Supplementary Material (ESI) for Chemical Communications

SUPPLEMENTARY INFORMATION FOR:

Using Ring Strain to Inhibit a Decomposition Path: First Synthesis of an Alkyl-BIAN ligand (Alkyl-BIAN = bis(alkyl)acenaphthenequinonediimine)

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Synthesis of Cypr-BIAN.

a) By transimination.

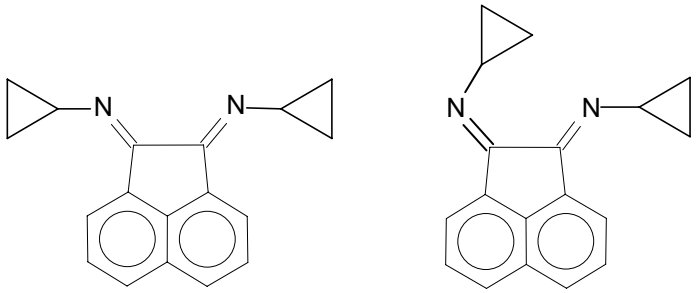
Given the low boiling point of cyclopropylamine (49-50 °C) and the absence of any reaction at room temperature, the reaction had to be performed either in an autoclave, under 10 bar N_2, or, more conveniently in a vessel closed with a Teflon valve, of the kind commonly employed to store dry deuterated solvents. A 1.5 molar excess of cyclopropylamine over the stoichiometric is sufficient to shift completely the reaction on the side of the cyclopropyl derivative. Complex (3,5-$Cl_2C_6H_3$-BIAN)$ZnCl_2$ was prepared as previously described in: M. Gasperini, F. Ragaini, S. Cenini, *Organometallics* **2002**, *21*, 2950-2957.

To a 50 mL vessel as described above was added (3,5-$Cl_2C_6H_3$-BIAN)$ZnCl_2$ (1.00 g, 1.65 mmol). The flask was evacuated and filled with dinitrogen three times after which cyclopropylamine (0.35 mL, 4.96 mmol) and dry methanol (20 mL) were added. The flask was closed and heated at 60 °C for 12 h in an oil bath. Both the starting and final complex are very little soluble in methanol, but the exchange was anyway complete in the given time. The yellow solid was collected by filtration in the air and was suspended in methanol at 50 °C to remove colored impurities, after which (Cypr-BIAN)$ZnCl_2$ was collected by filtration again and dried in vacuo (623 mg, 95 % yield). Anal. calcd. for $C_{18}H_{16}N_2Cl_2Zn$: C, 54.51; H, 4.07; N, 7.06. Found: C, 54.54, H, 4.17; N, 6.82. For the ^1H NMR signals see Table 1.

The compound so obtained was suspended in CH_2Cl_2 (100 mL) in a separating funnel and a saturated sodium oxalate solution (20 mL) was added. Shaking was continued until the yellow foamy solid which initially formed at the interface completely dissolved. The organic phase was separated, dried with sodium sulfate and evaporated *in vacuo* to give the

analytically pure colorless product (344 mg, 80 % overall yield). Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.65; H, 6.17; N, 10.38. m.p. = 111 °C. MS (70 ev): *m/z*: 260 (M^+).

The free ligand Cypr-BIAN exists in solution as a mixture of two isomers, the *syn-anti* and then *anti-anti* ones. Contrary, to Ar-BIAN ligands, in which the *syn-anti* isomer is usually not present or is present only in small amount, here the *syn-anti* isomer predominates, although the initial relative ratio changes from one preparation to the other, and the isomerization process between the two is very slow, taking days at room temperature to reach equilibrium. The ^{1}H NMR and ^{13}C NMR signals of both isomers are reported in the following.



anti-anti *syn-anti*

For the ^{1}H NMR signals see Table 1.

^{13}C NMR signals were attributed by ^{13}C-^{1}H NMR (HMQC with BIRD). Attribution is given when unequivocal. The resolution in the aromatic region was not sufficient to distinguish *para* and *meta* carbons. δ = 128.69 (CH), 128.43 (CH), 128.22 (CH), 128.15 (CH), 127.75 (CH), 126.92 (CH, *syn-anti* isomer, C-para-*syn*), 123.95 (CH, *anti-anti* isomer, C-ortho), 123.19 (CH, *syn-anti* isomer, C-ortho-*anti*), 118.03 (CH, *syn-anti* isomer, C-ortho-*syn*), 77.83 (C), 77.41 (C), 76.99 (C), 37.01 (CH Cypr, *anti-anti* isomer), 36.16 (CH Cypr, *syn-anti* isomer, C-*anti*), 33.78 (CH Cypr, *syn-anti* isomer, C-*syn*), 11.89 (CH_2 Cypr, *syn-anti* isomer, C-*syn*), 11.57 (CH_2 Cypr, *syn-anti* isomer, C-*anti*), 10.84 (CH_2 Cypr, *anti-anti* isomer).

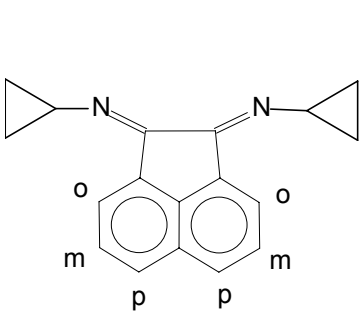
b) By direct reaction of acenaphthenequinone and cyclopropylamine.

To a 50 mL vial with a Teflon valve, of the kind commonly used to store dry deuterated solvents, were added acenaphthenequinone (547 mg, 3.00 mmol) and molecular sieves 3 Å (about 2.5 g). The vial was evacuated and filled with dinitrogen three times, after which cyclopropylamine (624 μL, 9.00 mmol) and dry methanol (20 mL) were added. The vial was closed and heated at 60 °C in an oil bath for 7 h with occasional swirling.

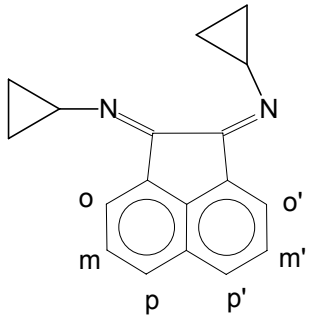
Acenaphthenequinone was only partly soluble at the beginning of the reaction, but a clear yellow-orange solution was formed during the heating time. The solution was filtered by the aid of a cannula and the molecular sieves washed with methanol (2 × 5 mL). The combined solutions were evaporated *in vacuo,* the resulting solid was almost completely dissolved in refluxing heptane (20 mL), and the solution was filtered while hot by the aid of a cannula. Upon cooling the product precipitated out as almost colorless needles, which were collected by filtration and washed with cold hexane (2 × 3 mL). 524 mg, 2.01 mmol, 67.0 % yield. The so obtained Cypr-BIAN (characterization as above) is analytically pure and melts at the same temperature (111 °C) of the perfectly pure compound, but still contains a very little amount of impurities, as evidenced by a pale yellow color. A colorless material (with the same m.p.) can be obtained by a further recrystallization from heptane. The initial heptane solution and hexane washings were evaporated *in vacuo*. The yellow solid mostly contains additional Cypr-BIAN, but is not analytically pure. It is pure enough to be employed in most synthetic applications or can be recrystallized again to afford more analytically pure product.

Table 1

^{1}H NMR signals of the two isomers of Cypr-BIAN and of its $ZnCl_2$ and palladium complexes.[a]



anti-anti



anti-syn

Compound	o	m	p	o'	m'	p'	C-H *anti*	C-H *syn*	CH_2
anti-anti isomer	8.27 d (J = 7.02)	7.70 dd (J = 8.33, 7.02)	7.97 d (J = 8.33)	-	-	-	3.88 psept (J ~ 3.5)	-	1.0-1.3 m
syn-anti isomer	8.15 d (J = 7.23)	7.62 pt	7.94 d (J = 8.27)	7.85 d (J = 6.38)	7.65 pt	7.87 d (J = 8.11)	3.95 psept (J ~ 3.5)	5.52 psept (J ~ 3.5)	1.0-1.3 m
$ZnCl_2$(Cypr-BIAN)	8.39 d (J = 7.51)	8.23 d (J = 8.34)	7.88 pt	-	-	-	4.09 psept	-	1.20-1.30 m 1.05-1.15 m
[Pd(Cypr-BIAN)(η^3-$CH_2C(CH3)CH_2$)][PF_6][b]	8.59 d (J = 7.34)	8.41 (J = 8.32)	7.94 pt				4.06 psept		1.38-1.45 m, 1.00-1.05 m

[a] In $CDCl_3$ at RT, 300 MHz, J values in Hz. Attribution based on COSY and NOESY spectra. [b] In DMSO-d_6. Additional signals: 3.40 (s, 2H, H_{syn}), 3.30 (s, 2H, H_{anti}), 2.17 (s, 3H, CH_3).

Crystal data for $[PF_6][Pd(C_3H_5)_2C_{12}H_8(C_4H_7)]$, monoclinic, space group $P2_1/n$, a = 8.600(1), b = 13.217(2), c = 18.918(3) Å, β = 91.575(4), V = 2149.65(7) $Å^3$, Z = 4, D_c = 1.75 g cm^{-3}, μ (Mo-Kα) = 1.002 mm^{-1}. Graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) was used with generator settings 45 kV and 40 mA. Experimental procedure: 20251 reflections (3804 unique, Rint = 0.0669) with 2θ < 50° were measured at T = 120 K on a Bruker SMART diffractometer (ω-scan mode) equipped with a CCD area-detector, using a yellow crystal of approximate dimensions 0.4 x 0.2 x 0.1 mm, mounted in air but protected by the cooling N_2 stream during the data collection. Data were corrected for Lorentz-polarization and absorption effects (empirical absorption corrections by SADABS: G. M. Sheldrick, available on line at: http:\\shelx.uni-ac.gwdg.de\axs\). The structures were solved by direct methods (A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.* 1999, **32**, 115) and refined with full-matrix least-squares (G. M. Sheldrick, SHELXL97; Program for Structure Refinement, University of Göttingen, Germany, 1997). Hydrogens were fixed on the riding C atoms, except for the allylic hydrogens, whose positional and thermal parameters were refined freely. Anisotropic displacement parameters were assigned to all atoms but the hydrogens. The final agreement factors (for I > 2 σ(I)) were R_1 = 0.0467 (0.0695 for all data) and R_{2W} = 0.1179 (0.1347 for all data); maximum/minimum Δρ = 1.3/-1.9 e $Å^3$, close to Pd.