidence for the formation of two out of the possible three isomers is observed for 3 and 4. In addition, the formation of a cationic Pt triscarbene complex ([PtCl3(C(NMe2)-5-C6H3S2)3]Cl, 4d) is observed for the reactions done with group 6 transition metal dimethylamino carbene complexes. The orientation of the carbene substituents in 4d is unknown.

Compounds 3 were synthesized using P3W (see ESI,† Fig. S1) and Pt(COD)Cl2 in DCM. The cis isomer 3 was obtained with evidence for the isolation of two-out-of-three possible geometric stereoisomers that are inseparable. The two isomers are 3a (yield 64%) and 3b (yield 13%), obtained in the ratio 5 : 1 as determined by integrating the 1H NMR spectrum resonances (ESI,† Fig. S9).

Compounds 4 were isolated from transmetallation reactions using P4Cr/W along with Pt(COD)Cl2 or cis-[PtCl2(NCMe)2] in DCM. The preferred reaction conditions are employed by reacting P4Cr with Pt(COD)Cl2 in DCM, to produce 4 in 71% yield. Excess PtCl2 and Pt(COD)Cl2 are removed by washing the reaction precipitate with minimal amounts of DCM, chloroform and ether. Two-out-of-three possible geometric stereoisomers of the cis-biscarbene complex of 4 are obtained.

The two isomers, 4a (yield 39%) and 4b (yield 8%), are accompanied by the triscarbene complex (4d, yield 24%) in the ratio 5 : 1 : 3 as determined by integrating 1H NMR spectrum resonances (ESI,† Fig. S11). Compounds 4 only dissolve in DMSO and partly in chlorinated solvents (e.g. DCM and CDCl3), hence the more insoluble 4d could be purified by washing the precipitate with a variety of solvents. In an attempt to purify 4, a short silica gel filter using acetone as eluent produced only the decomposition product (NMe2)C(O)-5-C6H3S2 (5, yield 24%).

The solubility of PtII FCCs decrease (1 > 2) with an increase in the number of thiophene units in the annulated spacer (1 < 2). A decrease in solubility is also seen when changing the heteroatom substituent from ethoxy- (2) to amino- (3, 4).

The mechanism for obtaining a PtII mononuclear biscarbene complex from Pt(COD)Cl2 requires the substitution of the η1-COD ligand, leaving two cis empty coordination sites on the metal. A stepwise mechanism is likely followed were the COD ligand remains partially coordinated (η1-COD), still bound to the metal through one of the two double bonds of cyclooctadiene, as the first carbene ligand coordinates. Coordination of the second carbene ligand, to the PtII metal, completely displaces the COD ligand. Further substitution would require that the trans effect of a carbene ligand is relatively stronger than that of a chloro ligand.8
Spectroscopic characterization

NMR spectra were recorded in CDCl$_3$, CD$_2$Cl$_2$ and (CD$_3$)$_2$SO, depending on the solubility of the compounds. $^1$H NMR data are summarized in Table 1. The aromatic proton adjacent to the carbene carbon is most affected by the coordination of the carbene fragment. In 1 this is seen in the resonance of H3 and even more so in H4 of 2 (ESI† Fig. S6 and S7). Due to conjugation in the thiopeptide ring of 1, H5 is also shifted significantly downfield. The methylene resonances of Pt(II) ethoxycarbene complexes appear as broadened peaks instead of quartets. One such broad peak/unresolved quartet is observed in the $^1$H NMR spectrum of 1 and two in the case of 2, resonating ca. 0.6 ppm apart (Fig. S6 and S7, ESI†). Due to the bulky nature of thienylenes and the cis-orientation of the two carbene ligands in the square planar structure of the platinum complexes, the peak broadening is ascribed to restricted rotation of the OEt group around the carbene carbon, more pronounced in 2 (larger TT spacer) compared to 1 (T spacer). The broad signals of 2 are duplicated indicating different electronic environments for the ethoxy substituents. Recording the NMR spectrum of 2 in a different solvent, e.g. CD$_2$Cl$_2$ or at a lower temperature (2 °C) did not significantly improve the resolution of the spectra.

In the $^1$H NMR spectrum of 3a, a double duplication of the carbene ligand resonances is observed in a 1:1 ratio (ESI† Fig. S9), for the compound 3b. The two cis-bis-carbene isomers are not separable. The difference between the two stereoisomers 3a and 3b can be visualized by restricting rotation around the Pt-C$_{carb}$ bond. In 3a a structure is assigned whereby each amino substituent is on the same side as the sulphurs in the adjacent TT ring, of the two carbene ligands (Fig. 2). The 1:1 ratio of the aromatic proton resonances of 3b indicates that the molecule constitutes of two different carbene ligands. In 3b one ligand has the same conformation as the TT substituents in 3a, but the other TT substituent is rotated around the C$_{carb}$-C$_{TT}$ bond to take up a position where the amino substituent is on the opposite side of the sulphurs in the TT ring. The greatest difference is observed for the NH and H4 proton resonances of 3a and 3b. Two significantly different NH resonances are observed, hence H-bonding interactions are suspected. Because three geometric stereoisomers are possible for 3 (Fig. 2), 3b is expected to be one of the minor isomers. A third isomer 3c, with both amino substituents on opposite sides of the sulphurs in the TT rings, was not observed.

In solution, the TT spacers may rotate and the major product (3a) is expected to be the energetically favoured compound where the amino groups are on the same side as the sulphurs of the TT-rings. This is also the favoured orientation for group 6 transition metal amino carbene complexes.21,22 Compound 3b is presumed to be the result of both intra- and intermolecular NH interactions and H-bonding interactions with polar solvents (DMSO-d$_6$ or THF), causing restricted rotation in the molecule. Single crystal X-ray diffraction confirms the molecular structure of this minor isomer 3b (vide infra), and is obtained due to the preferential crystallisation of this compound. The possibility of a cationic triscarbene monochlorido Pt(II) complex for 3, similar to those reported earlier by us,4 is excluded due to the 1:1 integration of the carbene ligand’s protons. Similarly, the trans-bis-carbene isomer would be expected to yield only one set of duplicate signals and is therefore also ruled out as the possible product of 3b.

$^1$H NMR spectra of mixtures of 4a, 4b and 4d in CDCl$_3$ were recorded (ESI† Fig. S11). DMSO was employed as a deuterated solvent for $^1$H NMR spectroscopy of the least soluble, purified fraction 4d (ESI† Fig. S12). Poor resolution and peak broadening are observed for 4d, ascribed to small differences in chemical shifts of protons as more than one of the same carbene ligand is present in the macromolecule, along with the impact of bulky carbene substituents restricting rotation in the molecule.

### Table 1 $^1$H NMR chemical shifts (δ) of the Pt FCCs

| Complex | H3 | H4 | H5 | H4′ | H5′ | OEt$^a$ | NH$_2$/NMe$_2$$^f$ |
|---------|----|----|----|-----|-----|--------|-----------------|
| 1$^e$   | 8.69 | 7.28 | 8.09 |     |     | 5.60, 1.59 |                  |
| 1$^g$   | 8.68 | 7.31 | 8.13 |     |     | 5.54, 1.59 |                  |
| 2$^e$   | 9.08 | 7.35 | 7.44 | 9.08 | 7.39 | 5.77, 5.18, 1.59 |                |
| 2$^g$   | 9.03 | 7.39 | 7.49 | 5.73, 5.21, 1.58 |       |          |                  |
| 3a$^f$  | 8.26 | 7.40 | 7.66 |     |     | 10.77, 10.61 |                  |
| 3b$^f$  | 8.56, 8.46 | 7.46, 7.43 | 7.73, 7.72 |   |     | 11.42, 11.18 |                  |
| 4a$^e$  | 8.06 | 7.35 | 7.45 |     |     | 4.22, 3.86 |                  |
| 4a$^g$  | 8.00 | 7.45 | 7.73 |     |     | 4.06, 3.77 |                  |
| 4b$^e$  | 7.61 | 7.29 | 7.38 |     |     | 3.30    |                  |
| 4b$^g$  | 7.80 | 7.41 | 7.70 |     |     | 4.15, 3.65 |                  |
| 4d$^{df}$ | 7.65, 7.37 | 7.26, 6.78 | 7.37, 6.87 |   |     | 4.10, 3.63, 3.38, 3.30 |            |

$a$ Proton chemical shifts for the ethoxy fragment are reported with the first value being the chemical shift of the methylene group, and the second the chemical shift of the methyl group. In the case of 2 there are two values for the methylene groups. $^b$ NMR data recorded in CD$_2$Cl$_2$. $^c$ NMR data recorded in (CD$_3$)$_2$SO. $^d$ Proton chemical shifts for the NH$_2$ fragments of 3a and 3b. In the case of 4 the chemical shifts represent the methyl groups of NMe$_2$. $^e$ Broadened resonances observed. The first values reported being the chemical shifts of the two carbene fragments opposite each other and the second the chemical shifts of the carbene fragment trans to a chloro ligand.
In (CD$_3$)$_2$SO the 2 : 1 ratio of the two carbene ligands when compared with the corresponding biscarbene complexes.

Two of the three geometric isomers of the cis-biscarbene complex (4a/b, Fig. 2) are identified in the reaction mixture. The sharp, resolved signals of the biscarbene complexes are clearly distinguishable from the broadened signals of the triscarbene complex (Fig. S11, ESI†). The major cis-biscarbene isomer (4a) has the NMe$_2$ fragments rotated away from the sulphur atoms in the TT spacers and the minor isomer (4b) has the NMe$_2$ fragments rotated to the same side as the sulphur atoms in the TT spacers. A single crystal of 4a could be isolated to confirm the molecular structure (vide infra). Hydrogen bonding interactions closer than 2.6 Å are absent in the solid state structure of 4a and did not affect the rotations in the molecule. The third isomer 4c with two different orientations of the NMe$_2$ fragments, would result in duplicated proton resonances in a 1 : 1 ratio (similar to 3b), and is not observed. The individual proton resonances of 4a are more downfield compared to 4b (Fig. S11, ESI†). Two significantly different NMe$_2$ resonances are observed for 4a in CDCl$_3$, ca. 0.3 ppm apart, that are more downfield compared to the single resonance of 4b at 3.30 ppm (Table 1). In (CD$_3$)$_2$SO both NMe$_2$ fragments of 4a and 4b appear as two signals, respectively.

A cationic triscarbene complex structure for 4d is further supported by the poorer solubility of the complex in deuterated solvents and the upfield shifts of the TT proton resonances when compared with the corresponding biscarbene complexes. In (CD$_3$)$_2$SO the 2 : 1 ratio of the two carbene ligands trans to each other and one carbene ligand trans to Cl are observed from proton integration 2 : 3 (2H + 1H) : 2 : 1 : 1 in the aromatic region (Fig. S12, ESI†), for the three thienothiophene carbene subtituents. The resonances of the two trans carbene ligands are chemically equivalent and more downfield than the third carbene ligand (trans to Cl). The three NMe$_2$ fragments in 4d resonate as four peaks (Table 1), with the two trans NMe$_2$ signals appearing as two broad signals (0.47 ppm apart) more downfield compared to the two broad signals of NMe$_2$ trans to Cl (0.08 ppm apart).

$^{13}$C NMR data are summarized in Table 2. The carbene carbon chemical shifts of the Pt$^{iv}$ ethoxy carbene complexes (1 and 2) are at 235.2 and 233.2 ppm, respectively, comparable to the Pt$^{iv}$ ethoxy-FCC ([PtCl$_2$(OEt)$_2$]-C$_5$H$_4$NMe$_2$)$_2$, 238.5 ppm in CD$_2$Cl$_2$).$^8$ Compared to the carbene carbon signals of PtCl$_2$ bisalkoxycarbene complexes with aliphatic carbene substituents (Fig. 1c, ca. 278 ppm in CDCl$_3$)$^6$ and mononuclear Pt-bisethoxy carbene complexes with cyclic amine substituents (Fig. 1d, ca. 198 ppm in CDCl$_3$)$^7$ 1 and 2 are shifted significantly upfield and downfield, respectively. The carbene carbon chemical shift of 2 is ca. 36 ppm downfield from the corresponding signal in the analogue aminocarbene complex 3a (196.5 ppm), measured in ([CD$_3$)$_2$SO]; commensurate with the strong shielding effect of the amino-substituent of the carbene carbon atom, compared to an ethoxy substituent.$^9$

Carbon chemical shifts are very similar in 1 and 2, with the carbene carbon resonance slightly more downfield in 1. The methyl resonance in 1 is duplicated. Broad signals are obtained for the carbene carbon and C4 resonance of 2 (ESI† Fig. S8).

Compound 3b was isolated as a mixture with 3a as the major component and no $^{13}$C NMR data were obtained for this complex, or the insoluble 4d. 2D NMR spectroscopy was employed to assign especially the aromatic resonances for the complex mixtures (ESI†).

**Molecular structures**

Crystallizations of the platinum(n) complexes 1, 2, 3b and 4a, precursor P4$_W$ and the oxidized ester-product 5 were carried out from saturated DCM solutions of the compounds, layered with hexane. The structures of P4$_W$ and 5 are reported in the ESI†. Due to the poor solubility of 3, the compound was crystallized from a large amount of THF layered with hexane. Single crystal X-ray diffraction studies confirmed the molecular structures (Fig. 3). Selected bond lengths, angles and torsion angles are reported in Table 3, employing the atom numbering scheme as used in the NMR assignments. The single crystal X-ray diffraction data set for 2 is of too poor quality to publish, but the molecular structure is included in the ESI† Fig. S19 to prove atom connectivity and to use as proof of the molecule’s conformation. The square planar cis-Pt dichloride fragment of 1 and 2 is attached to two thiophenes and two [2,3-β]TTs respectively, each through an ethoxy carbene carbon.

In 3b and 4a, the square planar cis-Pt dichloride fragment is attached to two [2,3-β]TT spacers, in the case of the former

| Complex | C2 | C3 | C4 | C5′ | C5 | C$_{carb}$ | OEt$^b$ |
|---------|----|----|----|-----|----|------------|--------|
| 1$^a$   | 150.5 | 143.4 | 130.4 | 142.5 | 235.2 | 80.5, 14.8, 14.8 |
| 2$^a$   | c | c | 140.2 | 153.6 | 122.1 | 131.9 | 233.2 | 80.1, 14.9 |
| 3a$^a$  | c | c | 124.2 | 130.8 | 121.0 | 130.9 | 196.5 |

$^a$ NMR data recorded in CD$_2$Cl$_2$. $^b$ Carbon chemical shifts for the ethoxy fragment are reported with the first value being the chemical shift of the methylene group, and the second the chemical shift of the methyl group. Assignments could not be made unambiguously. $^c$ NMR data recorded in (CD$_3$)$_2$SO.

**Table 2.** $^{13}$C NMR chemical shifts (δ) of the Pt FCCs
through aminocarbene carbons and the latter through dimethylamino-carbene carbons.

The ethoxycarbene complexes 1 and 2 have the anti-isomer arrangement in the solid state with their ethyl groups and metal moiety on the same side of the (M)Ccarb–O(Et) bonds.23–26 In both structures the ethoxy substituents appear on the same side as the thienylene spacer’s adjacent sulphur atom. In the case of the aminocarbene complex 3b, the first amino group is on the same side as its thienylene spacer’s adjacent sulphur atom and the second on the opposite side of its thienylene spacer’s adjacent sulphur atom. For 4aW, the dimethylamine group is on the same side as the sulphur atoms in the TT spacer (ESI† Fig. S19), contradictory to what is observed for 4a and 3b. The averaged Pt–C carb bond lengths for Pt-carbene complexes in this study, 1, 3b and 4a, are the same and independent of the type of thienylene spacer or ethoxy/amino/dimethylamine group present in the molecule (1.966(8), 1.966(3) and 1.987(9) Å respectively). Compared to a PtIII bisethoxycarbene complex [PtCl2(C(OEt)-C(6H4)NMe2)] with an averaged Pt–Ccarb bond length of 1.935 (16) Å, the former is slightly longer in length.8

In Pt cationic tris-dimethylaminocarbene complexes ([PtCl2{(C(NMe2)-p-C6H4NMe2)2}[W(CO)3Cl]− and [PtCl(C(NMe2)-p-C6H4NMe2)2][PF6]−] the carbene ligands trans to each other have longer averaged Pt–Ccarb bond lengths, 2.053(4) and 2.055(4) Å respectively, compared to their singular carbene ligand trans to Cl, 1.975(6) and 1.973(4) Å respectively. The Pt–Ccarb bond lengths in Pt cationic tris-dimethylaminocarbene complexes are longer compared to Pt bincarbone complexes (1, 3b, 4a and [PtCl2{(C(OEt)-p-C6H4NMe2)2}]).8

The Ccarb–C2/C5 bond lengths of 1 are shorter compared to 3b and 4a (Table 3), confirming that the ethoxycarbene complex is more dependent on electron density from the thienylene substituent to stabilize the carbene carbon compared to amino- and dimethylaminocarbene complexes. For 3b, NH···S intramolecular interactions are observed (Fig. S20, ESI†) for the sulfur of the thienylene spacer that is cis to the NH2 unit. This is not possible if the sulfurs of the thienylene spacer are trans to

| Complex | 1a | 3b | 4a |
|---------|----|----|----|
| Bond lengths |     |     |    |
| M–Ccarb | 1.986(7), 1.945(9) | 1.968(3), 1.964(2) | 1.993(9), 1.98(1) |
| Ccarb–O/N | 1.285(9), 1.34(1) | 1.303(4), 1.297(4) | 1.30(1), 1.29(1) |
| C2–C3 | 1.42(1), 1.39(1) | 1.451(4), 1.449(4) | 1.46(1), 1.49(1) |
| C3–C4 | 1.47(1), 1.43(1) | 1.378(4), 1.383(4) | 1.39(1), 1.37(2) |
| C4–C5 | 1.44(1), 1.40(1) | 1.445(4), 1.414(4) | 1.43(1), 1.42(1) |
| S–C2 | 1.35(1), 1.36(2) | 1.396(4), 1.375(4) | 1.37(2), 1.36(2) |
| S–C5 | 1.728(7), 1.77(1) | 1.703(3), 1.712(3) | 1.71(1), 1.73(1) |
| Bond angles |     |     |    |
| M–Ccarb–O/N | 126.0(6), 127.5(6) | 119.1(2), 121.3(2) | 122.8(7), 125.5(7) |
| Ccarb–C2/C5–C3/C4 | 113.0(7), 118.2(3) | 118.1(3), 118.2(3) | 119.9(9), 118.6(8) |
| Ccarb–C2/C5 | 117.25, 90.15 | 117.25, 90.15 | 117.25, 90.15 |
| Ccarb–C2/C5–C3/C4 | 72.75, 11.15 | 72.75, 11.15 | 72.75, 11.15 |

* First set of data reported for first carbene fragment and the second for the second carbene fragment. ** First mean plane drawn through C2, C3, C4 and C5, and the second through M, Ccarb and O/N. † Mean plane drawn through C2, C3, C4 and C5 of each thienylene.
the NH₂ unit, instead intermolecular hydrogen bonding interactions occur between TT-H4 and NH with the oxygen of a co-crystallized THF molecule (2.510 and 2.091 Å, respectively). Thus, two different orientated TT spacers are observed.

**Catalytic hydrosilylation**

The well-studied and documented a hydrosilylation model reaction with phenylacetylene and triethylsilane is depicted in Scheme 2.†-11,14,27,28 Six possible products have been reported for the reaction; triethyl(1-phenylvinyl)silane (α-isomer), (E)-triethyl-(styryl)silane (β-E-isomer), (Z)-triethyl(styryl)silane (β-Z-isomer), hydrogenated products (styrene and ethylbenzene) and a dehydrogenative silylation product (triethyl(phenylethynyl)silane). PtII NHC catalysts display almost exclusive selectivity for the β-E or α-isomers.†,11,14,27,29,30 Due to the lack of solubility and the ambiguity with regards to the purity/molecular structure of the aminocarbene complexes 3 and 4, only the well-defined ethoxy-FCCs 1 and 2 were evaluated as catalyst precursors for phenylacetylene hydrosilylation with triethylsilane. The reactions in Tables 4 and 5 were performed in toluene-d₈, except for the neat experiments (entries 14 and 15, Table 4). A stability test was performed for 2 (entry 1, Table 4), in the absence of any substrate. After heating the reaction tube with 2 for 6 hours at 80 °C, no decomposition indicative of a Pt-catalyzed carbene self-dimerization product is observed.†,31

Optimisation of the hydrosilylation reaction conditions were performed using 2 (entries 3–10, Table 4). The optimal reaction conditions were found to be 0.3 mol% catalyst loading at 80 °C for 2 hours (entry 9). Complete conversion was reached within this time, compared to some of the most active catalysts where 6 hours are required.† Pronounced selectivity for the β-E-isomer was observed, as have been reported for most PtII catalysed hydrosilylation reactions.†,14,31 In the case of entry 9, product distribution (β-E/α/β-Z) is determined as 74/23/3 (see NMR spectrum in Fig. S22, ESI†). By-products from the reaction; styrene, ethylbenzene and triethyl(phenylethynyl)silane, are reported in Table S8, ESI†.

Styrene formed (up to 7% yield) during most of the optimisation reactions, as long as the catalyst loading is high enough (>0.2 mol%) and the reaction time long enough (>1 h). Ethylbenzene was not observed and triethyl(phenylethynyl)silane is mostly observed in trace amounts (<1% yield). Changing the catalyst precursor to 1 (entry 11, Table 4) leads to a slight improvement in the % conversion and yield, but the selectivity is not influenced. The insignificantly different behaviour leads to the conclusion that there is virtually no difference between the reactivity of the T- and TT-substituted carbene ligands. However, the presence of the Fischer carbene ligand is required for catalytic activity, as determined from comparison to the performance of the platinum precursors, K₂PtCl₄ (entry 12) and cis-[PtCl₂(NCMe)₂] (entry 13).

Observation of plausible intermediates of platinum complexes containing chelated acyclic aminocarbene ligands during hydrosilylation catalysis, has been reported previously.† These intermediates represent either products of oxidative addition of the H-Si bond of the hydrosilane to the catalyst precursor’s core or a product of the 1,2-alkyne insertion into the Pt-H bond of the catalyst core, already containing the silyl fragment (see Scheme S2, ESI†). K₂PtCl₄ and cis-[PtCl₂(NCMe)₂] did not perform as well as our platinum catalyst precursors, 2 and 1, that display pronounced selectivity for one-to-two products. Performing the reactions neat (solvent free) with 2 (entry 14) and 1 (entry 15), led to reaction completion. No yield could be calculated for these reactions, but the product distribution could be determined as a ratio. Compared to entries 9 and 11, respectively, slightly more β-E-isomer and less β-Z-isomer formed. Complex 2 displayed high functional group tolerance as substrate screening was investigated (Table 5). Compared to hydrosilylation with phenylacetylene as substrate, entries 1–5 led to higher % yields of the hydrosilylation isomeric products.

Entry 7, carried out with N-Boc-propargylamine as substrate, yielded less hydrosilylation isomeric products. No products are obtained when using propargylamine and bis(trimethylsilyl)acetylene as substrates. Because of the high % yields obtained, the reaction time of selected substrates was decreased with the aim to decrease % yields to enable comparisons. The % yields of entries 9 and 12 (Table 5) were insignificantly influenced by the time change. In the case of internal alkyne, 3-hexyne (entry 10) and amine-functionalised alkyne, N-Boc-propargylamine (entry 11), a decrease in activity is seen, more extreme in the case of the latter. Selectivity of 2 for the β-E-isomer is better in entries 1, 2, 4 and 5 (Table 5), compared to hydrosilylation with phenylacetylene as substrate. The NMR spectrum of entry 5, Table 5 is displayed in Fig. S27, ESI†. Complete selectivity for the β-E-isomer is observed when the internal alkyne 3-hexyne is used as substrate, as the expected α-isomer formation is not possible. Selectivity for the β-E-isomer is poorer in the cases where 3-TMSO-1-propyne (entry 3) and N-Boc-propargylamine (entry 7) are used as substrates (TMSO = trimethylsilyloxide, Boc = tert-butoxycarbonyl). When the reaction time of selected substrates is decreased, a slightly higher selectivity for the β-E-isomer is observed. Assignments of ²H NMR signals (Table S7, ESI†), for products obtained during hydrosilylation were made according to literature reports: phenylacetylene,14,14,35,37 1-hexyne,38–41 3-hexyne,42–45 3-TMSO-1-propyne,46 5-hexyn-1-ol38 and 5-chloro-1-pentyne.47 The only evidence of a dehydrogenative silylation product is observed as a byproduct in the reaction using phenylacetylene as a substrate (triethyl(phenylethynyl)silane, 1.23 (9H, t, ²J 7.9)).†

Comparison of the catalytic performance of 2 and 1 with recent examples of PtII NHC catalysts for this benchmark hydrosilylation reaction, reveals superior selectivity of the PtII FCCCs 1 and 2 in the majority of cases.11,14,27,29,30 Similarly,
This study reports the first utilization of Fischer carbene ligands coordinated to a PtII metal centre, as molecular catalyst precursors for alkylene hydroisilylation reactions. The PtII FCCs 1 and 2 were tested as catalyst precursors for the benchmark reaction of phenylacetylene with triethylsilane. Both (pre)catalysts exhibited good activity as complete conversion was reached in a short period of time, and a high functional group tolerance for the reaction of phenylacetylene with triethylsilane. Both (pre)catalysts exhibited good activity as complete conversion was reached in a short period of time, and a high functional group tolerance for the reaction of phenylacetylene with triethylsilane.

Conclusions

The number of carbene ligands that coordinate to the PtII metal, depends on the steric and electronic properties of the carbene ligand as determined by its substituents. In this study, mostly neutral mononuclear PtII-biscarbene complexes were obtained (1, 2, 3a/b and 4a/b) from carbene transfer via group 6 FCC precursors. In the case of both the Pt-biscarbene complexes 3 and 4, two geometric stereoisomers are observed. The cis-isomer is negligible, the possibility of alkylene insertion into the Pt–Si bond, is discarded.

The formation of the β-Z-isomer is negligible, the possibility of alkylene insertion into the Pt–Si bond, is discarded. Finally, the recyclability of 2 was investigated. A catalytic experiment was done in duplicate with 0.3 mol% catalyst loading at 80 ºC for 2 hours in toluene-d8. After reaction completion/full conversion, substrates phenylacetylene and triethylsilane were added again, with the same equivalents as employed in the first batch reaction. This procedure was repeated four times, and the reaction still ran to completion and no decrease in activity was observed.

Table 4 Optimization of hydroisilylation using phenylacetylene and triethylsilane (variation of catalyst loading, temp., time, and catalyst precursor: 1, 2, cis-[PtCl2(NCMe)2], K2PtCl4)

| Entry | Catalyst precursor | Catalyst loading (mol%) | Time (h) | Temp. ( ºC) | Conv. (%) | Total% yieldb/TON/TOF (h–1) | Product distribution β-Z/ε-Z/β-ε (%) |
|-------|--------------------|-------------------------|----------|-------------|-----------|-----------------------------|-----------------------------------|
| 1d    | 2                  | 2                       | 6        | 80          | 0         | 0/0/0                       | 0/0/0                             |
| 2d    | —                  | —                       | 6        | 80          | 25        | 1/0/0                       | 100/0/0                          |
| 3d    | 2                  | 1                       | 6        | 80          | 98        | 83/83/14                    | 74/24/2                          |
| 4     | 2                  | 0.5                     | 6        | 80          | 97        | 91/182/30                  | 75/23/2                          |
| 5d    | 2                  | 0.3                     | 6        | 80          | 99        | 87/290/48                  | 75/23/2                          |
| 6d    | 2                  | 0.2                     | 6        | 80          | 90        | 39/195/33                  | 41/56/3                          |
| 7d    | 2                  | 0.3                     | 6        | 40          | 16        | 5/17/3                     | 60/40/0                          |
| 8d    | 2                  | 0.3                     | 3        | 80          | 98        | 83/283/94                  | 74/24/2                          |
| 9d    | 2                  | 0.3                     | 2        | 80          | 94        | 81/270/135                | 74/23/3                          |
| 10d   | 2                  | 0.3                     | 1        | 80          | 48        | 41/137/137                | 71/27/2                          |
| 11d   | 1                  | 0.3                     | 2        | 80          | 98        | 83/277/138                | 73/23/4                          |
| 12d   | K2PtCl4            | 0.3                     | 2        | 80          | 13        | 0/0/0                       | 0/0/0                            |
| 13    | cis-[PtCl2(NCMe)2] | 0.3                     | 2        | 80          | 52        | 44/147/73                 | 50/45/5                          |
| 14    | 2                  | 0.3                     | 2        | 80          | —         | —                           | 76/22/2                          |
| 15    | 1                  | 0.3                     | 2        | 80          | —         | —                           | 77/22/1                          |

a Conversion as determined by NMR integration based on the two substrates (phenylacetylene and triethylsilane) and referenced to internal standard anisole. b Yield as determined from NMR integration based on the limiting substrate (most of the time phenylacetylene). c Experiments not performed in duplicate. d Substrate loading = 0. e An unidentified precipitate was observed. f Reactions were performed neat (no solvent). Complete conversion was observed, however no yield could be calculated.

Table 5 Substrate functional group tolerance and product distribution dependence on time (with 2 as catalyst precursor at 0.3 mol% catalyst loading in toluene-d8 at 80 ºC)

| Entry | Substrate | Time (h) | Conv. (%) | Total% yieldb/TON/TOF (h–1) | Product distribution β-Z/ε-Z/β-ε (%) |
|-------|-----------|----------|-----------|-----------------------------|-----------------------------------|
| 1     |           | 2        | 99        | 94/313/157                  | 76/21/3                          |
| 2     |           | 2        | 100       | 100/333/167                 | 99/0/1                           |
| 3     | TMSO      | 2        | 99        | 94/313/157                  | 61/37/2                          |
| 4     | HO        | 2        | 99        | 98/327/163                  | 88/11/1                          |
| 5a    | Cl        | 2        | 100       | 87/290/145                  | 81/16/3                          |
| 6     |            | 2        | 6         | 0/0/0                       | 0/0/0                            |
| 7     |            | 2        | 73        | 73/243/122                  | 69/31/0                          |
| 8a    | TMS–TMS   | 2        | 13        | 0/0/0                       | 0/0/0                            |
| 9     |            | 1        | 98        | 95/317/317                  | 86/12/2                          |
| 10    |            | 1        | 86        | 86/287/287                  | 99/0/1                           |
| 11    | Boc–NH    | 1        | 38        | 36/120/120                  | 72/28/0                          |
| 12    |            | 1        | 99        | 96/320/320                  | 89/10/1                          |

a An unidentified precipitate was observed.
alkyne substrates. At optimal reaction conditions, product distribution $[\beta$-$E]/[\beta$-$Z]$ was determined as 73/23/4 and 74/23/3, respectively. Notably, this selectivity is an improvement on that of known Pt$^\text{II}$ NHC complexes, with comparable activity. The possibility of excluding solvent use in neat hydrosilylation reactions with 1/2 as catalyst precursors, proved possible with the additional advantage of improved selectivity for the $\beta$-$E$-isomer, while 2 can be reused for at least four batch hydrosilylation reactions, without any evidence of decomposition or decreased reactivity.

### Experimental

#### General

All operations were carried out using standard Schlenk techniques or vacuum line techniques under an inert atmosphere of nitrogen or argon, using oven-dried glassware. Silica gel 60 (particle size 0.063–0.20 mm) was used as resin (stationary phase) for all column chromatography separations.

#### Chemical reagents and solvents

THF and diethyl ether were distilled over sodium wire and benzophenone under N$_2$ (g) atmosphere, hexane over sodium wire and DCM over CaH$_2$. Other chemicals were used as they were commercially supplied by Sigma Aldrich and Strem Chemicals. The n-ButLi used in syntheses was from a stock 1.6 M solution in THF.

Boron trifluoride etherate was distilled before use. Pt(COD)Cl$_2$, cis-[PtCl$_2$(NMe$_2$)$_2$] and group 6 FCC precursors were prepared according to literature procedures. The synthesis and characterization of [Cr(CO)$_5${C(OEt)-2-C$_4$H$_3$S}], [Cr(CO)$_5${C(NH$_2$)-5-C$_6$H$_3$S$_2$}], and [W(CO)$_5${C(NH$_2$)-5-C$_6$H$_3$S$_2$}] are reported in the ESI.

#### Synthesis and characterization of Fischer carbene complexes

##### Synthesis of platinum(II) ethoxycarbene complexes of thiophene

Excess $\text{PdCl}_2$ (3.00 g, 9.0 mmol) and Pt(COD)Cl$_2$ (1.53 g, 4.1 mmol) were dissolved in 20 mL dried DCM (degassed for 15 min) and allowed to reflux under an inert atmosphere at 50 ℃ for 24–30 hours. The solvent was removed under vacuum and the reaction mixture dissolved in a minimal amount of DCM. The product was cannula filtered and triturated with hexane. The product was repeatedly washed with large amounts of dry ether to separate unreacted Pt(COD)Cl$_2$ from 1 (listed in ESI, Table S2), before being dried under vacuum.

1: $\delta^1$H (400.13 MHz; CDCl$_3$; Me$_4$Si) 8.09 (2 H, d, $^3J$$_\text{F-H}$ 4.7, H5), 7.28 (2 H, d, $^3J$$_\text{F-H}$ 4.7, 3.7, H4), 8.69 (2 H, d, $^3J$$_\text{F-H}$ 3.7, H3), 5.60 (4 H, s, br, CH$_2$), 1.59 (6 H, t, $^3J$ 6.8, CH$_3$). $\delta^1$C(125.75 MHz; (CD$_3$)$_2$SO; Me$_4$Si) 196.5 (C$_4$), 150.8 (C$_5$), 146.0 and 145.8 (C$_3$ and C$_2$), 121.2 (C$_1'$). $\delta$$_\text{N(J)}$ KBr pellet/cm$^{-1}$ 3294s, br (v$_\text{a}$) and 3210s, br (v$_\text{a}$). $\delta^1$H (500.13 MHz; (CD$_3$)$_2$SO; Me$_4$Si) 10.77 and 10.61 (2H + 2H, s, br, NH$_2$), 8.26 (2H, s, H$_4$), 7.66 (2H, d, $^3J$$_\text{F-H}$ 5.3, H5'), 7.40 (2 H, d, $^3J$$_\text{F-H}$ 5.3, H4). $\delta^1$C(125.75 MHz; (CD$_3$)$_2$SO; Me$_4$Si) 196.5 (C$_5$), 150.8 (C$_5$), 146.0 and 145.8 (C$_3$ and C$_2$), 130.9 (C$_5$'), 121.0 (C$_4'$). m/z (C$_4$H$_8$NO$_2$Cl$_2$S$_2$Pt, 600.49 g mol$^{-1}$) calculated: 677.7935, found: 677.7938 (96% [M + Br$^-$]).

3b: $\delta^1$H (500.13 MHz; (CD$_3$)$_2$SO; Me$_4$Si) 11.42 and 11.18 (2H + 2H, s, br, NH$_2$), 8.56 and 8.46 (2H, s, H$_4$), 7.73 and 7.72 (2H, d, $^3J$$_\text{F-H}$ 5.3, H5), 7.46 and 7.43 (2 H, d, $^3J$$_\text{F-H}$ 5.3, H4).

##### Synthesis of platinum(II) dimethylamine-carbene complexes of thiophene

The same reaction method was applied to excess $\text{PdCl}_2$ (0.17 g, 0.4 mmol) and Pt(COD)Cl$_2$ (0.06 g, 0.2 mmol). Instead of using large amounts of ether, the product was repeatedly washed with minimal amounts of chloroform, followed by a single ether wash. Dissolved in DCM, the product (in ESI, Table S3) was dried on MgSO$_4$, filtered and dried under vacuum.

2: $\delta^1$H (400.13 MHz; CDCl$_3$; Me$_4$Si) 9.08 (2 H, s, H$_4$), 7.44 (2 H, d, $^3J$$_\text{F-H}$ 5.2, H5'), 7.35 (2 H, s, br, H$_4$), 5.77 and 5.18 (2H + 2H, s, br, CH$_3$), 1.59 (6 H, s, br, CH$_3$). $\delta^1$H (500.13 MHz; CDCl$_3$; Me$_4$Si) 9.03 (2 H, s, H$_4$), 7.49 (2H, d, $^3J$$_\text{F-H}$ 5.1, H5'), 7.39 (2 H, s, br, H$_4$), 5.73 and 5.21 (2H + 2H, s, br, CH$_3$), 1.58 (6 H, s, br, CH$_3$). $\delta^1$C(400.13 MHz; CD$_2$Cl$_2$; Me$_4$Si) at 2 ℃ 0.05 (2 H, s, H$_4$), 7.49 (2 H, s, br, H$_5$'), 7.39 (2 H, s, br, H$_4$), 5.73 and 5.14 (2H + 2H, s, br, CH$_3$), 1.61 (6 H, s, br, CH$_3$). $\delta$($^1^3$C) (125.75 MHz; CD$_2$Cl$_2$; Me$_4$Si) 233.2 (br, C$_\text{carb}$), 153.6 (C$_5$), 140.2 (C$_4$), 152.3 and 148.3 (C$_3$ and C$_2$), 131.9 (C$_5'$), 122.1 (C$_4'$), 80.1 (C$_2$), 14.9 (CH$_3$). m/z (C$_4$H$_8$NO$_2$Cl$_2$S$_2$Pt, 658.56 g mol$^{-1}$) calculated: 691.8747, found: 691.8950 (35%, [M + Cl$^-$]).
4a: δ^1H (300.13 MHz; CDCl3; Me4Si) 8.06 (2H, s, H4), 7.45 (2H, d, δ 5.3, H5'), 7.35 (2H, d, δ 5.3, H4'), 4.22 and 3.86 (6H + 6H, s, NCH3). δ^13C (75.468 MHz, CDCl3; Me4Si) 166.41 (δ(NMe2)(C)(O)), 145.95 (C5), 121.8 and 121.8 (C4), 141.1 and 140.2 (C3 and C2), 128.6 (C5'), 120.3 (C4'), 38.0 (br, NMe2). m/z ([C5H5N2Cl2S4Pt] +, [M + Na]+), calculated: 234.0091, found: 234.0023 (100%, [M + Na]+).

4b: δ^1H (400.13 MHz; CDCl3; Me4Si) 7.61 (2H, s, H4), 7.38 (2H, d, δ 5.3, H5'), 7.29 (2H, d, δ 5.3, H4'), 3.30 (12H, s, NMe2). δ^13C (125.75 MHz; CDCl3; Me4Si) 78.0 (2H, s, H4), 7.70 (2H, d, δ 5.2, H5'), 7.41 (2H, d, δ 5.2, H4'), 4.15 and 3.65 (6H + 6H, s, NMe2).

4c: δ^1H (300.13 MHz; CD3)2SO; Me4Si) 7.65 (2H, s, br, H4′ (trans to carbene ligand) + H4 (trans to Cl)), 7.26 (2H, s, br, H4′ (trans to carbene ligand)), 6.87 (1H, s, br, H5′ (trans to Cl)), 6.78 (1H, s, br, H4′ (trans to Cl)), 4.10 and 3.63 (6H + 6H, s, br, NMe2 (trans to carbene ligand)), 3.38 and 3.30 (3H and 3H, s, br, NCH3 (trans to Cl)).

5: ν̇C=O(hexane)/cm⁻¹ 1639m, br (C=O stretching vibration).

Catalytic hydrosilylation reactions
A high pressure NMR tube fitted with a J. Young valve, was charged with the (prec)atalyst precursor, alkylene, triethylysilane and internal standard in toluene-d8 under an atmosphere of argon, before heating. Each reaction contained triethylsilane (0.25 mmol), anisole (27.0 mL), 0.2 mL toluene-d8 and 0.25 mmol, and was integrated in the proton NMR spectra to represent three protons (area: 3.34–3.31 or 3.36–3.30 ppm). No triethylsilane was added in entry 1 (Table 4) and entries 14 and 15 (Table 4) were done solvent free. After a predetermined time at a certain temperature (80 °C, except entry 7, Table 4, was performed at 40 °C), the NMR data are collected and analysed. Reaction conditions applied to individual reactions are reported in Table S8, ESL. After the reactions were completed the solutions appeared pale yellow, indicating the presence of hydrosilylation isomeric products that formed.

A descriptive example for a performed catalytic run (entry 9, Table 4) is as follows: 0.3 mol% of 2, phenylacetylene (27.5 μL, 0.25 mmol), triethylysilane (40.0 μL, 0.25 mmol), anisole (27.0 μL, 0.25 mmol) and 0.2 mL toluene-d8 was added to a high pressure NMR tube, under an atmosphere of argon. The sealed NMR tube was then placed in an oil bath set at 80 °C for 2 hours. The NMR tube is allowed to reach RT before NMR spectra were collected. Catalytic reactions were performed in duplicate, unless stated otherwise, and the averaged results reported.

Characterization and analytical data
Ultraviolet spectra could not be obtained for 1, 3, 4 and 5 (these compounds are yellow to colourless when diluted to 0.01 mM in 10 mL of DCM and 3 and 4 are insoluble in DCM). 4d did not ionize during mass spectrometric (MS) analysis. Dimerization of 1 through bridging chlorido ligands was observed in the MS of the sample.

Nuclear magnetic resonance spectroscopy. NMR spectra were recorded on Bruker AVANCE 500, Ultrasound Plus 400 AVANCE 3 and Ultrashield 300 AVANCE 3 spectrometers, at 25 °C. The 1H NMR spectra were recorded at 500.139, 400.13 or 300.13 MHz, and the 13C NMR spectra at 125.75, 100.613 or 75.468 MHz, respectively. CDCl3, CD2Cl2 and (CD3)2SO were used as solvent. For the samples measured in CDCl3, chemical shifts (reported as δ (ppm) downfield from Me4Si) are referenced at 7.26 ppm for δH and 77.0 ppm for δC. The CD2Cl2 reference signals are at 5.32 ppm for δH and 54.0 ppm for δC, and the (CD3)2SO reference signals are at 2.50 ppm for δH and 39.5 ppm for δC. An additional low temperature 1H NMR spectrum of 2 was measured in CD2Cl2 at 2 °C. The toluene-d8 reference signal is at 2.09 ppm for δH (hydrosilylation reactions). Coupling constants (J) are reported in Hz. Preparation of the samples was carried out under Ar(g) and the NMR tubes were sealed before data collection. The 1H NMR data are reported in the format: chemical shift (integration, multiplicity, coupling constant, assignment) and the 13C NMR data in the format: chemical shift (assignment), in the order of assignments. The spectral coupling patterns are: s – singlet, d – doublet, t – triplet and br – broad.

First-order analysis was carried out to assign signals of the 1H NMR spectra. Additional 2D [1H, 13C] COSY NMR experiments were done where confirmation of the proton assignments were required. Assigning the carbon chemical shifts, obtained from proton-decoupled 13C NMR spectra, was possible with the assistance of 2D [1H, 13C] HSQC and 2D [1H, 13C] HMBC NMR experiments (see ESI, † Section S3). Standard Bruker pulse programs were used in the experiments.

Fourier-transform infrared spectroscopy. Infrared spectroscopy was performed on a Bruker ALPHA FT-IR spectrophotometer with a NaCl cell, using dried hexane as solvent. Insoluble samples were measured in the solid state (KBr pellets). KBr pellets are pressed from dry homogeneously powdered KBr containing sample in 0.2–1% concentration. The absorptions were measured from 400–4000 cm⁻¹. The IR data are reported in the format: absorption intensity (assignment) in the order of highest to lowest wavenumber. The wave intensities are: w – weak, m – medium, s – strong, sh – shoulder and br – broad.

High-resolution mass spectrometry. Mass spectral analyses were performed on a Waters® Synapt G2 high definition mass spectrometer (HDMS) that consists of a Waters Acuity Ultra Performance Liquid Chromatography (UPLC®) system hyphenated to a quadrupole-time-of-flight (QTOF) instrument. Data acquisition and processing was carried out with MassLynxTM (version 4.1) software. A leucine encephalin solution (2 pg μL⁻¹, m/z 555.2693) was used as an internal lock mass control standard.
to compensate for instrumental drift and ensure good mass accuracy. The internal control was directly infused into the source through a secondary orthogonal electrospray ionization (ESI) probe to allowing intermittent sampling. Flow injection analysis (FIA, 0.4 mL min⁻¹ flow rate) with the injection volume set at 5 μL. Samples were made up in ultra-purity liquid chromatography methanol to an approximate concentration of 10 μg mL⁻¹. The methanol was spiked with 0.1% formic acid and used throughout the 1 min run. The capillary voltage for the ESI source was set at 2.8 kV and 2.6 kV for positive and negative mode ionization, respectively. The source temperature was set at 110 °C, the sampling cone voltage at 25 V, extraction cone voltage at 4.0 V and cone gas (nitrogen) flow at 10.0 L h⁻¹. The desolvation temperature was set at 300 °C with a gas (nitrogen) flow of 600.0 L h⁻¹. The mass to charge ratios (m/z) were measured in the range of 50–1500 Da with the raw data presented in the form of a centroid profile (scans collected every 0.3 seconds). A negative electron spray was employed as the ionization technique, but positive electron spray was required for the 1 min run. The capillary voltage for the ESI source was set at 2.8 kV and 2.6 kV for positive and negative mode ionization, respectively. The source temperature was set at 110 °C, the sampling cone voltage at 25 V, extraction cone voltage at 4.0 V and cone gas (nitrogen) flow at 10.0 L h⁻¹. The desolvation temperature was set at 300 °C with a gas (nitrogen) flow of 600.0 L h⁻¹. The mass to charge ratios (m/z) were measured in the range of 50–1500 Da with the raw data presented in the form of a centroid profile (scans collected every 0.3 seconds). A negative electron spray was employed as the ionization technique, but positive electron spray was required for 5. The MS data are reported in the format: calculated mass, found mass (percentage intensity, fragmentation) in the order of highest to lowest mass to charge ratio.

**UV-Vis spectroscopy**

Measurements were performed on 10 mL DCM solutions of 0.01 mM analyte concentration at 25 °C. Absorptions were measured in the range 200–1000 nm using a UV-Vis spectrophotometer Spectec 200 plus. WinASPECT PLUS (version 4.2) software was used for data visualization.

**X-ray diffraction analysis**

Single crystal diffraction data for P₄W₁, 2, 3b and 5, were collected at 150 K on a Bruker D8 Venture diffractometer with a kappa geometry goniometer and a Photon 100 CMOS detector using a Mo-Kα 1μs.macro focus source. Data were reduced and scaled using SAINT and absorption intensity corrections were performed using SADABS (APEX III control software).54 Single crystals of 1 and 4a were analyzed on a Rigaku XtalLAB Synergy R diffractometer, with a rotating-anode X-ray source and a HyPix CCD detector. Data reduction and absorption were carried out using the CrysalisPro (version 1.171.40.23a) software package.55 X-ray diffraction measurements were all performed at 150 K (except for 4a at 293 K) using an Oxford Cryogenics Cryostat. All structures were solved by an intrinsic phasing algorithm using SHELX56 and were refined by full-matrix least-squares methods based on F² using SHELXL.57 All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealized positions and refined using riding models. The X-ray crystallographic coordinates for the structures of compounds P₄W₁, 1, 2, 3b, 4a and 5 have been deposited at the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers CSD 2061163–2061168.

**Conflicts of interest**

There are no conflicts to declare.

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