

Supplementary Material

**Table T1.**  $^{31}\text{P}\{^1\text{H}\}$  and selected  $^1\text{H}$  NMR data for the amidine complexes in  $\text{CDCl}_3$  at  $27^\circ\text{C}$  ( $\delta$  in ppm,  $J$  in Hz).

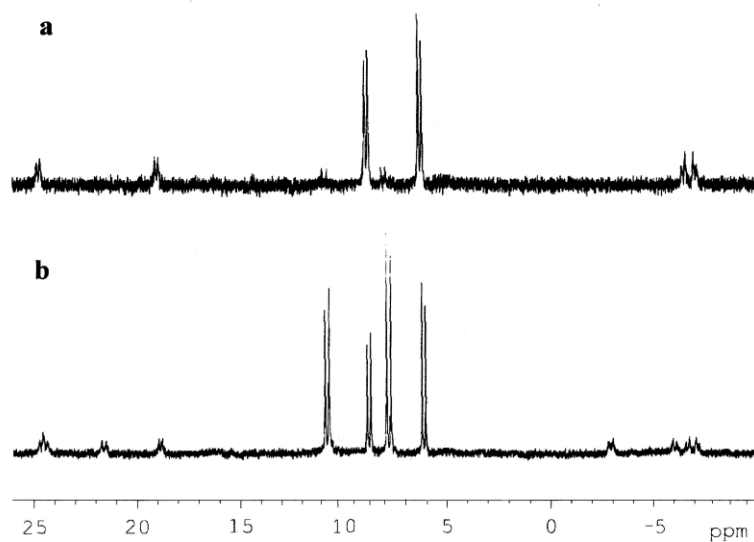
| Compound | $\text{P}_\text{A}$ ( $^1J_{\text{PPt}}$ ) | $\text{P}_\text{B}$ ( $^1J_{\text{PPt}}$ ) | $^2J_{\text{PP}}$ | H6   | H5   | N4H  |
|----------|--------------------------------------------|--------------------------------------------|-------------------|------|------|------|
| 1a       | 8.99 (3477)                                | 7.77 (3419)                                | 24.8              | 7.20 | 6.02 | 5.72 |
| 1b       | 9.03 (3486)                                | 7.77 (3417)                                | 24.9              | 7.14 | 6.22 | 6.05 |
| 1c       | 9.66 (3473)                                | 8.02 (3384)                                | 24.9              | 7.12 | 6.03 | 5.89 |
| 1d       | 8.91 (3513)                                | 6.62 (3402)                                | 25.2              | **   | 5.93 | 6.07 |
|          |                                            |                                            |                   | H2   | H8   | N6H  |
| 2a       | 11.33 (3385)                               | 10.86 (3417)                               | 24.7              | 8.11 | 7.81 | 5.44 |
| 2b       | 10.95 (3263)                               | 10.70 (3370)                               | 24.5              | 8.28 | 7.95 | 6.32 |
| 2c*      | 11.18 (3262)                               | 9.66 (3365)                                | 24.8              | -    | -    | -    |
| 2d*      | 10.77 (3341)                               | 7.78 (3359)                                | 24.7              | -    | -    | -    |

\* in  $\text{CH}_2\text{Cl}_2$  solution; \*\* in the range of the Ph resonances.

**Table T2.** Comparison of bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) of the amidine fragment in complexes *cis*-[(PMePh<sub>2</sub>)<sub>2</sub>PtNH=C(Me){9-MeAd(-2H)}]NO<sub>3</sub> (3a in ref [9]), *cis*-[(PPh<sub>3</sub>)<sub>2</sub>PtNH=C(Me){9-MeAd(-2H)}]NO<sub>3</sub> (3b in ref [9]), *cis*-[(PPh<sub>3</sub>)<sub>2</sub>PtNH=C(Ph){9-MeAd(-2H)}]NO<sub>3</sub> (4 in ref. [10]) and in the two molecules of **6b**.

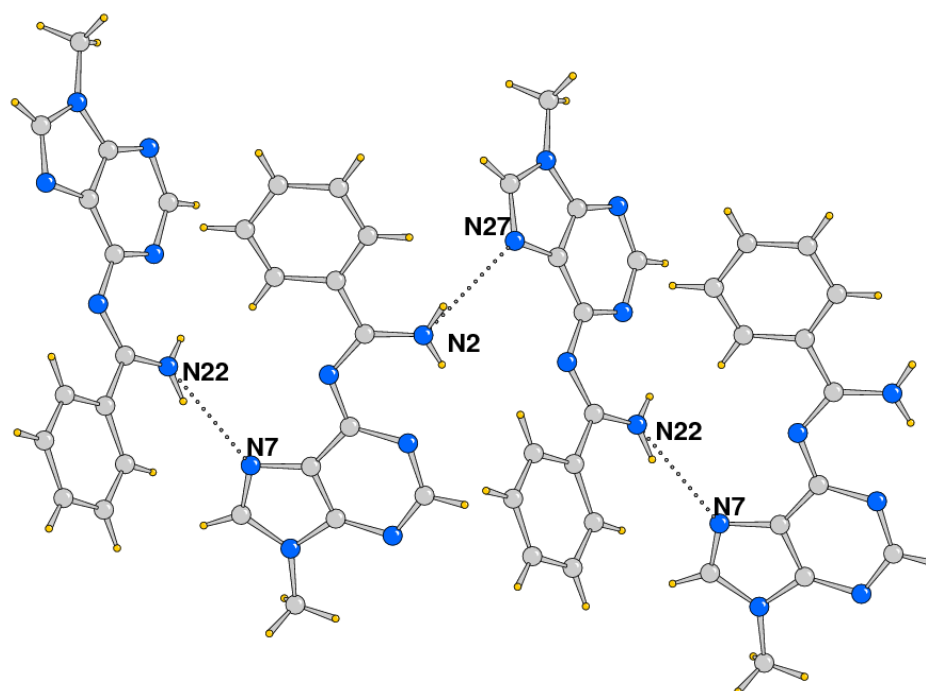
|                |                      | 2a                   | 2b                   | 6b         |            |
|----------------|----------------------|----------------------|----------------------|------------|------------|
|                | <u>3a</u> in ref [9] | <u>3b</u> in ref [9] | <u>4</u> in ref [10] | molecule A | molecule B |
| N(1)-C(6)      | 1.357(7)             | 1.397(10)            | 1.388(9)             | 1.361(4)   | 1.353(4)   |
| C(6)-N(6)      | 1.355(8)             | 1.319(9)             | 1.341(9)             | 1.368(4)   | 1.376(5)   |
| N(6)-C(3)      | 1.335(8)             | 1.358(11)            | 1.308(9)             | 1.319(5)   | 1.333(4)   |
| C(3)-N(2)      | 1.292(7)             | 1.279(11)            | 1.295(8)             | 1.324(5)   | 1.334(5)   |
| C(3)-C(10)     | 1.523(9)             | 1.509(11)            | 1.504(10)            | 1.497(5)   | 1.493(5)   |
| N(1)-C(6)-N(6) | 127.3(6)             | 127.7(8)             | 127.2(8)             | 123.2(4)   | 124.4(3)   |
| C(6)-N(6)-C(3) | 122.4(6)             | 123.1(8)             | 124.0(7)             | 122.0(4)   | 121.3(3)   |
| N(6)-C(3)-N(2) | 128.0(6)             | 126.5(8)             | 126.5(8)             | 126.8(4)   | 126.3(4)   |

**Figure S1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR of a mixture of *cis*-[(PPh<sub>3</sub>)<sub>2</sub>Pt(μ-OH)]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, 9-MeAd and Ph<sub>2</sub>C(H)CN (molar ratio 1:2:20), in CDCl<sub>3</sub>: *a*) fresh solution; *b*) after 8 days at r.t.

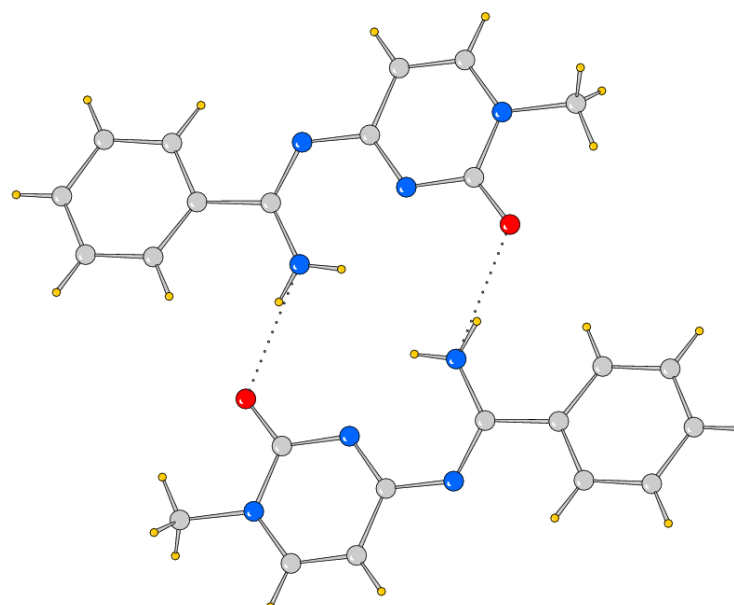


**Figure S2.**  $^1\text{H}$ ,  $^{15}\text{N}$  HMQC NMR spectrum (evolution time 5.5 msec) of NH<sub>2</sub>-C(Ph){1-MeCy(-2H)} (**5b**) in CDCl<sub>3</sub>.

**Figure S3.** Packing of the molecules of **6b** connected by H-bonds.



**Figure S4.** Packing of the molecules **5b** connected by H-bonds.



**Figure S5.** NOESY NMR spectrum of **3b** in DMF-*d*<sub>7</sub> solution at –55°C.

