This article is published as part of the Dalton Transactions themed issue entitled:

Self-Assembly in Inorganic Chemistry

Guest Editors Paul Kruger and Thorri Gunnlaugsson

Published in issue 45, 2011 of Dalton Transactions



Image reproduced with permission of Mark Ogden

Articles in the issue include:

PERSPECTIVE:

Metal ion directed self-assembly of sensors for ions, molecules and biomolecules Jim A. Thomas Dalton Trans., 2011, DOI: 10.1039/C1DT10876J

ARTICLES:

Self-assembly between dicarboxylate ions and a binuclear europium complex: formation of stable adducts and heterometallic lanthanide complexes James A. Tilney, Thomas Just Sørensen, Benjamin P. Burton-Pye and Stephen Faulkner Dalton Trans., 2011, DOI: 10.1039/C1DT11103E

Structural and metallo selectivity in the assembly of [2 × 2] grid-type metallosupramolecular species: Mechanisms and kinetic control Artur R. Stefankiewicz, Jack Harrowfield, Augustin Madalan, Kari Rissanen, Alexandre N. Sobolev and Jean-Marie Lehn Dalton Trans., 2011, DOI: 10.1039/C1DT11226K

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research <u>www.rsc.org/dalton</u>

Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 12146

PAPER

9-Anthracenyl-substitued pyridyl enones revisited: photoisomerism in ligands and silver(I) complexes[†]

Edwin C. Constable,* Guoqi Zhang, Catherine E. Housecroft* and Jennifer A. Zampese

Received 11th April 2011, Accepted 13th May 2011 DOI: 10.1039/c1dt10618j

In solution, (*E*) to (*Z*)-isomerism is facile both in 3-(9-anthracenyl)-1-(pyridin-4-yl)propenone, **2**, and in its silver(1) complex $[Ag(2)_2]^+$. The crystal structures of (*E*)-**2**, (*Z*)-**2** and $[Ag\{(E)-2\}_2][SbF_6]$ are presented, and the roles of edge-to-face and face-to-face π -interactions in the lattice are discussed. Solution NMR spectroscopic data suggest that the driving force for (*E*) to (*Z*) isomerization is intramolecular π -stacking of the pyridine and anthracene domains. The reversed enone 3-(9-anthracenyl)-1-(pyridin-4-yl)propen-3-one, (*E*)-**3**, and the silver(1) complex $[Ag\{(E)-3\}_2][SbF_6]$ have been prepared and characterized, including a single crystal X-ray determination of the latter. Surprisingly, no π -stacking between anthracene or pyridine domains is observed in the solid state, and the crystal packing is dominated by Ag...F, CH_{anthracene}... π -pyridine and CH...F interactions. In contrast to (*E*)-**2** and $[Ag\{(E)-2\}_2]^+$, neither (*E*)-**3** nor $[Ag\{(E)-3\}_2]^+$ undergoes photoisomerization in solution.

Introduction

Anthracenyl substituents are commonly incorporated in supramolecules and conjugates to engineer defined and desired photophysical characteristics.^{1,2} We have previously observed that 3-(9-anthracenyl)-1-(pyridin-2-yl)propen-1-one, 1, (Scheme 1) undergoes photochemical (E) to (Z)-isomerism in solution, and that the conjugation between the anthracenyl substituent and the C=C bond of the enone plays a critical role.³ Coordination of (E)-1 to platinum(II) involves both the pyridine N-donor and the alkene functionality, preventing the coordinated ligand from undergoing photoisomerization.⁴ Recently, Ogawa has demonstrated (Z)–(E)isomerism of 2-(9-anthracenylmethylene)-1-indanones in the solid state.⁵ Rather surprisingly, ligand 2 (the 4-pyridyl analog of 1) has not previously been described. We report here the syntheses and structures of (E)-2, (Z)-2 and (E)-3 (Scheme 1), and the retention of a photoisomerizable C=C bond on going from (E)-2 to $[Ag\{(E)-2\}_2]^+$. We also describe the effects of photolysis of (E)-3 and $[Ag\{(E)-3\}_2]^+$.

Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer; chemical shifts are referenced to residual solvent peaks with respect to TMS = δ 0 ppm. Absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. Finnigan MAT 8400 and Bruker esquire 3000^{plus} mass spectrom-

Department of Chemistry, University of Basel, Spitalstrassse 51, CH-4056 Basel, Switzerland. E-mail: catherine.housecroft@unibas.ch, edwin. constable@unibas.ch; Fax: +41 61 267 1018; Tel: +41 61 267 1008 † CCDC reference numbers 821504–821507. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10618j



Scheme 1 Structure of ligands (*E*)-1, (*E*)-2 and (*E*)-3 with numbering schemes for NMR spectroscopic assignments.

eters were used to record fast atom bombardment (FAB) and electrospray ionization (ESI) mass spectra; a Shimadzu FTIR-8400S spectrophotometer was used to record IR spectra with solid samples using a Golden Gate diamond ATR accessory. UV irradiation was performed using a Philips HPR 125 lamp (230V/125W, E27, UV-A).

Compound (E)-2

4-Acetylpyridine (0.605 g, 5.00 mmol) and anthracene-9carbaldehyde (1.03 g, 5.00 mmol) were dissolved in EtOH (10 cm³). The solution was stirred as aqueous KOH (0.336 g, 6.00 mmol in 4.0 cm³ H₂O) was added. The mixture was stirred at room

temperature overnight, during which time a yellow precipitate formed. The solid was collected by filtration, washed with EtOH and dried in vacuo. The crude solid was recrystallized from hot EtOH to give orange crystals (1.05 g, 70.0%). m.p. 168-170 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.86 (overlapping d (J = 15.9 Hz) and $d_{(AB)}$ (J = 6.0 Hz), 3H, H^{a/b+A2}), 8.50 (s, 1H, H^{B10}), 8.27 (d, J = 8.5 Hz, 2H, H^{B1}), 8.04 (d, J = 8.3 Hz, 2H, H^{B4}), 7.82 $(d_{(AB)}, J = 6.1 \text{ Hz}, 2H, H^{A3}), 7.57-7.51$ (overlapping, 4H, $H^{B2+B3}),$ 7.49 (d, J = 15.9 Hz, 1H, H^{a/b}). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 189.2 (C^{C=O}), 151.2 (C^{A2}), 144.1 (C^{a/b}), 131.5 (C^{B4a/B9a}), 130.1 (C^{a/b}), 129.9 (C^{B4a/B9a}), 129.5 (C^{B9}), 129.3 (C^{B10}), 129.25 (C^{B4}), 127.0 (C^{B2/B3}), 125.7 (C^{B2/B3}), 125.2 (C^{B1}), 121.8 (C^{A3}), C^{A4} not observed. IR (solid, cm⁻¹): 3046 w, 1662 s, 1597 s, 1587 s, 1576 m, 1441 w, 1411 m, 1355 m, 1334 w, 1291 m, 1266 m, 1208 m, 1063 w, 1024 m, 973 s, 930 w, 892 m, 804 s, 784 m, 731 s. UV/VIS λ_{max}/nm (5.0 × $10^{-6} \text{ mol dm}^{-3}$, CH₂Cl₂), 256 ($\varepsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} 133$), 351 (4.58), 368 (5.80), 388 (5.88), 430sh (3.20). ESI MS (CH₂Cl₂/MeOH) m/z $705.6 [2M + Na + 2MeOH]^+, 641.2 [2M + Na]^+ (calc. 641.2), 332.2$ $[M + Na]^+$ (base peak, calc. 332.1), 310.3 $[M + H]^+$ (calc. 310.1). Found C 84.34, H 5.16, N 4.61; C₂₂H₁₅NO 0.25EtOH requires C 84.22, H 5.18, N 4.37%.

Compound (Z)-2

(E)-2 (8.0 mg, 0.026 mmol) was dissolved in $CDCl_3$ (0.6 cm³) in an NMR tube. The tube was exposed to sunlight for 3 days, after which time the solvent was removed. The residue was redissolved in $CH_2Cl_2/MeOH$ (1.0 cm³, 3:1 v/v) in a small vial, and the solvent was allowed to evaporate slowly. Over a period of 3 days, X-ray quality yellow needles formed which were collected by filtration, washed with MeOH and dried in vacuo. (Z)-2 was isolated as yellow needles (6.5 mg, 81%). m.p. 160-162 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.26 (s, 1H, H^{B10}), 8.12 (d, J = 5.6 Hz, 2H, H^{A2}), 8.08 (d, J = 12.1 Hz, 1H, $H^{a/b}$), 8.02 (d, J = 8.7 Hz, 2H, $H^{B1/B4}$), 7.89 (d, J = 8.4 Hz, 2H, H^{B1/B4}), 7.48 (m, 2H, H^{B2/B3}), 7.43 (m, 2H, $H^{B2/B3}$), 7.21 (d, J = 12.1 Hz, 1H, $H^{a/b}$) 7.02 (d, J = 5.6 Hz, 2H, H^{A3}). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 193.4 (C^{C=0}), 149.5 (C^{A2}), 141.3 (C^{a/b}), 130.9 (C^{B4a/B9a}), 130.7 (C^{a/b}), 129.3 (C^{B4a/B9a}), 129.5 (C^{B9}), 129.0 (C^{B1/B4}), 128.1 (C^{B10}), 126.5 (C^{B2/B3}), 125.3 (C^{B1/B4}), 125.1 ($C^{B2/B3}$), 120.5 (C^{A3}), C^{A4} not observed. UV/VIS (5.8×10^{-6} mol dm^-3, CH_2Cl_2) λ_{max}/nm 257 ($\epsilon/10^3$ dm^3 mol^{-1} cm^{-1} 124), 349sh (4.83), 368 (6.21), 388 (6.21), 417 (3.90). ESI MS (CH₂Cl₂/MeOH) m/z 332.1 [M + Na⁺] (base peak, calc. 332.1), 310.2 [M + H]⁺ (calc. 310.1). Found C 84.71, H 5.06, N 4.51; C₂₂H₁₅NO requires C 85.41, H 4.89, N 4.53.

$[Ag{(E)-2}_2][SbF_6]$

AgSbF₆ (17.1 mg, 0.050 mmol) was dissolved in MeOH (4 cm³) and a solution of (*E*)-**2** (30.9 mg, 0.10 mmol) in CH₂Cl₂ (8 cm³) was added. The reaction mixture was stirred at room temperature for 10 min and was then filtered. The filtrate was left to evaporate slowly at room temperature. Red crystals of X-ray quality formed over a period of 3–7 days, were collected by decanting the solvent and were washed with MeOH three times and dried in air. [Ag{(*E*)-**2**}₂][SbF₆] was isolated as red crystals (33.2 mg, 69.2%). ¹H NMR (400 MHz, CD₃CN) δ (ppm) 8.81 (d_(AB), *J* = 6.1 Hz, 4H, H^{A2}), 8.74 (d, *J* = 16.0 Hz, 2H, H^{a/b}), 8.62 (s, 2H, H^{B10}), 8.32 (m, 4H, H^{B1/B4}), 8.12 (m, 4H, H^{B1/B4}), 7.93 (d_(AB), *J* = 6.1 Hz, 4H, H^{A3}), 7.61–

7.54 (m, 8H, H^{B2+B3}), 7.54 (d, J = 16.0 Hz, 2H, H^{a/b}). ¹³C NMR (126 MHz, CD₃CN) δ (ppm) 188.6 (C⁼⁰), 152.5 (C^{A2}), 144.0 (C^{a/b}), 130.1 (C^{B1/B4}), 130.0 (C^{B10}), 128.5 (C^{B2/B3}), 128.2 (C^{a/b}), 126.6 (C^{B1/B4}), 126.1 (C^{B2/B3}), 123.4 (C^{A3}), quaternary C not resolved. IR (solid, cm⁻¹): 3054 w, 1669 s, 1653 m, 1590 s, 1558 s, 1424 m, 1357 w, 1295 w, 1265 s, 1230 w, 1209 m, 1063 w, 1038 w, 1015 m, 984 m, 965 m, 852 s, 814 s, 744 m, 733 s. ESI MS (CH₂Cl₂/MeOH) *m/z* 727.2 [M – SbF₆]⁺ (calc. 727.1), 416.0 [M – SbF₆ – **2**]⁺ (calc. 416.0), 310.1 [**2** + H]⁺ (base peak, calc. 310.1). Found C 54.74, H 3.20, N 3.03; C₄₄H₃₀AgF₆N₂O₂Sb requires C 54.92, H 3.14, N 2.91%.

$[Ag{(Z)-2}_2][SbF_6]$

(Z)-2 (30.9 mg, 0.10 mmol) was dissolved in CH₂Cl₂ (8 cm³) and a solution of AgSbF₆ (17.1 mg, 0.050 mmol) in MeOH (4 cm³) was added. The reaction mixture was stirred at room temperature for 10 min and then filtered. The filtrate was allowed to evaporate at room temperature, and an orange precipitate formed in 3 days. This was collected by decanting the solvent, was washed with MeOH and dried in air. $[Ag\{(Z)-2\}_2][SbF_6]$ was isolated as an orange solid (36.0 mg, 75.0%). ¹H NMR (500 MHz, CD₃CN) δ (ppm) 8.41 (s, 2H, H^{B10}), 8.32 (d_(AB), J = 6.1 Hz, 4H, H^{A2}), 8.07 (overlapping m, 6H, H^{a/b} + H^{B1/B4}), 8.00 (m, 4H, H^{B1/B4}), 7.48 (overlapping m, 10H, $H^{a/b} + H^{B2+B3}$), 7.34 (d_(AB), J = 6.1 Hz, 4H, H^{A3}). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 193.0 (C^{C=0}), 151.2 (C^{A2}) , 144.9 (C^{A4}) , 142.4 $(C^{a/b})$, 132.1 $(C^{B9/B9a/B4a})$, 131.2 $(C^{a/b})$, 129.75 (C^{B9/B9a/B4a}), 129.7 (C^{B1/B4}), 128.2 (C^{B10}), 127.2 (C^{B2/B3}), 126.5 (C^{B1/B4}), 126.3 (C^{B2/B3}), 122.0 (C^{A3}), one quaternary C not observed. IR (solid, cm⁻¹): 1665 m, 1595 m, 1443 w, 1418 m, 1232 m, 1217 m, 1001 m, 893 m, 841 w, 785 m, 778 m, 745 s, 735 s, 724 s, 653 s. UV/VIS λ_{max}/nm (2.9 × 10⁻⁶ mol dm⁻³, acetone), 348 sh ($\varepsilon/10^3$ dm³ mol⁻¹ cm⁻¹ 8.38), 368 (11.3), 385 (12.0), 416 sh (6.31). ESI MS (MeOH) m/z 641.3 $[Na(2)_2]^+$ (base peak, calc. 641.2), 332.1 [Na(2)]⁺ (calc. 332.1). FAB MS (NBA matrix) m/z 727.1 [M - SbF_6^{+} (calc. 727.1) 416.0 [M – $SbF_6 - 2$]⁺ (base peak, calc. 416.0). Found C 54.11, H 3.29, N 2.86; C44H30AgF6N2O2Sb·H2O requires C 53.91, H 3.45, N 2.82%.

Compound (E)-3

9-Acetylanthracene (1.10 g, 5.00 mmol) and pyridine-4carbaldehyde (0.535 g, 5.00 mmol) were suspended in EtOH (15 cm³). The mixture was stirred as aqueous KOH (0.336 g, 6.00 mmol in 4.0 cm³ H₂O) was added, and was then stirred at room temperature overnight. A yellow solid formed which was collected by filtration, washed with EtOH and dried in vacuo. (E)-3 was isolated as a yellow solid (0.800 g, 51.8%). m.p. 179-180 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.58 (d, J = 5.9 Hz, 2H, H^{A2}), 8.56 (s, 1H, H^{B10}), 8.06 (m, 2H, H^{B4}), 7.85 (m, 2H, H^{B1}), 7.48 (m, 4H, H^{B2+B3}), 7.37 (d, J = 16.3 Hz, 1H, $H^{a/b}$), 7.25 (d, J = 5.7 Hz, 2H, H^{A3}), 7.14 (d, J = 16.3 Hz, 1H, $H^{a/b}$). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 199.9 (C^{C=O}), 150.8 (C^{A2}), 144.3 (C^{a/b}), 141.7 (C^{A4}), 133.9 (C^{B9}), 132.8 (C^{a/b}), 131.3 (C^{B4a/B9a}), 129.2 (C^{B4a/B9a}), 129.0 (C^{B4}), 128.6 (C^{B10}), 127.2 (C^{B2/B3}), 125.8 (C^{B2/B3}), 125.1 (C^{B1}), 122.2 (C^{A3}). IR (solid, cm⁻¹): 3054 w, 1642 s, 1624 m, 1593 m, 1548 w, 1447 w, 1414 m, 1356 m, 1289 w, 1265 m, 1231 m, 1215 s, 1185 s, 1168 w, 1152 m, 1143 w, 1091 w, 1013 w, 982 s, 948 w, 885 s, 845 s, 811 s, 728 s, 694 s, 670 s. UV/VIS λ_{max}/nm (5.0 \times 10^{-6} mol dm^{-3}, CH_2Cl_2), 256 (ε/10³ dm³ mol⁻¹ cm⁻¹ 150), 276 sh (24.2), 347 (5.88), 365 (7.20),

384 (6.40). ESI MS (CH₂Cl₂/MeOH) m/z 641.2 [2M + Na]⁺ (calc. 641.2), 332.2 [M + Na]⁺ (base peak, calc. 332.1), 310.3 [M + H]⁺ (calc. 310.1). Found C 83.84, H 5.15, N 4.44; C₂₂H₁₅NO·0.3H₂O requires C 83.79, H 5.01, N 4.44%.

$[Ag{(E)-3}_2][SbF_6]$

(E)-3 (30.9 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (8 cm³) and a solution of $AgSbF_{6}$ (17.1 mg, 0.050 mmol) in MeOH (4 cm³) was added. The reaction mixture was stirred at room temperature for 10 min and was then filtered. The filtrate was left to evaporate slowly at room temperature for one week during which time yellow plates formed. The product was collected by decanting the solvent, was washed with MeOH and dried in air. $[Ag\{(E)-3\}_2][SbF_6]$ was isolated as a yellow crystalline solid (30.2 mg, 62.9%). ¹H NMR (500 MHz, CD₃CN) δ (ppm) 8.70 (s, 1H, H^{B10}), 8.51 (d_(AB), J = 5.9 Hz, 4H, H^{A2}), 8.15 (d, J = 8.5 Hz, 4H, H^{B1/B4}), 7.84 (d, J = 8.3 Hz, 4H, $H^{B1/B4}$), 7.54 (m, 8H, H^{B2+B3}), 7.48 (d, J = 16.3 Hz, 2H, $H^{a/b}$), 7.42 (d, J = 5.8 Hz, 4H, H^{A3}), 7.16 (d, J = 16.3 Hz, 2H, H^{a/b}). ¹³C NMR (126 MHz, CD₃CN) δ (ppm) 201.1 (C^{C=0}), 152.1 (C^{A2}), 145.3(C^{a/b}), 143.6 (C^{A4}), 135.3 (C^{B9}), 134.6 (C^{a/b}), 132.5 (C^{B4a/B9a}), 130.2 (C^{B1/B4}), 130.1 (C^{B10}), 129.5 (C^{B4a/B9a}), 128.3 (C^{B2/B3}), 127.1 (C^{B2/B3}), 126.1 (C^{B1/B4}), 123.8 (C^{A3}). IR (solid, cm⁻¹): 1657 s, 1609 s, 1445 w, 1426 m, 1352 m, 1287 w, 1229 w, 1207 s, 1191 s, 1172 s, 1150 s, 1113 m, 1069 w, 965 s, 970 w, 846 m, 818 s, 735 s, 668 s. UV/VIS λ_{max}/nm (2.5 × 10⁻⁶ mol dm⁻³, CH₃CN), 253 ($\epsilon/10^3$ dm³ mol⁻¹ cm⁻¹ 316), 272sh (50.4), 345 (11.6), 364 (15.6), 383 (13.6). ESI MS (MeCN/MeOH) m/z 727.2 [M – SbF₆]⁺ (base peak, calc. 727.1), 641.3 $[Na + 2(3)]^+$ (calc. 641.2), 332.1 $[3 + Na]^+$ (calc. 332.1), 310.1 [3 + H]⁺ (calc. 310.1). Found C 54.44, H 3.13, N 2.92; C44H30AgF6N2O2Sb requires C 54.92, H 3.14, N 2.91%.

Crystal structure determinations

Data were collected on a Stoe IPDS instrument. The data reduction, solution and refinement used Stoe IPDS software⁶ and SHELXL97.⁷ ORTEP figures were drawn using Ortep-3 for Windows.⁸ Structures were analysed using Mercury v. 2.3.^{9,10} See the ESI for crystallographic data in cif or other electronic format.[†]

(*E*)-2

C₂₂H₁₅NO, *M* = 309.35, yellow block, triclinic, space group *P*Ī, *a* = 10.5404(16), *b* = 12.2631(19), *c* = 14.022(2) Å, *α* = 64.884(11), *β* = 77.234(12), *γ* = 70.989(12)°, *U* = 1544.3(4) Å³, *Z* = 4, *D_c* = 1.331 Mg m⁻³, μ (Mo-K*α*) = 0.081 mm⁻¹, *T* = 173 K. Total 35812 reflections, 6696 unique, *R_{int}* = 0.0387. Refinement of 6154 reflections (433 parameters) with *I* > 2*σ*(*I*) converged at final *R₁* = 0.0398 (*R*1 all data = 0.0436), w*R*₂ = 0.1039 (*wR*2 all data = 0.1066), gof = 1.059.

(*Z*)-2

C₂₂H₁₅NO, M = 309.35, yellow block, monoclinic, space group $P2_1/c$, a = 10.0453(13), b = 17.701(3), c = 9.1880(12) Å, $\beta = 108.582(10)^\circ$, U = 1548.6(4) Å³, Z = 4, $D_c = 1.327$ Mg m⁻³, μ (Mo-K α) = 0.081 mm⁻¹, T = 173 K. Total 30644 reflections, 3511 unique, $R_{int} = 0.0478$. Refinement of 3277 reflections (217 parameters) with $I > 2\sigma(I)$ converged at final $R_1 = 0.0425$ (*R*1 all data = 0.0455), w $R_2 = 0.1081$ (wR2 all data = 0.1101), gof = 1.085

$[Ag\{(E)-2\}_2][SbF_6]$

C₄₄H₃₀AgF₆N₂O₂Sb, *M* = 962.33, orange block, monoclinic, space group *C*2/*c*, *a* = 34.842(3), *b* = 7.2479(4), *c* = 16.1272(13) Å, β = 114.900(6)°, *U* = 3694.0(5) Å³, *Z* = 4, *D*_c = 1.730 Mg m⁻³, μ(Mo-Kα) = 1.334 mm⁻¹, *T* = 173 K. Total 58504 reflections, 5091 unique, *R*_{int} = 0.0687. Refinement of 5022 reflections (273 parameters) with *I* > 2σ(*I*) converged at final *R*₁ = 0.0392 (*R*1 all data = 0.0396), w*R*₂ = 0.1043 (*wR*2 all data = 0.1046), gof = 1.086.

$[Ag{(E)-3}_2][SbF_6]$

C₄₄H₃₀AgF₆N₂O₂Sb, *M* = 962.33, yellow plate, monoclinic, space group *C*2/*c*, *a* = 40.453(6), *b* = 9.9935(15), *c* = 9.4455(14) Å, β = 103.001(11)°, *U* = 3720.6(9) Å³, *Z* = 4, *D*_c = 1.718 Mg m⁻³, μ(Mo-Kα) = 1.324 mm⁻¹, *T* = 173 K. Total 42865 reflections, 4501 unique, *R*_{int} = 0.0874. Refinement of 4366 reflections (275 parameters) with *I* > 2σ(*I*) converged at final *R*₁ = 0.0322 (*R*1 all data = 0.0331), w*R*₂ = 0.0876 (*wR*2 all data = 0.0884), gof = 1.082.

Results and discussion

Synthesis and characterization of isomers of 2

Ligand (E)-2 was prepared by the reaction between 4acetylpyridine and anthracene-9-carbaldehyde in EtOH in the presence of KOH. After recrystallization from hot EtOH, (E)-2 was isolated as deep yellow crystals in 70% yield. The base peak in the electrospray mass spectrum appeared at m/z 332.2 and was assigned to $[M + Na]^+$. The solution ¹H and ¹³C NMR spectra of a freshly dissolved sample of (E)-2 in CDCl₃ showed one set of signals and were assigned by 2D techniques (see below). A CDCl₃ solution of (E)-2 was kept in the dark for 3 days, and the ¹H NMR spectrum of the sample after this period was unchanged. The same NMR tube was then exposed to sunlight for 10 h. Changes in the ¹H NMR spectrum were observed which were consistent with partial conversion of (E)-2 to (Z)-2. Signals in the NMR spectra were assigned using COSY, DEPT, HMBC and HMQC spectra. Due to the overlap of one alkene signal with that for HA2 in each spectrum (Fig. 1), it proved difficult to unambiguously assign the former as either H^a or H^b from the NOESY spectrum. The HMBC spectrum was similarly ambiguous. The alkene protons give rise to resonances at δ 8.86 and 7.49 ppm (J = 15.9 Hz) in (*E*)-2, and at δ 8.08 and 7.21 ppm (*J* = 12.1 Hz) in (*Z*)-2. The coupling constants are diagnostic of the (E) or (Z) isomer.³ Fig. 1 shows that the resonances for the pyridine protons undergo significant shifts to lower frequency and this suggests that in the (Z) isomer, the pyridine ring lies over the anthracene substituent, so that protons HA2 and HA3 experience the effects of the ring current of the anthracene π -system. Once formed, (Z)-2 is stable in solution with respect to conversion back to (E)-2. We have no evidence to suppose that isomerization occurs in the solid state. Crystals of (E)-2 (see below) stored for several months and then dissolved in CDCl₃ gave a ¹H NMR spectrum typical of (E)-2.

X-Ray quality crystals of (E)-2 were grown by slow evaporation of a CH₂Cl₂/MeOH solution of the compound and the structure determination confirmed the (E) configuration. The asymmetric unit contains two independent molecules (A and B), and molecule A is depicted in Fig. 2. Bond parameters are unexceptional (caption to Fig. 2). The pyridylenone units are slightly twisted, and angles between the pyridine ring and alkene unit are 21.06(12)



Fig. 1 500 MHz NMR spectra in $CDCl_3$ (* = residual $CHCl_3$) of (*E*)-**2** (top, with traces of the (*Z*)-isomer), and (*Z*)-**2** (bottom, with minor amounts of the (*E*)-isomer). For remaining signal assignments, see experimental section.



Fig. 2 Structure of one of the two independent molecules of (*E*)-2; ellipsoids plotted at 40% probability level. Selected bond parameters (which are similar in both molecules): O1a–C17a = 1.2167(14), N1a–C22a = 1.3294(15), N1a–C18a = 1.3343(16), C15a–C16a = 1.3357(15), C14a–C15a = 1.4687(15), C16a–C17a = 1.4797(15) Å; C22a–N1a–C18a = 116.63(10), O1a–C17a–C16a = 121.23(10), O1a–C17a–C20a = 119.60(10), C15a–C16a–C17a = 119.27(10), C16a–C15a–C14a = $127.82(11)^\circ$.

and 28.65(12)° in molecules A and B, respectively. The alkene unit is twisted with respect to the plane of the anthracene by 50.28(12) and 54.81(12)° in molecules A and B, respectively. The mutual twisting of the aromatic domains appears to have its origins in the crystal packing. Molecules A and B associate through $CO \cdots HC$ non-classical hydrogen bonds (C21aH21a $\cdots O1b$ = 2.50, C21a...O1b = 3.3817(17) Å, C21a-H21a...O1b = 154° ; $C16aH16a \cdots O1b = 2.66, C21a \cdots O1b = 3.6041(17) \text{ Å}, C16a H16a \cdots O1b = 171^{\circ}$). In addition, pyridine hydrogen atom H19b (molecule B) is directed towards the π -system of the anthracene unit of molecule A. The packing of molecules in the lattice features face-to-face π -interactions of pairs of molecule A pyridine rings (separation between planes of rings containing N1a and N1 a^{i} = 3.39 Å, symmetry code i = 1 - x, 1 - y, 1 - z), and face-to-face π -stacking of pairs of molecule B anthracene domains (separation between planes = 3.43 Å).

A solution of (E)-2 in CDCl₃ was exposed to sunlight for 3 days. Once solvent had been removed, the residue was dissolved in CH₂Cl₂/MeOH and slow evaporation yielded yellow needles suitable for X-ray structure determination. The molecular structure of (Z)-2 is shown in Fig. 3, and the data in the captions to Fig. 2



Fig. 3 Structure of (*Z*)-2; ellipsoids plotted at 40% probability level. Selected bond parameters: O1-C6 = 1.2156(14), N1-C1 = 1.3335(16), N1-C5 = 1.3384(17), C7-C8 = 1.3355(16), C6-C7 = 1.4719(15), C8-C9 = 1.4794(15) Å; C1-N1-C5 = 116.89(10), O1-C6-C7 = 122.78(10), O1-C6-C3 = 118.44(10), C7-C6-C3 = 118.78(9), $C8-C7-C6 = 125.62(10)^{\circ}$.

and 3 reveal that the bond parameters in (*Z*)-2 are similar to those in (*E*)-2. The pyridylenone unit in (*Z*)-2 is essentially planar, the largest deviation from the least squares plane through the nonhydrogen atoms being 0.23 Å for atom O1. As in (*E*)-2, the alkene substituent is twisted with respect to the plane of anthracene (angle between the least squares planes of the anthracene and alkene units is 65.01(7)°). The crystal packing involves face-to-face π -stacking of anthracene domains (symmetry codes *x*, *y*, *z* and -x, 1 - y, 2 - z) at a separation of 3.53 Å, but in contrast to the packing in (*E*)-2, no face-to-face interactions involving the pendant pyridines is observed. Instead, pairs of pyridine rings face one another across an inversion centre (N1 ··· H1aⁱC1ⁱ = 2.83 Å) and are sandwiched between anthracene domains which associate through oblique CH_{anthracene} ··· $\pi_{pyridine}$ interactions (CH ··· centroid = 2.82 Å).^{11,12}

The change in orientation of the pyridine ring with respect to the anthracene unit observed within a molecule in the solid state on going from (*E*)-**2** to (*Z*)-**2** does not explain the dramatic shifts observed in solution for the pyridine ¹H NMR resonances (protons H^{A2} and H^{A3}). These data are, however, consistent with the fact that, in solution, intramolecular interactions are dominant and lead to the pyridine ring lying over the anthracene domain.

Complexes of silver(I) with (E)-2 and (Z)-2

A CH₂Cl₂ solution of (*E*)-**2** was added to a MeOH solution of AgSbF₆ and the mixture was stirred at room temperature for 10 min. After filtration, the filtrate was allowed to evaporate slowly at room temperature. Crystals suitable for X-ray analysis formed within a week. Fig. 4 shows the structure of the centrosymmetric cation. The Ag1–N1 bond distance of 2.1102(17) Å is typical, and the N1–Ag1–N1ⁱ bond angle is constrained by symmetry to 180°. The [SbF₆]⁻ ion is disordered and has been modelled as a 'top' with each of the equatorial F atoms having fractional occupancies of 0.5. Two symmetry related Ag… F contacts involving non-disordered F atoms (Ag1…F1ⁱⁱ = Ag1…F1ⁱⁱⁱ = 2.942(4) Å,



Fig. 4 Structure of the $[Ag\{(E)-2\}_2]^*$ cation in $[Ag\{(E)-2\}_2][SbF_6]$; ellipsoids plotted at 40% probability level and H atoms omitted. Symmetry code i = -x, 2 - y, 1 - z. Selected bond parameters: Ag1–N1 = 2.1102(17), C3–C6 = 1.507(3), O1–C6 = 1.219(2), C6–C7 = 1.475(3), C7–C8 = 1.340(3) Å; O1–C6–C7 = 122.75(17), O1–C6–C3 = 119.04(18), C7–C6–C3 = 118.19(17), C8–C7–C6 = 120.32(18), C7–C8–C9 = 127.83(19)°.

symmetry codes ii = -x, y, $\frac{1}{2} - z$, iii = x, 2 - y, $\frac{1}{2} + z$) are shorter than the sum of the van der Waals radii (3.19 Å) and result in the coordination environment of the silver atom being best considered as square planar (angles $N1-Ag1 \cdots F1^{ii}$ = 90.32(9), N1–Ag1 \cdots F1ⁱⁱⁱ = 89.68(9)°). The Ag \cdots F interactions lead to the formation of chains of alternating cations and anions running along the crystallographic *c*-axis. The backbone of the cation has a wave-like appearance, and the angle between the least squares planes of the pyridine and anthracene units of each coordinated ligand is 37.95(9)°. The cations intercalate with one another (Fig. 5), thereby optimizing face-to-face π interactions between alternating pyridine and anthracene domains, at separations of 3.40 and 3.43 Å. This packing places the Ag atoms over one another along the *b*-axis, with the shortest Ag \cdots Ag distances (7.2479(4) Å) being approximately twice the pyridine · · · anthracene separations.



Fig. 5 Packing of $[Ag\{(E)-2\}_2]^*$ cations in $[Ag\{(E)-2\}_2][SbF_6]$ showing intercalation of pyridine and anthracene domains.

The ¹H NMR spectrum of a CD₃CN solution of freshly dissolved crystals of $[Ag\{(E)-2\}_2][SbF_6]$ was consistent with the presence of one ligand environment. The appearance of two doublets, each with J = 16.0 Hz, confirmed that the ligand was in an (E)-configuration. After the solution had been standing in sunlight for 10 h, the ¹H NMR spectrum was again recorded and confirmed the presence of both $[Ag\{(E)-2\}_2]^+$ and $[Ag\{(Z)-2\}_2]^+$ in a ratio of 1:2 based on integrals of the signals for H^{B10}. When a CD₃CN solution of $[Ag\{(E)-2\}_2][SbF_6]$ was irradiated with a UV lamp for 20 min, the ratio of coordinated E to Z ligand was 1:7.5. The (Z)-configuration of the coordinated ligand was unambiguously assigned from a pair of doublets with diagnostic coupling constants of 12 Hz, although these signals overlapped with those of the anthracenyl protons (see experimental section). We are not able to distinguish between isomerization of the free ligand after dissociation, or isomerization of the complex (Scheme 2) and furthermore, cannot distinguish between the presence of



Scheme 2 The formation of $[Ag\{(Z)-2\}_2]^*$ may arise in solution by isomerization of the complex or free ligand.

the Z ligand in the putative complexes $[Ag\{(Z)-2\}\{(Z)-2\}]^+$ and $[Ag\{(Z)-2\}_2]^+$. The ¹H NMR spectrum of a 1:1 mixture of the two homoleptic complexes was a superimposition of the spectra of $[Ag\{(E)-2\}_2]^+$ and $[Ag\{(Z)-2\}_2]^+$ indicating that the individual signals of the *E* and *Z* ligands in the homo- and heteroleptic complexes are isochronous, or that the heteroleptic complex is not formed.

The most significant changes in the spectrum on going from $[Ag\{(E)-2\}_2]^+$ and $[Ag\{(Z)-2\}_2]^+$ are in the chemical shifts of signals arising from the pyridine and alkene protons. These differences resemble those observed upon isomerization of the free ligand (Fig. 1). In the complexes, resonances for HA2 and H^{A3} appear at δ 8.81 and 7.93 ppm for $[Ag\{(E)-2\}_2]^+$, and at δ 8.32 and 7.34 ppm for $[Ag\{(Z)-2\}_2]^+$. The signal for one of the two alkene protons moves to lower frequency (δ 8.74 to 8.07 ppm) as the coordinated ligand switches from (E) to (Z) isomer. $[Ag\{(Z)-2\}_2][SbF_6]$ was also prepared by reaction of AgSbF₆ and (Z)-2 and the ¹H NMR spectrum agreed with the subspectrum which appears when $[Ag\{(E)-2\}_2]$ [SbF₆] is left to stand in CD₃CN solution. The $[Ag\{(Z)-2\}_2]^+$ ion is stable in solution with respect to any isomerization process, and the ${}^{13}C$ NMR spectrum of [Ag{(Z)- 2_{2} [SbF₆] was readily assigned using 2D methods. It proved difficult to obtain a ¹³C NMR spectrum of $[Ag\{(E)-2\}_2][SbF_6]$ in the absence of the (Z)-isomer, and the ${}^{13}C$ NMR spectrum of $[Ag\{(E)-2\}_2]$ [SbF₆] was assigned from a mixture of isomers.

Synthesis and characterization of (E)-3

We have previously noted that while 3-(9-anthracenyl)-1-(pyridin-2-yl)propen-1-one undergoes photochemical isomerization in solution, the 'reversed' enone, 3-(9-anthracenyl)-1-(pyridin-2yl)propen-3-one does not. This suggests that the direct attachment of the alkene to the anthracene domain is a requirement for isomerization. In order to explore whether this is a more general phenomenon, we prepared (E)-3 (Scheme 1) by the reaction of 9-acetylanthracene with pyridine-4-carbaldehyde under basic conditions. Yellow (E)-3 was isolated in moderate yield. The base peak in the ESI mass spectrum appeared at m/z 332.2 and was assigned to $[M + Na]^+$. A less intense peak at m/z 310.3 arose from $[M + H]^+$. The ¹H NMR spectrum exhibited two doublets, each with $J_{\rm HH} = 16.3$ Hz, consistent with an (E)-configuration for the C=C bond. The solution ¹H and ¹³C NMR spectra (see experimental section) were fully assigned by COSY, NOESY, HMQC and HMBC techniques. Resonances for protons H^{B4} and H^{B1} (Scheme 1) were distinguished using a NOESY cross peak between H^{B4} and H^{B10} .

A CDCl₃ solution of (*E*)-**3** was irradiated with UV light for 2 h. The ¹H and ¹³C NMR spectra of the resultant solution were consistent with the presence of (*E*)-**3** as the dominant species. There were no peaks that could be assigned to (*Z*)-**3**. Most notably,

in the ¹H NMR spectrum there were no doublets for the alkene protons with coupling constants characteristic of a (Z)-isomer. However, subspectra accounting for about 10% of the sample based on integration of the pyridine HA3 signals were observed. Analysis using COSY, HMQC and HMBC techniques showed the presence of three species in addition to (E)-3. A comparison with the literature identified two components as anthraquinone^{13,14} and 10H,10'H-[9,9'-bianthracenylidene]-10,10'-dione (Scheme 3).14 In the ¹H NMR spectrum, the third component shows a diagnostic pair of COSY correlated doublets (δ 8.50 and 7.02 ppm, J = 5.7Hz) assigned to pyridine protons, and COSY correlated doublets (δ 7.51 and 6.30 ppm, J = 16.0. Hz) assigned to an (E)-alkene functionality. HMBC cross peaks between the latter and a ¹³C NMR signal at δ 199.8 ppm can be assigned to a C=O group adjacent to the C=C bond. However, complete characterization of this product has not been possible.



Scheme 3 Decomposition resulting from the photolysis of (*E*)-3.

Treatment of AgSbF₆ with two equivalents of (E)-**3** resulted in the formation of a yellow crystalline product. In the ESI mass spectrum, the base peak at m/z 727.2 was assigned to $[M - SbF_6]^+$, and the isotope pattern was in accord with that simulated. The ¹H and ¹³C NMR spectra were consistent with the presence of a single ligand environment and were assigned by 2D methods. Differences in solubilities of ligand and complex necessitated that the spectra were recorded in CDCl₃ and CD₃CN, respectively. Even so, a comparison of the spectra is made in Fig. 6, and illustrates only a relatively minor perturbation of the signals upon formation of the complex. The retention of a 16.3 Hz coupling constant for the alkene protons H^a and H^b confirms that the (*E*)-configuration of the ligand is maintained. This was further confirmed by a structural determination of $[Ag\{(E)-3\}_2][SbF_6]$.

X-Ray quality crystals of $[Ag\{(E)-3\}_2][SbF_6]$ were grown by slow evaporation of a CH₂Cl₂/MeOH solution of the complex. Fig. 7 depicts the molecular structure of the cation, confirming a linear coordination environment about the silver(1) centre. The asymmetric unit contains half a cation (atom Ag1 resides on an



Fig. 6 500 MHz NMR spectra of (E)-3 (top) in CDCl₃ (* = residual solvent) and of $[Ag\{(E)$ -3 $\}_2][SbF_6]$ (bottom) in CD₃CN. For atom labelling, see Scheme 1.



Fig. 7 Structure of the $[Ag\{(E)-3\}_2]^*$ cation in $[Ag\{(E)-3\}_2][SbF_6]$; ellipsoids plotted at 30% probability level and H atoms omitted. Symmetry code i = 1 - x, 1 - y, -z. Selected bond distances and angles: Ag1-N1 = 2.1375(18), O1-C8 = 1.209(3), C3-C6 = 1.469(3), C6-C7 = 1.330(3), C7-C8 = 1.479(3) Å; C7-C6-C3 = 125.34(19), C6-C7-C8 = 122.39(19), O1-C8-C7 = 120.92(19), O1-C8-C9 = 120.80(19), C7-C8-C9 = 118.28(18)°.

inversion centre and thus the N-Ag-Nⁱ bond angle is constrained to 180°) and half an anion (the two halves of the $[SbF_6]^-$ ion are related by a 2-fold axis). The anion is disordered and has been modelled over two sites with 0.7 and 0.3 fractional occupancies. The Ag–N bond lengths of 2.1375(18) Å in $[Ag\{(E)-3\}_2][SbF_6]$ are comparable with 2.1102(17) Å found for corresponding bonds in $[Ag\{(E)-2\}_2][SbF_6]$. As in the latter, the coordination geometry around the silver(I) ion in $[Ag\{(E)-3\}_2][SbF_6]$ is best thought of as square planar because of the presence of two short $Ag \cdots F$ contacts (Ag1 \cdots F3 = Ag1 \cdots F3ⁱ = 2.687(5) Å). These interactions do not support chains of cations and anions as in $[Ag\{(E)\}$ - 2_{2} [SbF₆]. Instead, the Ag atoms approach more closely (shortest $Ag \cdots Ag = 4.7227(7)$ Å) resulting in stacks of cations running along the *c*-axis (Fig. 8). The stacking results in atom Ag1 being sandwiched between two pyridine rings of adjacent cations with concomitant weak Ag $\cdots \eta^2$ -pyridine interactions: Ag $1 \cdots C1^{iii}$ = $Ag1 \cdots C1^{iv} = 3.483(3), Ag1 \cdots C2^{iii} = Ag1 \cdots C2^{iv} = 3.554(3) Å.$ These distances are somewhat longer than in previously reported Ag $\cdots \eta^2$ -arene (including pyridine) contacts,¹⁵⁻¹⁸ and significantly lengthened with respect to those observed for $Ag\cdots\eta^{i}\text{-arene}$ contacts.^{19,20} An analysis of silver(I) ··· arene (excluding heterocycles) complexation by Kochi and coworkers reveals that the typical separation between the Ag atom and aromatic ring plane is 2.41 \pm 0.05 Å.²¹ In [Ag{(*E*)-3}₂][SbF₆], the separation is much longer (3.56 Å). The pyridine and anthracene units of each coordinated ligand are twisted 86.18(9)° with respect to one another, and this contrasts with the smaller twist angle observed in



Fig. 8 Packing of cations in $[Ag\{(E)-3\}_2][SbF_6]$ viewed down the (a) *b*-axis, and (b) *c*-axis.

 $[Ag\{(E)-2\}_2][SbF_6]$ (see above). The difference is, naturally, associated with the crystal packing. Despite the potential for π -stacking between anthracene and pyridine domains, the crystal packing in $[Ag\{(E)-3\}_2][SbF_6]$ is dominated by the Ag... F interactions described above, $CH_{anthracene} \cdots \pi$ -pyridine contacts (C20–H20a... centroid of ring with N1ⁱⁱ = 2.663 Å, symmetry code ii = x, y, 1 + z), and CH... F contacts.

A CD₃CN solution of $[Ag\{(E)-3\}_2][SbF_6]$ was exposed to sunlight for 3 days and the ¹H NMR spectrum was recorded. Although the spectrum revealed $[Ag\{(E)-3\}_2][SbF_6]$ to be the predominant species, at least two minor components had formed. Both subspectra contained signals assigned to pyridine and (E)-CH=CH domains, but the lack of corresponding singlets for anthracenyl H^{B10} protons suggested the products resulted from photo-decomposition of $[Ag\{(E)-3\}_2]^+$. The photolysis was repeated using a UV lamp, irradiating for 2 h. Under these conditions, $[Ag\{(E)-3\}_2]^+$ was almost completely destroyed and a complex mixture of products resulted, the major component of which was anthraquinone.¹³

Conclusions

We have shown that (*E*) to (*Z*)-isomerism readily occurs in 3-(9-anthracenyl)-1-(pyridin-4-yl)propenone, **2**, and in its silver(1) complex $[Ag(2)_2]^+$ in solution. The crystal structures of (*E*)-**2**, (*Z*)-**2** and $[Ag\{(E)-2\}_2][SbF_6]$ are presented. In both isomers of the ligand and in the complex, the solid state packing features face-to-face π -stacking of pyridine and/or anthracene units, and in (*Z*)-**2** CH_{anthracene} $\cdots \pi_{pyridine}$ interactions are also important. NMR spectroscopic data indicate that (*E*) to (*Z*) isomerization is facilitated by intramolecular π -stacking of the pyridine and anthracene domains. The enone (E)-**3**, the 'reversed' isomer of (E)-**2**, and the silver(1) complex $[Ag\{(E)$ -**3** $_{2}][SbF_{6}]$ have been synthesized. The solid state structure of the complex exhibits no π stacking between anthracene or pyridine domains, and instead, the crystal packing is dominated by Ag \cdots F, CH_{anthracene} $\cdots \pi$ -pyridine and CH \cdots F contacts. Neither (E)-**3** nor $[Ag\{(E)$ -**3** $\}_{2}]^{+}$ undergoes photoisomerization in solution. Irradiation with a UV lamp results in ligand decomposition. For the free ligand, the products are anthraquinone, 10H, 10'H-[9,9'-bianthracenylidene]-10, 10'-dione and a third product (Scheme 3). Photodecomposition of $[Ag\{(E)$ -**3** $\}_{2}]^{+}$ leads to a mixture of products, with anthraquinone being the dominant component.

Acknowledgements

We thank the Swiss National Science Foundation and the University of Basel for financial support. GZ thanks the Novartis Foundation, formerly Ciba-Geigy Jubilee Foundation, for support. Peter Kopecky is thanked for recording the 500 MHz NMR spectra.

References

- P. V. Slitikov, A. V. Petrov, E. N. Rasadkina and E. E. Nifant'ev, *Russ. J. Gen. Chem.*, 2010, **80**, 69.
- 2 P. K. Bhowmik, A. K. Nedeltchev and H. Han, *Mol. Cryst. Liq. Cryst.*, 2009, **501**, 125.
- 3 E. C. Constable and D. R. Smith, Tetrahedron, 1996, 52, 935.
- 4 P. Marqués-Gallego, H. den Dulk, J. Brouwer, H. Kooijman, A. L. Spek, O. Roubeau, S. J. Teat and J. Reedijk, *Inorg. Chem.*, 2008, 47, 11171.
- 5 J. Harada, M. Harakawa, S. Sugiyama and K. Ogawa, *CrystEngComm*, 2009, 11, 1235.
- 6 Stoe & Cie, IPDS software v 1.26, Stoe & Cie, Darmstadt Germany, 1996.
- 7 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 8 L. J. Farrugia, J. Appl. Crystallogr., 1997, 30, 565.
- 9 I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, 58, 389.
- 10 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, J. Appl. Crystallogr., 2008, 41, 466.
- 11 M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama and H. Suezawa, *CrystEngComm*, 2009, 11, 1757.
- 12 M. Nishio, CrystEngComm, 2004, 6, 130.
- 13 H. Fidder, A. Lauer, W. Freyer, B. Koeppe and K. Heyne, J. Phys. Chem. A, 2009, 113, 6289.
- 14 T. Yamaji, T. Saito, K. Hayamizu, M. Yanagisawa and O. Yamamoto, Spectra Database for Organic Compounds, http://riodb01.ibase.aist.go.jp/sdbs/.
- 15 E. C. Constable, C. E. Housecroft, M. Neuburger, S. Reymann and S. Schaffner, *Eur. J. Inorg. Chem.*, 2008, 3540.
- 16 S. Kim, J. S. Kim, S. K. Kim, I.-H. Suh, S. O. Kang and J. Ko, *Inorg. Chem.*, 2005, 44, 1846.
- 17 P. Pérez-Galán, N. Delpont, E. Herrero-Gómez, F. Maseras and A. M. Echavarren, *Chem.-Eur. J.*, 2010, 16, 5324.
- 18 M. L. Gallego, M. s Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, P. Cornago and R. M. Claramunt, *Eur. J. Inorg. Chem.*, 2005, 4370 and references therein.
- 19 D. L. Reger, J. R. Gardinier and M. D. Smith, *Inorg. Chem.*, 2004, 43, 3825 and references therein.
- 20 R. Koschabek, R. Gleiter and F. Rominger, *Eur. J. Inorg. Chem.*, 2006, 609.
- 21 S. V. Lindeman, R. Rathore and J. K. Kochi, *Inorg. Chem.*, 2000, 39, 5707.