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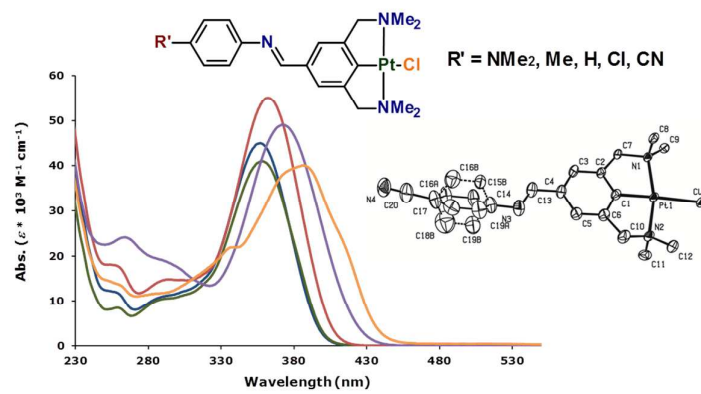


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Inductively the Pt-moiety in these organometallic benzyldene anilines is a very strong electron-withdrawing group, but mesomerically a very strong electron-donating group.

Organometallic Benzylidene Anilines: Donor-Acceptor Features in NCN-Pincer Pt(II) Complexes with a 4-(*E*)-[(4-*R*-phenyl)imino]methyl substituent^{¶†}

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Abstract

A series of organometallic 4, 4'-substituted benzylidene aniline complexes 4-ClPt-3,5-(CH₂NMe₂)₂C₆H₂CH=NC₆H₄R'-4', abbreviated as PtCl[NCN(CH=NC₆H₄R'-4')-4], with R' = NMe₂, Me, H, Cl, CN) (**1–5**, respectively), was synthesized *via* a Schiff-base condensation reaction involving reaction of PtCl[NCN(CH=O)-4] (**7**) with the appropriate 4-R'-substituted aniline derivative (**6a–e**) in toluene. The resulting arylplatinum(II) products were obtained in 75–88% yield. Notably, product **2** was also obtained in 68% yield from *a reaction in the solid state* by grinding solid **7** with aniline **6b**. The structures of **2**, **4**, and **5** in the solid state (single crystal X-ray diffraction) showed a non-planar geometry, in particular for compound **5**. The electronic interaction between the donor benzylidene fragment PtCl(NCN-CH) and the *para*-R' aniline substituent through the azomethine bridge was studied with NMR and UV/Vis spectroscopy. Linear correlations were found between the azomethine ¹H, the ¹⁹⁵Pt NMR and various ¹³C NMR chemical shifts, and the substituent parameters σ_F and σ_R of R' at the aniline site. In common with organic benzylidene anilines, the azomethine ¹H NMR chemical shift showed anomalous substituent behavior. The ¹⁹⁵Pt NMR chemical shift of the platinum center can be used as a probe for the electronic properties of the delocalized π -system of the benzylidene aniline framework, to which it is connected. The dual substituent parameter treatment of the azomethine ¹³C NMR shift gave important insight into the unique behaviour of the Pt-pincer group as a substituent. Inductively, it is a very strong electron-withdrawing group, whereas mesomerically it behaves like a very strong electron donating group.

Introduction

The introduction of transition metals in organic materials with important optical properties continues to attract the interest of current research.^[1] Herein, the possibility to engineer the redox properties of a metal center embedded in its ligand surrounding is an important tool. In the presence of other electro-active groups it is possible to transport charge from the metal center (donor) to the ligand backbone (acceptor), or *vice versa*. The nature of the backbone or spacer separating the electroactive groups, including the metal center, is very important in this process.

Within our current research on stilbenoid NCN-pincer platinum complexes **A**, PtCl[NCN(C₂H₂C₆H₄-R'-4')-4] (R' = NMe₂, OMe, SiMe₃, H, I, CN, NO₂; Fig. 1),^[2, 3] it has been shown that the functional group R' tunes the electronic properties of the metal center, and that the entire PtCl(NCN) fragment^[4, 5] can be regarded as an electron donating group. Previous results using PtX(NCN-COOH-4) (X = Cl, I) had already indicated that, qualitatively, the Hammett σ_p parameter of a PtI substituent can be considered as to be of comparable strength to that of a NMe₂ group, *i.e.* acts as a π -donor.^[6] In the stilbenoid complexes the donor-acceptor groups are connected via alternating carbon-carbon single and double bonds only. Although benzylidene anilines are isoelectronic with stilbenes, regarding their π -electronic structure, their properties can be strongly different.^[7, 8] Therefore it became of interest to study how the physical and electronic properties of these complexes would change when the ethen-1,2-diyl linker in the stilbenoid complexes (**A**) is replaced by an isoelectronic carbon-nitrogen double bond (**B**) as the linker, see Fig. 1.

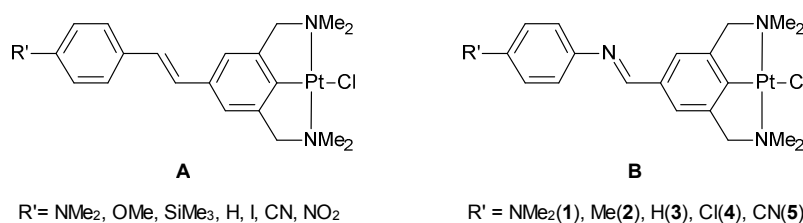
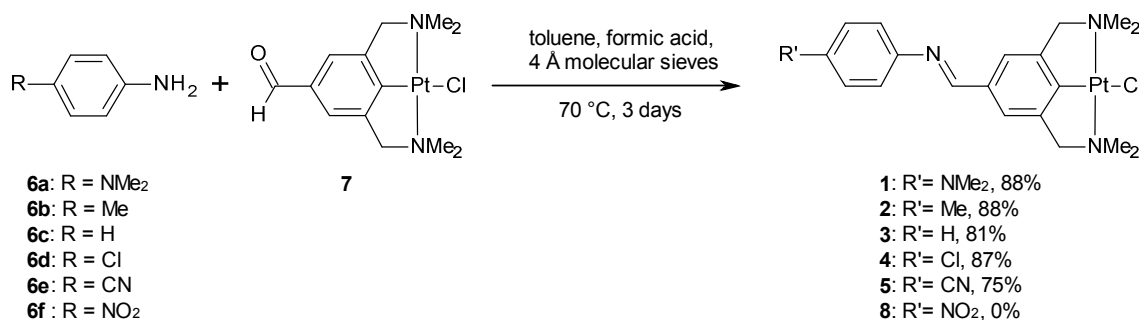


Fig. 1 NCN-pincer platinum(II) chloride benzylidene fragment in a R'-substituted stilbene, **A**, and a benzylidene aniline, **B**.

It must be noted that a great variety of *ortho*-cyclometalated imine complexes,^[9, 10] and complexes with a benzylidene aniline as a monodentate coordinating ligand^[11-13] have been reported but only a limited number of *para*-metalated benzylidene aniline complexes incorporating a metal-carbon σ -bond.^[14-17] Ferrocenylimines are well

known organometallic benzylidene aniline-type complexes which find use in cyclometalation reactions.^[18-20] However, to our knowledge, the synthesis and structures of *para*-metalated benzylidene aniline complexes in the solid state have not been reported thus far.

Previous studies revealed that the *para*-aldehyde functionality of PtCl(NCN-CH=O-4),^[2] **7**, can be readily converted into R' substituted stilbenes (see A in Fig.1). In the present study we report its direct conversion into a [(4-R'-phenyl)imino]methyl one using substituted anilines **6** in a Schiff-base condensation reaction (Scheme 1).



Scheme 1. Schiff-base condensation reaction of **6a–f** and **7**, giving **1–5**.

We describe the synthesis and structural characterization of a series of these 4-platinum benzylidene aniline complexes and compare their physical and electronic properties with those of their organometallic stilbenoid and corresponding organic benzylidene anilines^[7, 21] analogues.

Results and discussion

Synthesis. Reactions of 4-formyl-2,6-bis[(dimethylamino)methyl]phenyl platinum(II) chloride (**7**)^[2] with the respective *p*-substituted anilines **6a–f** (Scheme 1) were performed in dry toluene with a drop of formic acid as catalyst. Molecular sieves (4Å) were used to capture the released water (Na₂SO₄ and MgSO₄ were not effective). The respective complexes **1–5** were obtained pure, and in crystalline form after an easy work-up procedure in moderate to good yield (75 – 88%). Compounds **2–5** were stable when stored under air, but **1** (R' = NMe₂) slowly hydrolysed upon

several weeks of storage. Complexes **1–5** were fully characterized by NMR, UV/Vis, ATR-IR, and mass spectroscopy, as well as elemental analysis. The synthesis of **8** ($R' = \text{NO}_2$) was also attempted, but under the above-described reaction conditions complete conversion of **7** did not occur. Furthermore, attempts to separate pure **8** from the reactants failed. Prolonged reaction times, higher reaction temperatures as well as the addition of extra 4-nitroaniline to the reaction mixture did not drive the reaction to completion.

It is interesting to note that both Schiff-base condensation reactions^[22, 23] and the synthesis of pincer-metal compounds^[24] can be performed using solvent-free conditions. The applicability of this potentially Green method was tested for the synthesis of **2** involving of grinding of a mixture of solid organometallic aldehyde **7** (1 equiv) and aniline **6b** (1.2 equiv) in a Schlenk flask at room temperature, see experimental section. Monitoring of the reaction progress by ^1H NMR indicated that gradual formation of **2** (1h 27%, 5 days 68%) occurred. Neither decomposition nor formation of side products due to the high pressures exerted on the reactants during grinding was observed.

Structures in the solid state. For **2**, **4** and **5** crystals suitable for single crystal X-ray structure determinations were obtained by slow concentration of CD_2Cl_2 solutions of the respective compounds (evaporation in air). Displacement ellipsoid plots of the molecules are depicted in Fig. 2 and typical bond lengths and angles are listed in Table 1.

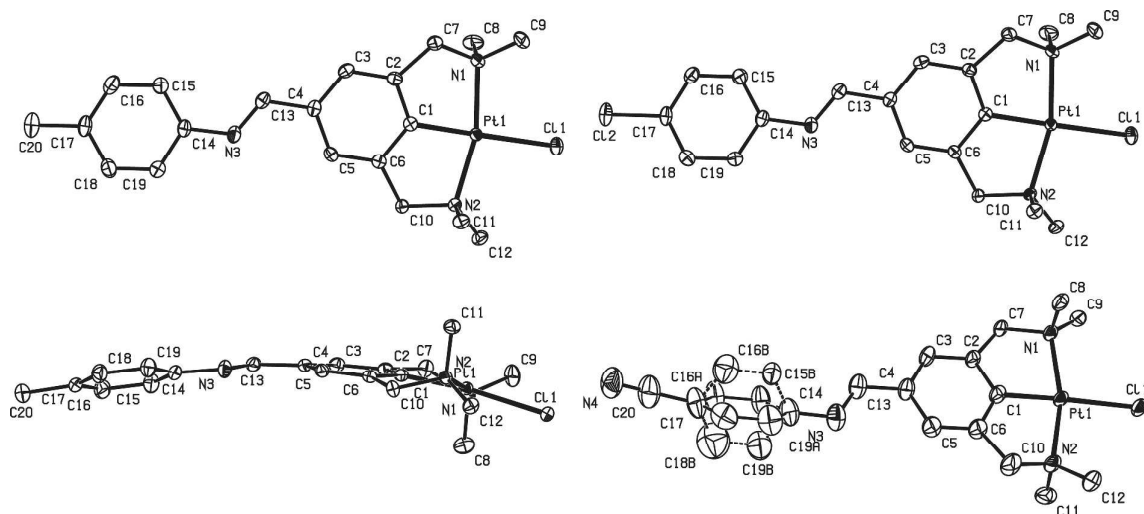


Fig. 2 Displacement ellipsoid plot (50% probability level) of **2** (top left and bottom left), **4** (top right), and **5** (bottom right). Hydrogen atoms have been omitted for clarity. For **5** the minor disorder component is drawn with dashed lines.

Compounds **2** and **4** are isostructural and possess an overall bent shape, *i.e.* the (Pt)C1 carbon atoms are 0.3700(17) and 0.3824(19) Å (for residues **2** and **4**, respectively) beneath the least-squares plane of the central double bond (C4-C13-N3-C14) (Fig. 2). For carbon atom C17 the distances are 0.2808(18) and 0.289(3) Å, respectively. A bent shaped conformation in benzylidene anilines has been observed previously for Ni(η^5 -C₅H₅)(PBU₃)(SC₆H₄N=CHC₆H₄CH₃-4') where the methylbenzylidene group is bent away from the rest of the molecule to avoid steric crowding.^[16] The same is likely to be the case here. Despite rather similar cell parameters, compound **5** is not isostructural with **2** and **4**, and has different packing. Compound **5** crystallizes with a disordered aniline fragment (Fig. 2). This type of disorder is rather common in *para*-substituted benzylidene aniline derivatives and will be commented below.

Comparison of the structural features of the NCNPtCl fragments of **2**, **4**, and **5** with earlier reported [PtCl(NCN)] complexes^[2, 25-28] show a similar distorted square planar geometry around the Pt nucleus, in which the carbon atoms of the benzylic substituents (C7 and C10) are positioned above and below the plane defined by C1-N1-Pt1-N2-C11. For the two five-membered metallacycles, which are slightly puckered, torsion angles for Pt1-N1-C7-C2 and Pt1-N2-C10-C6 have magnitudes between 26.6(6) and 32.9(2)°. The Pt1-C1 distances of **2**, **4**, and **5** are in the range of 1.9139(16) to 1.919(2) Å.^[26]

It is known that the molecular structure of substituted organic benzylidene anilines in the solid state can be non-planar, since both the aniline fragment A and benzylidene fragment C (Fig. 3) can rotate with respect to the azomethine fragment B (torsion angles θ and φ , respectively).^[8, 29] The conformational changes are controlled by the electronic and/or steric effects induced by the substituents on the aniline or benzylidene ring.^[30] Indeed, for complexes **2** (R' = Me), **4** (R' = Cl) and **5** (R' = CN) significant rotation of fragments A (θ (C13-N3-C14-C15 and C13-N3-C14-C19) 17.2(3) – 57.9(12)°) but quite small rotations of C (φ (C3-C4-C13-N3 and C5-C4-C13-N3) 1.1(9) – 1.7(3)°) are observed (Table 1).

Table 1 Selected bond lengths [\AA], angles [$^\circ$] and torsion angles [$^\circ$] of **2**, **4** and **5**

	2 [R' = Me]	4 [R' = Cl]	5 [R' = CN]
Pt1-C1	1.9139(16)	1.919(2)	1.915(5)
Pt1-N1	2.0922(14)	2.0931(19)	2.089(4)
Pt1-N2	2.0865(14)	2.0867(18)	2.083(4)
Pt1-Cl1	2.4116(4)	2.4132(6)	2.4037(12)
C4-C13	1.467(2)	1.463(3)	1.462(7)
C13-N3	1.273(2)	1.279(3)	1.285(8)
C14-N3	1.416(2)	1.413(3)	1.402(8)
C1-Pt1-N1	82.03(6)	81.88(8)	82.13(19)
C1-Pt1-N2	82.06(6)	82.11(8)	82.3(2)
C1-Pt1-Cl1	173.95(5)	173.85(7)	176.56(15)
N1-Pt1-N2	164.07(5)	163.98(7)	164.45(16)
Pt1-N1-C7-C2	-29.35(16)	-29.7(2)	32.1(5)
Pt1-N2-C10-C6	-32.72(15)	-32.9(2)	26.6(6)
C4-C13-N3-C14	-173.86(16)	-173.3(2)	-177.8(5)
C3-C4-C13-N3	173.52(17)	173.7(2)	177.0(6)
C5-C4-C13-N3 (φ)	-1.5(3)	-1.7(3)	-1.1(9)
C13-N3-C14-C15 (θ)	17.2(3)	22.1(4)	46.8(8) ^[a] / -57.9(12) ^[b]
C13-N3-C14-C19	-166.67(18)	-162.6(2)	-134.7(6) ^[a] / 123.5(12) ^[b]
Angle between planes [C1-C2-C3-C4-C5-C6] and [C14-C15-C16-C17-C18-C19] [$^\circ$]			
	20.52(8)	24.59(11)	44.7(3) ^[a] / 58.5(5) ^[b]

[a] Major disorder component (81.4(7)% occupancy); [b] Minor disorder component (18.6(7)% occupancy).

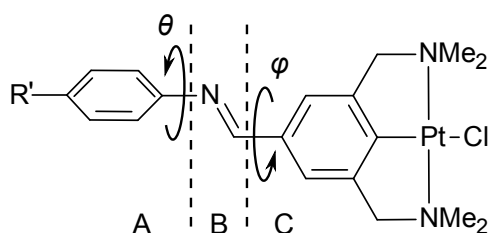


Fig. 3 Representation of the three fragments of the benzylidene aniline pincer platinum complex; R'-substituted aniline ring A, azomethine bridge B, and NCN-pincer platinum fragment C. Torsion angles θ and φ .

The marked difference between these torsion angles θ and φ results from a combination of steric, inductive and mesomeric effects, and is in agreement with

earlier obtained crystallographic data for other substituted organic benzylidene anilines.^[29, 31-33] When going through the series from the more electron donating (ED) Me-group to the more electron withdrawing (EW) CN-group, φ hardly changes while θ becomes larger. Particularly noteworthy is the large θ angle between fragments A and B in **5**. According to Nakai and coworkers^[33] such large twist angles of θ can be explained by the strong intramolecular charge transfer interaction between the lone-pair electrons of the azomethine nitrogen atom and the EW group at the aniline ring. The energetically unfavorable twisting from molecular planarity, which affects the intramolecular charge transfer stabilization between the *para*-substituents, is compensated for by the stabilization resulting from the nitrogen lone-pair electron interaction with the electron deficient aniline ring.

Table 2 Selected intermolecular distances [Å] and angles [°] for **2**, **4** and **5**

Compnd.	X(I)-H(I)→Cg(J)	X-H... π interactions			X-H...Cg ^[d]	X...Cg ^[e]
		H...Cg ^[a]	H_perp ^[b]	γ ^[c]		
2	C(19)-H(19)→Cg(3) ^[f1]	2.77	2.724	9.90	159	3.6664(19)
4	C(19)-H(19)→Cg(3) ^[f1]	2.74	2.700	9.25	160	3.641(3)
5	C(12)-H(12A)→Cg(3) ^[f2]	2.71	2.662	10.43	168	3.670(7)

Compnd.	D-H...A	Potential H bonds ^[g]			
		D-H ^[h]	H...A ^[h]	D...A ^[h]	D-H...A ^[i]
2	C(10)-H(10A)...Cl(1) ^[f3]	0.99	2.76	3.7429(17)	171
	C(10)-H(10B)...Cl(1) ^[f1]	0.99	2.71	3.5286(18)	140
4	C(10)-H(10A)...Cl(1) ^[f3]	0.99	2.75	3.726(2)	169
	C(10)-H(10B)...Cl(1) ^[f1]	0.99	2.69	3.517(3)	141
5	C(9)-H(9A)...Cl(1) ^[f1]	0.98	2.82	3.735(5)d	156
	C(11)-H(11B)...Cl(1) ^[f4]	0.98	2.83	3.650(7)	142

[a] Distance between H(I) and ring centroid Cg(J) (Å). [b] Perpendicular distance of H(I) on ring J (Å). [c] Angle between H(I)→Cg(J) vector and normal plane J (°). [d] Angle defined by X(I), H(I), and Cg(J) (°). [e] Distance between X(I) and Cg(J) (Å). [f] Symmetry operations: [f1] x, 1/2-y, 1/2+z; [f2] x, 3/2-y, -1/2+z; [f3] -x, 1-y, 1-z; [f4] 2-x, 1/2+y, 1/2-z. [g] D = Donor, H = Hydrogen, A = Acceptor. [h] Distance [Å]. [i] Angle [°].

The presence of a less EW or moderate ED substituent on the aniline ring reduces the twist angle θ , as is found in **2** and **4**. In **5** the bond length N3-C14 is slightly shorter while the distance N3-C13 is larger, compared to **2** and **4**. Probably in **5** the strong intramolecular charge transfer interaction between the lone-pair electrons of the

azomethine nitrogen atom and the cyano group results in a substantial contribution of a quinoid resonance structure.

From the aromatic ring interaction analysis of the three independent structures, close interactions between aromatic planes with distances around 3.5 Å (or shorter) appeared not to be present in the crystal. Therefore we conclude that there is no attractive aromatic ring π - π -stacking between neighboring molecules. In contrast, all three structures show an intermolecular interaction of an aromatic hydrogen atom with the π -system of a neighboring molecule (Table 2), referred to as an intermolecular Ar-H \cdots π -interaction^[34] (X-H \cdots Cg(π -Ring)). Such interactions were also observed in solid state structures of other substituted organic benzylidene anilines.^[35]

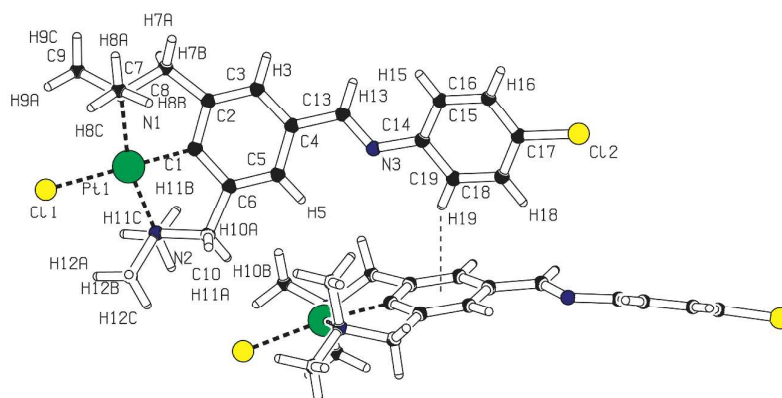


Fig. 4 Intermolecular Ar-H \cdots π -interaction of H(19) with neighboring aromatic plane for **4**

In Fig. 4 this is shown as an example for **4**, in which the aromatic proton of C19-H19 interacts with the neighboring aromatic ring. In all the structures intermolecular C-H \cdots Cl-M interactions are also found between both the CH₂ (in **2** and **4**) or the CH₃ (in **5**) protons of the (dimethylamino)methyl groups of fragment A with a neighboring metal-bound chloride and *vice versa*, with distances ranging from 2.71 to 2.83 Å (Table 2; example shown for **2** in Fig. 5).

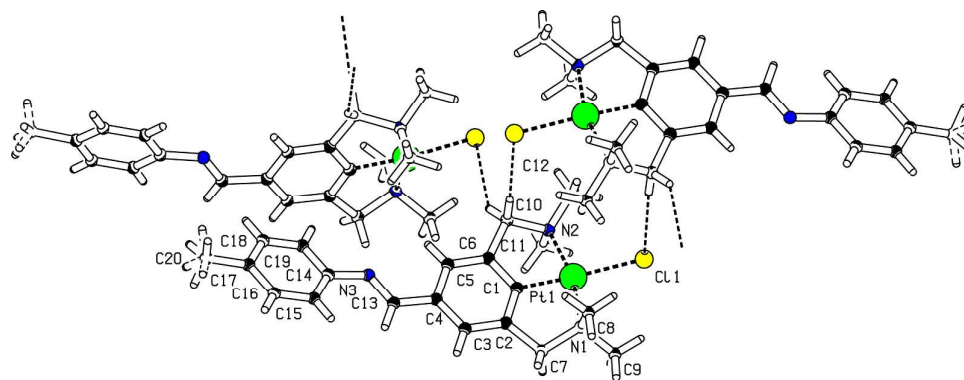


Fig. 5 Intermolecular C–H···Cl–M interaction displayed for **2** which are commonly observed in NCN-pincer platinum(II)^[2] and other metal complexes.^[36, 37]

Spectroscopic characterization. Selected NMR data of Pt complexes **1–5** have been compiled in Table 3. The substituent induced chemical shifts (SCS) observed in the ¹H, ¹³C{¹H}, and ¹⁹⁵Pt{¹H} NMR spectra have been examined by both a single substituent (Eq. 1) and a dual substituent parameter (DSP) method (Eq. 2),^[21] using Hammett constant σ_p and modified Swain-Lupton constants (σ_F, σ_R),^[38] respectively.

$$\text{SCS} = \rho\sigma_p + \text{constant} \quad (\text{Eq. 1})$$

$$\text{SCS} = \rho_F\sigma_F + \rho_R\sigma_R + \text{constant} \quad (\text{Eq. 2})$$

SCS are the ¹H, ¹³C{¹H}, or ¹⁹⁵Pt{¹H} NMR chemical shifts of the atom of interest from the substituted compound, in the present study **1** (R' = NMe₂), **2** (R' = Me), **4** (R' = Cl) and **5** (R' = CN) relative to that observed for compound **3** (R' = H), while σ_F and σ_R are the field inductive and resonance parameters, respectively, for the aromatic ring *para*-substituent (Table 4). As an example, the azomethine proton shift in the ¹H NMR spectra of **1–5** (Table 3) is strongly influenced by the electronic character of the substituents present on the benzylidene aniline backbone. The effect is much stronger in C₆D₆ than in CD₂Cl₂.

Table 3. Selected NMR data of PtCl[NCN(CH=NC₆H₄R'-4')-4] (**1–5**).^[a]

Compound	$\delta^1\text{H} (\text{HC}=\text{N})$		$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	$\delta^{195}\text{Pt}$	$\sigma_p (\sigma_F, \sigma_R)$
	CD ₂ Cl ₂ ^[b]	C ₆ D ₆ ^[c]	(C–Pt) ^[b]	(HC=N) ^[b]	(Pt) ^{[b],[d]}	Hammett ^[e]
1 (R' = NMe ₂)	8.40	8.58	151.4	157.03	–3125	–0.83 (0.15, –0.98)

2 (R' = Me)	8.36	8.41	152.4	160.62	-3115	-0.17 (0.01, -0.18)
3 (R' = H)	8.35	8.33	152.7	161.46	-3111	0.00 (0.03, 0.00)
4 (R' = Cl)	8.33	8.17	153.2	161.87	-3105	0.23 (0.42, -0.19)
5 (R' = CN)	8.31	7.98	154.3	163.47	-3090	0.66 (0.51, 0.15)

[a] δ in ppm, and $\tilde{\nu}$ in cm^{-1} ; [b] 43 mM solution in CD_2Cl_2 ; [c] 2.0 mM solution in C_6D_6 ; [d] Na_2PtCl_6 as external reference; [e] Values from ref. 39.

Linear correlations were found between the SCS and the single substituent parameter σ_p displayed in Table 4 and Fig. 6, reflecting the electronic interaction between substituent R' and the molecular backbone, either inductively or by resonance.

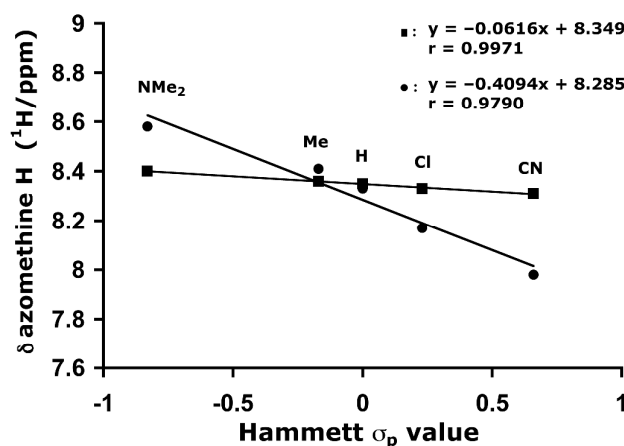


Fig. 6 Hammett correlation of the ^1H NMR chemical shift of the azomethine proton ($\text{CH}=\text{N}$) of **1–5** in CD_2Cl_2 (squares) and C_6D_6 (dots).

The correlations improved upon using the DSP method, accounting for the individual influences of the field inductive and resonance effect of the substituent on the electronic interactions in the molecule. The ρ_F/ρ_R values are close to one, indicating that field inductive and mesomeric effects are about equally strong. With ρ_F/ρ_R being larger than one, in most cases the inductive effect is slightly dominant. The exception is the chemical shift of the azomethine carbon atom (entry 3), which is more influenced by the mesomeric effect.

The positive ρ values in entries 3–5 (Table 4) reflect that the NMR signals of the respective atoms shift to lower field when R' becomes more EW in character, caused by decreased shielding of the atoms. In contrast, the azomethine proton shows an

opposite shift behavior, also referred to as the anomalous shift behavior of benzylidene anilines.^[38, 40-42] An explanation for this behavior is that the molecules have a non-planar geometry in solution. As pointed out above, the more EW R', the larger the twist angle θ is. Upon twisting, the π -cloud of the aniline ring induces shielding of the azomethine hydrogen, shifting the proton signal to higher field (Fig. 7). This reasoning is supported by the observation that the anomalous shift behavior is stronger in deuterated benzene (entry 2, Table 4). Twisting makes the azomethine hydrogen atom better accessible to solvent molecules, inducing a aromatic solvent-induced shift (ASIS)^[43] by the magnetic anisotropy of benzene.^[44-46] It is, however, also possible that bond polarization effects are responsible for the occurrence of anomalous NMR shift behavior.^[21, 47,48]

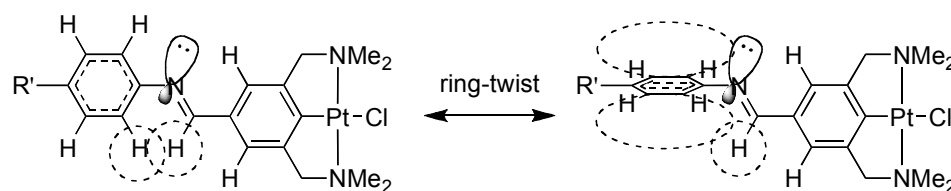


Fig. 7 Out of plane ring-twist increases shielding of the azomethine proton due to increased overlap of the π -cloud with the free electron pair of the azomethine nitrogen

Notable is the $\rho = 23$ value of the correlation of $\delta^{195}\text{Pt}\{^1\text{H}\}$ with the Hammett σ_p (entry 5), which is in close agreement with the $\rho = 25$ value, which was found in a similar correlation study for the isoelectronic stilbenoid pincer platinum complexes $\text{PtCl}[\text{NCN}(\text{C}_2\text{H}_2\text{C}_6\text{H}_4\text{-R}'\text{-4}')\text{-4}]$.^[2] This shows that the electronic influence exerted by the R'-substituents on the platinum center in both the benzylidene aniline and stilbenoid pincer platinum compounds is almost the same, despite the structural and conformational differences of these compounds.

Table 4. Correlation of the ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR SCS values *versus* the Hammett constant σ_p , and the dual substituent parameters σ_F and σ_R for **1–5** in CD_2Cl_2 .

Entry	Atom	$\rho(\sigma_p)$	$r^{[b]}$	$\rho_F(\sigma_F)$	$\rho_R(\sigma_R)$	$r^{[b]}$	ρ_F/ρ_R
1	H (CH=N)	-0.062 ± 0.003	0.9971	-0.068 ± 0.008	-0.059 ± 0.004	0.9974	1.16
2	H (CH=N) ^[a]	-0.41 ± 0.05	0.9790	-0.61 ± 0.03	-0.331	0.9993	1.85

					± 0.015		
3	C (CH=N)	4.3 ± 0.4	0.9858	2.9 ± 0.4	4.85 ± 0.20	0.9988	0.59
4	C (<i>ipso</i> to Pt)	1.92 ± 0.17	0.9889	2.4 ± 0.4	1.71 ± 0.19	0.9946	1.45
5	Pt	23 ± 3	0.9746	33 ± 6	19 ± 3	0.9878	1.68

[a] In C₆D₆; [b] Correlation coefficient.

Interestingly, the Hammett relations found allow the evaluation of the substituent character and strength of the Pt group, as it has been reported that the *substituent at the benzylidene moiety* affects the *sensitivity of the –C=N–¹³C NMR chemical shift to the substituent at the aniline moiety*.^[21] Thus, in plots of $\delta^{13}\text{C}$ (C=N) versus σ_{F} and σ_{R} of substituents at the aniline site, ρ_{F} was found to vary from 1.99 ± 0.28 (4-Me₂N group at the benzylidene site) to 2.81 ± 0.50 (4-nitro group at the benzylidene site). Parameter ρ_{R} varied from 5.20 ± 0.37 in presence of a benzylidene 4-Me₂N donor to 8.49 ± 0.65 in presence of a 4-benzylidene nitro acceptor.^[21] In this context, the ρ_{F} parameter of 2.9 ± 0.4 found here for the molecules with the 4-Pt substituent at the benzylidene site suggests that inductively a Pt substituent behaves like an EW group stronger than a nitro group. Given the formal +2 charge on Pt this is not unexpected. For the mesomeric case, the ρ_{R} value of 4.85 ± 0.20 suggests that the Pt substituent is stronger than a dimethylamino group. The Pt atom thus very readily donates electrons from its d orbitals to the organic π -system. Together, these two features render a Pt containing substituent an extraordinary and schizophrenic substituent: simultaneously it is positioned among the strongest electron donors and among the strongest electron acceptors. When attached to a π system like in the present case, the mesomeric effect dominates.

An UV/Vis spectroscopic study was performed in solvents of different polarity to further examine the properties of the benzylidene aniline pincer complexes **1–5** in solution (Table S1, Fig. 8). The complexes show a typical, strong absorption band at wavelengths around 350 – 392 nm, assigned to a π - π^* transition.^[49] At higher energies, around 290 (for **1** at 339 nm) and 260 nm weaker absorption bands are found for **1–5**, referred to in literature as superimposed absorptions from local excitations of the aniline and benzylidene fragments, respectively.^[49] Indeed the absorptions for substituted anilines and PtCl(NCN) complexes are found around these wavelengths.^[49,50] In MeCN a strong absorption band for **1–5** in the UV region was found around 202 – 207 nm, also observed by others.^[31]

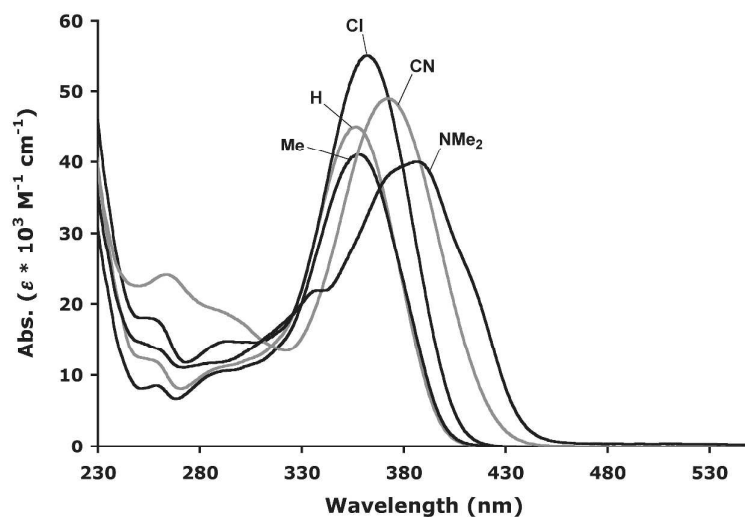


Fig. 8 UV/Vis absorption spectra for **1** (NMe₂), **2** (Me), **3** (H), **4** (Cl) and **5** (CN) in THF

Focusing on the long wavelength transitions, the highest energy maxima are found for the unsubstituted compound and the compound with the weakly donating methyl group. As usual, introduction of stronger *para*-substituents (either ED or EW) on the aniline fragment results in a bathochromic shift. No distinct solvatochromic behavior for **1–5** is observed, suggesting a non-polar ground state. When comparing the long wavelength maxima with those of benzylidene anilines bearing the same substituent at the aniline 4-position but without the Pt-substituent, a bathochromic shift is noted. Maxima of 376 (in chloroform), 321 (in cyclohexane), 312 (in chloroform) and 336 nm (in heptane) have been reported for benzylidene anilines bearing a Me₂N,^[7] Me,^[51] H^[7] or Cl^[52] group at the aniline 4-position, respectively. This indicates that the Pt-group affects the energy levels of the π electron system, presumably by virtue of its mesomeric electron donating properties. Note that this effect is much more pronounced for the compounds with weakly donating and accepting substituents. The Pt substituent induces a shift of 3720 cm⁻¹ (312 to 353 nm) for unsubstituted benzylidene aniline, while the shift is only 690 cm⁻¹ (376 to 386 nm) for the system with the strong dimethylamino donor.

The UV-Vis maxima of the Pt-benzylidene anilines are not too different from those of the 4'-substituted Pt-stilbenes. In dichloromethane as solvent, maxima of 371 (R' = NMe₂), 350 (R' = H), and 376 (R' = CN) have for instance been reported for the latter series of compounds.^[2] Hence, for a given substituent, the maxima do not differ by

more than ca. 15 nm. The details of the differences are not easy to disclose, as they involve effects as planarity, the stabilization of the LUMO by the electronegative imine nitrogen^[7] and specific interactions, like the one between the azomethine nitrogen lone pair and the cyano substituent.

None of the solutions containing **1–5** showed fluorescence, probably due to the twisting around the azomethine bond (*E-Z* isomerization), which was shown to be responsible for the absence of fluorescence in other organic benzylidene anilines.^[53, 54]

CONCLUSIONS

A useful and efficient synthetic route toward organometallic benzylidene anilines, comprising a common NCN-pincer platinum(II) chloride substituted benzylidene grouping condensed with a R' substituted aniline, is reported. Interestingly, the involved Schiff base condensation reaction occurs with retention of the Pt-C bond of the NCN-pincer platinum(II) chloride fragment. Preliminary experiments confirmed that these reactions can also be carried out under solvent-free conditions.

In common with other benzylidene anilines these platinum substituted benzylidene anilines exhibit bent and twisted structures in the solid state. The extent of twisting of the R'-substituted aniline ring with respect to the azomethine group depends on the nature of the substituent R'.

Despite the introduction of a nitrogen atom into the ethylene bridge and the occurrence of the twisting the electronic properties resemble those of stilbenoid pincer platinum complexes, the complete absence of fluorescence being a notable exception. The lowest energy absorptions in the electronic absorption spectra in the two types of compounds occur at not too different positions, and according to the dependence of the ¹⁹⁵Pt{¹H} NMR shift on the Hammett σ_p parameters, the sensitivity of the metal to the electronic properties of substituents at the other site of the molecule is highly comparable.

The dual substituent parameter treatment of the azomethine ¹³C NMR shift gave important insight into the unique behaviour of the Pt-moiety as a substituent.^{6,55}

Inductively, it is a very strong electron withdrawing group, whereas mesomerically it behaves like a very strong electron donating group.

EXPERIMENTAL SECTION

General. All reactions involving air- or moisture-sensitive reagents were performed by standard Schlenk techniques unless stated otherwise. Toluene and pentane were distilled from Na/benzophenone, CH₂Cl₂ was distilled from CaH₂ prior to use. The platinum precursor [PtCl(NCN-CHO-4)] (**7**) was prepared according to a published procedure.^[2] All other reagents were obtained commercially and were used without further purification. ¹H and ¹³C{¹H} NMR spectra were recorded at 25 °C on Bruker AC 300 NMR or Varian Inova 300 or Varian 400 spectrometers (operating frequencies: for ¹H spectra at 400 and 300 MHz; for ¹³C spectra at 101 and 75 MHz), chemical shifts are reported in ppm and referenced to residual solvent resonances. ¹⁹⁵Pt{¹H} NMR spectra were recorded on a Varian Inova 300 MHz NMR spectrometer (operating at 64.4 MHz), referenced to external Na₂PtCl₆ (1 M in D₂O, δ = 0 ppm).^[56] Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium (Mülheim a.d. Ruhr, Germany). ES-MS spectra were obtained from the Biomolecular Mass Spectrometry Group at the Utrecht University. Infrared spectra were recorded with a Perkin Elmer Spectrum 1 FT-IR spectrometer. UV/Vis spectra were collected on Cary 1 or Cary 5 spectrophotometers in spectrophotometric grade solvents (Acros), see Table S1.

General procedure for the synthesis of **1–5**.

To a sealed reaction tube containing 4 Å molecular sieves and aldehyde **7** in dry toluene (30 mL), the respective aniline **6a–f** was added. At room temperature formic acid (one drop) was added and the reaction mixture was heated to 70 °C and slowly stirred at this temperature for 3 days. The mixture was filtered and the residual molecular sieves were extracted with dichloromethane. The combined organic

fractions were evaporated to dryness *in vacuo*, and the residue was dissolved in a minimal amount of dichloromethane. Subsequently the product was precipitated with the addition of pentane. The product was isolated after centrifugation of the resulting suspension. When necessary the last steps were repeated to remove traces of residual aniline.

[PtCl(NCN-(CH=NC₆H₄-NMe₂-4')-4)] (1). 4-(Dimethylamino)aniline **6a**: 45 mg (0.42 mmol); aldehyde **7**: 125 mg (0.28 mmol). Yield: 132 mg (0.24 mmol, 88%) of **1** as a brown powder. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.40 (s, 1H; N=CH), 7.36 (s, 2H; ArH), 7.20 (d, ³J_{H,H} = 9.0 Hz, 2H; ArH), 6.75 (d, ³J_{H,H} = 8.7 Hz, 2H; ArH), 4.08 (s, ³J_{H,Pt} = 44.1 Hz, 4H; CH₂), 3.06 (s, ³J_{H,Pt} = 38.1 Hz, 12H; NCH₃), 2.97 (s, 6H; ArN(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 157.03 (C=N), 151.4 (C_{ipso}), 149.7, 144.4 (²J_{C,Pt} = 77.4 Hz; C_{ortho} to Pt), 141.7, 133.2, 122.2, 119.9 (³J_{C,Pt} = 34.9 Hz; C_{meta}), 113.3, 77.7 (²J_{C,Pt} = 63.2 Hz; NCH₂), 54.6 (N(CH₃)₂), 40.9 (ArN(CH₃)₂); ¹⁹⁵Pt{¹H} NMR (64 MHz, CD₂Cl₂): δ = -3125; IR (ATR): ν̄ = 2977, 2918, 2798 1676, 1613 (C=N), 1590, 1559, 1511, 1446, 1345, 1291, 1221, 1164, 1123, 1085, 1014, 943, 882, 834, 756, 724, 710 cm⁻¹; MS (ES+; CH₂Cl₂) *m/z* : 568.11 [M+H]⁺; elemental analysis calcd (%) for C₂₁H₂₉ClN₄Pt (568.01): C 44.40, H 5.15, N 9.86; found: C 44.61, H 5.11, N 9.93.

[PtCl(NCN-(CH=NC₆H₄-Me-4')-4)] (2). 4-Methylaniline **6b**: 45 mg (0.42 mmol); aldehyde **7**: 125 mg (0.28 mmol). Yield: 132 mg (0.24 mmol, 88%) of **2** as a light yellow powder. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.36 (s, 1H; N=CH), 7.38 (s, 2H; ArH), 7.19 (d, ³J_{H,H} = 8.1 Hz, 2H; ArH), 7.10 (d, ³J_{H,H} = 8.1 Hz, 2H; ArH), 4.09 (s, ³J_{H,Pt} = 45.6 Hz, 4H; CH₂), 3.07 (s, ³J_{H,Pt} = 38.4 Hz, 12H; NCH₃), 2.36 (s, 3H; ArCH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 160.62 (C=N), 152.4 (C_{ipso}), 150.3, 144.5 (²J_{C,Pt} = 79.6 Hz; C_{ortho}), 135.6, 132.6, 130.1, 120.9, 120.3 (³J_{C,Pt} = 34.9 Hz; C_{meta}), 77.7 (²J_{C,Pt} = 64.3 Hz; NCH₂), 54.6 (N(CH₃)₂), 21.0 (ArCH₃); ¹⁹⁵Pt{¹H} NMR (64 MHz, CD₂Cl₂): δ = -3115; IR (ATR): ν̄ = 3004, 2974, 2920, 1617 (C=N), 1577, 1560, 1503, 1466, 1452, 1432, 1421, 1402, 1366, 1313, 1291, 1277, 1212, 1169, 1149, 1108, 1085, 1027, 1014, 964, 945, 909, 875, 863, 844, 834, 815, 780, 736, 715 cm⁻¹; MS (ES+; CH₂Cl₂) *m/z* : 540.14 [M+2H]⁺; elemental analysis calcd (%) for C₂₀H₂₆ClN₃Pt (538.97): C 44.57, H 4.86, N 7.80; found: C 44.45, H 4.93, N 7.72.

[PtCl(NCN-(CH=NC₆H₄-Me-4')-4)] (2, solvent free procedure). Solid aldehyde **7** (30 mg, 0.067 mmol) and solid 4-methylaniline **6b** (8.6 mg, 0.08 mmol) were ground together in a Schlenk flask using an egg shaped magnetic stirrer. Reaction progress was followed by analyzing samples with ¹H NMR (δ aldehyde-H/ δ imine-H; 9.90/8.42 ppm, respectively). After 1 h stirring of the solid reaction mixture 27% of **2** was formed that increased to 68% after 5 days. Subsequent stirring (16h) of the mixture at 50 °C, followed by (16h) at the same temperature under vacuum did not increase product formation. No reaction workup was performed, yielding a mixture of compounds **2**, **6b** and **7** as a powder. ¹H NMR (300 MHz, C₆D₆): δ = 9.90 (s; CHO), 8.42 (s; N=CH), 7.34 (m; ArH), 7.08 (m; ArH), 6.90 (d, ³J = 8.0 Hz; ArH), 6.34 (d, ³J = 8.3 Hz; ArH) 3.27 (s, ³J(H-Pt) = 45.1 Hz; CH₂), 3.12 (s, ³J(H-Pt) = 45.7 Hz; CH₂), 2.67 (s, ³J(H-Pt) = 37.4 Hz; NCH₃), 2.60 (s, ³J(H-Pt) = 38.5 Hz; NCH₃), 2.16 (s; ArCH₃), 2.15 (s; ArCH₃);

[PtCl(NCN-CH=NC₆H₅-4)] (3). Aniline **6c**: 38 μ l (0.42 mmol); aldehyde **7**: 125 mg (0.28 mmol). Yield: 118 mg (0.22 mmol, 81%) of **3** as an off-white powder. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.35 (s, 1H; N=CH), 7.41–7.36 (m, 4H; ArH), 7.22–7.17 (m, 3H; ArH), 4.09 (s, ³J_{H,Pt} = 46.2 Hz, 4H; CH₂), 3.07 (s, ³J_{H,Pt} = 38.1 Hz, 12H; CH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 161.46 (C=N), 153.0, 152.7 (C_{ipso}), 144.5 (²J_{C,Pt} = 77.4 Hz; C_{ortho}), 132.5, 129.5, 125.7, 121.0, 120.4 (³J_{C,Pt} = 36.0 Hz; C_{meta}), 77.7 (²J_{C,Pt} = 64.3 Hz; NCH₂), 54.6 (N(CH₃)₂); ¹⁹⁵Pt{¹H} NMR (64 MHz, CD₂Cl₂): δ = -3111; IR (ATR): $\tilde{\nu}$ = 3011, 2984, 2921, 1616 (C=N), 1578, 1564, 1487, 1469, 1453, 1433, 1346, 1335, 1318, 1312, 1275, 1206, 1171, 1152, 1106, 1087, 1025, 1015, 974, 961, 945, 912, 883, 855, 836, 772, 737, 710, 699 cm⁻¹; MS (ES+; CH₂Cl₂) *m/z* : 525.11 [M+H]⁺; elemental analysis calcd (%) for C₁₉H₂₄ClN₃Pt (524.94): C 43.47, H 4.61, N 8.00; found: C 43.38, H 4.70, N 7.95.

[PtCl(NCN-(CH=NC₆H₄-Cl-4')-4)] (4). 4-Chloroaniline **6d**: 53 mg (0.42 mmol); aldehyde **7**: 125 mg (0.28 mmol). Yield: 136 mg (0.24 mmol, 87%) of **4** as a light yellow powder. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.33 (s, 1H; N=CH), 7.38 (s, 2H; ArH), 7.35 (d, ³J_{H,H} = 8.7 Hz, 2H; ArH), 7.14 (d, ³J_{H,H} = 8.7 Hz, 2H; ArH), 4.09 (s, ³J_{H,Pt} = 45.9 Hz, 4H; CH₂), 3.07 (s, ³J_{H,Pt} = 38.1 Hz, 12H; CH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 161.87 (C=N), 153.2 (C_{ipso}), 151.6, 144.6 (²J_{C,Pt} = 78.5 Hz; C_{ortho}),

132.2, 130.9, 129.5, 122.4, 120.5 ($^3J_{C,Pt} = 34.9$ Hz; C_{meta}), 77.6 ($(^2J_{C,Pt} = 62.1$ Hz; NCH₂), 54.6 (N(CH₃)₂); $^{195}Pt\{^1H\}$ NMR (64 MHz, CD₂Cl₂): $\delta = -3105$; IR (ATR): $\tilde{\nu} = 3003, 2973, 2920, 1611$ (C=N), 1587, 1573, 1558, 1483, 1452, 1430, 1421, 1402, 1366, 1332, 1312, 1289, 1166, 1149, 1085, 1007, 971, 960, 945, 909, 872, 839, 816, 745, 714, 673 cm⁻¹; MS (ES+; CH₂Cl₂) m/z : 559.09 [M+H]⁺; elemental analysis calcd (%) for C₁₉H₂₃Cl₂N₃Pt (559.39): C 40.80, H 4.14, N 7.51; found: C 40.69, H 4.18, N 7.46.

[PtCl(NCN-(CH=NC₆H₄-CN-4')-4)] (5). 4-Cyanoaniline **6e**: 49 mg (0.42 mmol); aldehyde **7**: 125 mg (0.28 mmol). Yield: 115 mg (0.21 mmol, 75%) of **5** as a yellow powder. 1H NMR (300 MHz, CD₂Cl₂): $\delta = 8.31$ (s, 1H; N=CH), 7.67 (d, $^3J_{H,H} = 8.7$ Hz, 2H; ArH), 7.40 (s, 2H; ArH), 7.22 (d, $^3J_{H,H} = 8.4$ Hz, 2H; ArH), 4.10 (s, $^3J_{H,Pt} = 45.6$ Hz, 4H; CH₂), 3.07 (s, $^3J_{H,Pt} = 37.8$ Hz, 12H; CH₃); $^{13}C\{^1H\}$ NMR (75 MHz, CD₂Cl₂): $\delta = 163.47$ (C=N), 157.0 (CN), 154.3 (C_{ipso}), 151.6, 144.7 ($^2J_{C,Pt} = 77.4$ Hz; C_{ortho}), 133.7, 131.8, 121.8, 120.8 ($^3J_{C,Pt} = 36.0$ Hz; C_{meta}), 119.5, 108.7, 77.6 ($^2J_{C,Pt} = 62.1$ Hz; NCH₂), 54.6 (N(CH₃)₂); $^{195}Pt\{^1H\}$ NMR (64 MHz, CD₂Cl₂): $\delta = -3090$; IR (ATR): $\tilde{\nu} = 3008, 2983, 2922, 2219$ (C≡N), 1615 (C=N), 1594, 1576, 1558, 1494, 1452, 1433, 1424, 1403, 1345, 1317, 1218, 1171, 1149, 1105, 1087, 1017, 986, 974, 959, 947, 882, 869, 841, 765, 727, 711 cm⁻¹; MS (ES+; CH₂Cl₂) m/z : 551.14 [M+2H]⁺; elemental analysis calcd (%) for C₂₀H₂₃ClN₄Pt (549.95): C 43.68, H 4.22, N 10.19; found: C 43.74, H 4.29, N 10.12.

[PtCl(NCN-(CH=NC₆H₄-NO₂-4')-4)] (8) (e.g. by repeated precipitations of the impure reaction product with pentane from dichloromethane followed by crystallization from toluene).

X-ray crystal structure determinations.

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin \theta/\lambda)_{max} = 0.65$ Å⁻¹ at a temperature of 150 K. The structures were solved with automated Patterson methods (program DIRDIF-99,^[57] compounds **2** and **5**). The initial coordinates of **4** were taken from the isostructural **2**. Refinement was performed with

SHELXL-97^[58] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in a difference Fourier map and refined with a riding model. In **5** the phenyl ring C14-C19 was refined with a disorder model with occupancy of 81.4(7) vs. 18.6(7)%. Geometry calculations and checking for higher symmetry was performed with the PLATON program.^[59]

Further details about the crystal structure determinations are given in Table S2.

CCDC 649683 (compound **2**), 649684 (compound **4**), and 649685 (compound **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif."

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Notes

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Electronic Supplementary Information (ESI) available: For ESI and crystallographic data of **2**, **4** and **5** in CIF or other electronic format see DOI: 10.yyyyyyyyyy. **Table S1**

for the UV/Vis data of PtCl[NCN(CH=NC₆H₄R'-4')-4], **1–5**. **Table S2** containing the experimental details for the X-ray crystal structure determinations of **2**, **4** and **5** and **Table S3** with Selected NMR and IR data of PtCl[NCN(CH=NC₆H₄R'-4')-4] (**1–5**) and a comment on the ATR IR data.

[†]Dedicated to Professor William (Bill) C. Kaska on the occasion of his 80th birthday. GvK thanks Bill for exciting times during various joint “Pincer Metal” projects in Utrecht and Santa Barbara.

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