Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2014

Revised version May 24th 2014

Supplementary information

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

Guido D. Batema,[a] Martin Lutz,[b], ‡ Anthony L. Spek,[b] § Cornelis A. van Walree,[a,c] Gerard P. M. van Klink,[a, d] and Gerard van Koten*[a]

Table S1. UV/Vis data of PtCl[NCN(CH=NC$_6$H$_4$R'-4')-4] **1**–**5**.[a]

Solvent	**1** (R' = NMe$_2$)	**2** (R' = Me)	**3** (R' = H)	**4** (R' = Cl)	**5** (R' = CN)
Acetonitrile	383 (40)	350 (47)	350	353	361
	335 (22)	234 (26)	254	293	244
	240 (23)	207 (47)	237	236	202
	204 (49)		203	205	
Dichloromethane	386 (40)	355 (41)	353 (25)	358 (32)	367 (37)
	334 (23)	245 (18)	254 (10)	292 (7)	246 (21)
	243 (24)			252 (12)	
Tetrahydrofuran	386 (40)	357 (41)	357 (45)	362 (55)	372 (49)
	339 (22)	292 (11)	292 (11)	294 (15)	294 (18)
	257 (14)	259 (9)	258 (12)	258 (18)	264 (24)
Ethyl acetate	381 (37)	354	354	358	367
	338 (20)	286	287	291	298
	280 (17)	254	255	257	265
	257 (20)				
Diethyl ether	384	354	354	360	368
	337	284	283	286	269
	237	233	254	252	
Benzene	392 (37)	359 (41)	357	362 (45)	372
	338 (22)	288 (10)	290	294 (11)	303
	283 (11)				

[a] Absorption wavelength (in nm) at room temperature in air-saturated solutions ($c \approx \times 10^{-5}$ M), absorption coefficient between brackets (ε in $\times 10^3$ M^{-1} cm^{-1}).

Table S2. Experimental details for the X-ray crystal structure determinations

compound	**2**	**4**	**5**

formula	$C_{20}H_{26}ClN_3Pt$	$C_{19}H_{23}Cl_2N_3Pt$	$C_{20}H_{23}ClN_4Pt$
fw	538.98	559.39	549.96
crystal colour	orange	orange	yellow
crystal size [mm^3]	0.39 × 0.18 × 0.09	0.27 × 0.27 × 0.09	0.30 × 0.15 × 0.08
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	18.2341(6)	18.1760(4)	18.3716(7)
b [Å]	8.9441(5)	8.9325(3)	9.1309(4)
c [Å]	11.9240(6)	11.8834(3)	11.5847(3)
β [°]	95.965(2)	94.713(3)	94.535(1)
V [Å^3]	1934.13(3)	1922.84(3)	1937.24(12)
Z	4	4	4
D_x [g/cm^3]	1.851	1.932	1.886
μ [mm^{-1}]	7.400	7.582	7.392
abs. corr. method	multi-scan	multi-scan	analytical
abs. corr. range	0.21 – 0.51	0.18 – 0.51	0.17 – 0.44
refl. (meas./unique)	41054 / 4438	53574 / 4417	23964 / 4433
param./restraints	233 / 0	230 / 0	276 / 60
R1/wR2 [I>2σ(I)]	0.0112 / 0.0229	0.0156 / 0.0327	0.0295 / 0.0671
R1/wR2 [all refl.]	0.0148 / 0.0239	0.0219 / 0.0343	0.0326 / 0.0683
S	1.072	1.055	1.151
extinction coeff.	0.00097(4)	-	-
ρmin/max [e/Å3]	–0.41 / 0.39	–0.99 / 0.45	–1.63 / 1.63

Table S3. Selected NMR and IR data of PtCl[NCN(CH=NC_6H_4R’-4')-4] (**1**–**5**).[a]

	$\delta\,^{1}$H (HC=N)		$\delta\,^{13}$C (C–Pt)[b]	$\delta\,^{13}$C (HC=N)[b]	$\delta\,^{195}$Pt (Pt)[b],[d]	σ_p (σ_F,σ_R) Hammett[e]	$\tilde{\nu}$ (C=N)
Compound	CD_2Cl_2[b]	C_6D_6[c]					

1 (R' = NMe$_2$)	8.40	8.58	151.4	157.03	–3125	–0.83 (0.15, -0.98)	1613
2 (R' = Me)	8.36	8.41	152.4	160.62	–3115	–0.17 (0.01, -0.18)	1617
3 (R' = H)	8.35	8.33	152.7	161.46	–3111	0.00 (0.03, 0.00)	1616
4 (R' = Cl)	8.33	8.17	153.2	161.87	–3105	0.23 (0.42, -0.19)	1611
5 (R' = CN)	8.31	7.98	154.3	163.47	–3090	0.66 (0.51, 0.15)	1615

[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. [1]

The respective ATR-IR spectra of the organometallic benzylidene anilines **1**–**5** show C=N stretch vibrations that are all slightly shifted to lower frequencies (around 1611 – 1617 cm^{-1}, Table S3) as compared to those of analogous organic benzylidene anilines (1635 – 1616 cm^{-1}).[2.3] This common feature points to a small change of the C=N bond order which may be caused by the presence of the electron donating NCN-pincer platinum(II) chloride grouping in each of these compounds. Furthermore, the narrow frequency range of the C=N stretch vibrations in the series **1**–**5** establishes that the electronic effect of substituent R' on the azomethine group is small which is a common feature of *para*-substituted organic benzylidene anilines.[3] No trend was observed between the C=N stretch frequencies and either the Hammett substituent parameter σ_p of **1**–**5** or the C=N bond lengths of **2**, **4**, and **5** (C13-N3, Table 1).

References

[1] C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.,* 1991, **91**, 165-195.
[2] N. Ebara, *Bull. Chem. Soc. Jpn.,* 1961, **34**, 1151-1158.
[3] K. Tabei and E. Saitou, *Bull. Chem. Soc. Jpn.,* 1969, **42**, 1440-1443.