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Synthesis and Structure of Pentamethylcyclopentadienyl Tungsten(V) Complexes Containing Functionalized 6,12-Epiiminodibenzo[*b,f*][1.5]diazocine Ligands

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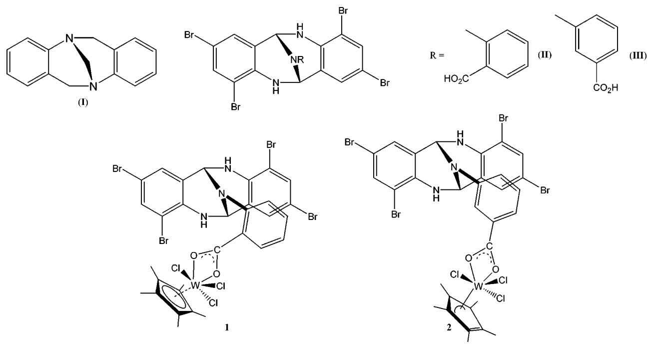
Summary: 2-Amino-3,5-dibromobenzaldehyde [3,5-Br_2-2-$H_2NC_6H_2CHO$] undergoes a self-condensation reaction in the presence of o- or m-anthranilic acid, affording the novel ligand systems [o- or m-(HO_2C)C_6H_4(μ_3-N)L] (L = [3,5-Br_2-2-HNC_6H_2-CH]$_2$). Further interaction with [CpWCl_4] in refluxing toluene affords the tungsten(V) complexes [Cp*WCl_3(η^2-O_2C)C_6H_4(μ_3-N)L], the X-ray crystal structures of which show pseudo-octahedral tungsten centers with the chelating syn carboxylate group of the new ligand system and a mer arrangement of chlorine atoms forming the base and an η^5- (for **1·MeCN**) or slipped, η^3- (for **2·3MeCN**) C_5Me_5 ligand at the apex.*

As part of a program aimed at the development of new ligand systems derived from anthranilic acid,[1] we have characterized carboxylates, amidobenzoates, imidobenzoates, imido/silyl esters, quinazoline ligands, as well as Schiff base complexes. We now describe a class of ligand system derived from the self-condensation of 2-amino-3,5-dibromobenzaldehyde in the presence of anthranilic acid, epiiminodibenzo[*b,f*][1,5]diazocines (see Chart 1). Such tricyclic ligands are of interest in supramolecular chemistry because of the defined orientation afforded to each aryl ring.[2] The best-known example of such a "molecular cleft" is Troger's base, 2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo-[6,*f*][1,5]diazocine (see **I**),[3] analogues of which continue to be of interest.[4] We also note that the self-condensation of *o*-aminobenzaldehyde leads to a variety of trimers and tetramers.[5] Ligands with related steric features, such as bulky anthracenyl-derived ligands, have also been found to be useful in late transition metal olefin polymerization, particularly when coordinated to nickel, and it is thought that such a ligand impacts a degree of steric protection thereby preventing binding of potentially poisonous donor groups.[6] Our ligands are only sparingly soluble in common organic solvents. In order to fully characterize this new ligand system, we have prepared the pentamethylcyclopentadienyl (Cp*, C_5Me_5) tungsten(V) derivatives, by reaction with [Cp*WCl_4],[7] which we recognize from our earlier work as a system which is prone to give highly crystalline products. The structures of both the *ortho*- and *meta*-anthranilic acid derived complexes are described herein.

Chart 1



Treatment of 2-amino-3,5-dibromobenzaldehyde (2 equiv) with *o*- or *m*-anthranilic acid in acidified refluxing ethanol afforded, after workup, the yellow ligands [*o*- or *m*-(HO_2C)-C_6H_4(μ_3-N)L] (L = [3,5-Br_2-2-HNC_6H_2CH]$_2$) in good yield (80−90%). In the absence of anthranilic acid, 2-amino-3,5-dibromobenzaldehyde is recovered unaltered (for X-ray data, see Supporting Information), suggesting that the reaction proceeds via an amino−imine intermediate as opposed to initially forming a dibenzo[*b,f*][1,5]diazocine ring (Scheme 1). Similar mechanistic schemes have been postulated for related systems involving the iminophosphorane *o*-(triphenylphosphoranylideneamino)benzaldehyde, 2-(PPh_3N), CHO−C_6H_4,[8] and the reaction of 5-aminothieno[2,3-*c*]pyridazine-6-carbaldehyde with primary amines.[9]

The reaction of [W(η-C_5Me_5)Cl_4] with in situ generated [*o*-(HO_2C)C_6H_4(μ_3-N)L] (**II**) in refluxing toluene afforded, after workup, red/brown prisms of the paramagnetic (d^1) complex

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(1) (a) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Dalton Trans.* **1997**, 3207. (b) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Dalton Trans.* **1997**, 3343. (c) Gibson, V. C.; Redshaw, C.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 79. (d) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *Inorg. Chem. Commun.* **2001**, *4*, 95. (e) Redshaw, C.; Elsegood, M. R. J. *Chem. Commun.* **2001**, 2016. (f) Humphrey, S. M.; Redshaw, C.; Holmes, K. E.; Elsegood, M. R. J. *Inorg. Chim. Acta* **2005**, *358*, 222.

(2) Field, J. D.; Turner, P.; Harding, M. M.; Hatzikominos, T.; Kim, L. *New J. Chem.* **2002**, *26*, 720.

(3) Tröger, J. *J. Prakt. Chem.* **1877**, *36*, 225.

(4) See for example: (a) Dolenský, B.; Valik, M.; Sýkora, D.; Král, V. *Org. Lett.* **2005**, *7*, 67. (b) Hansson, A.; Wixe, T.; Bergquist, K.-E.; Wärnmark, K. *Org. Lett.* **2005**, *7*, 2019. (c) Ashmore, J.; Bishop, R.; Craig, D. C.; Scudder, M. L. *Cryst. Growth Des.* **2007**, *7*, 47.

(5) (a) Jircitano, A. J.; Sommerer, S. O.; Shelley, J. J.; Westcott, B. L., Jr. *Acta Crystallogr.* **1994**, *C50*, 445. (b) Seidel, F.; Dick, W. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 2018.

(6) See for example: (a) Gibson, V. C.; Tomov, A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 719. (b) Gibson, V. C.; Tomov, A. *Chem. Commun.* **2001**, 1964.

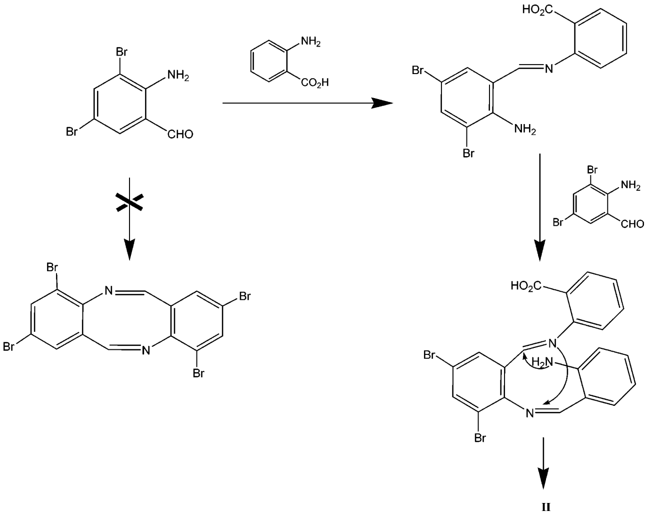
(7) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 953.

(8) Molina, P.; Arques, A.; Tárraga, A.; del Rosario Obon, M.; Foces-Foces, C.; Jagerovic, N.; Elguero, J. *Tetrahedron* **1998**, *54*, 997.

(9) Quintela, J. M.; Alvarez-Sarandés, R.; Peinador, C.; Maestro, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3557.

10.1021/om700810p CCC: $37.00

Scheme 1



$[W(\eta\text{-}C_5Me_5)Cl_3\{o\text{-}(O_2C)C_6H_4(\mu_3\text{-}N)L\}]$ (**1**) in ca. 53% isolated yield. The IR spectrum of **1** has a ν(N−H) stretch at 3321 cm^{-1}, together with a strong ν(C−N) stretch at 1259 cm^{-1}. There are also bands in the ν(C−O) region at 1697 and 1594 cm^{-1}. The X-band EPR spectrum (MeCN, 298 K) is sharp with $g = 1.897$. Similar treatment of $[W(\eta\text{-}C_5Me_5)Cl_4]$ with in situ generated $[m\text{-}(HO_2C)C_6H_4(\mu_3\text{-}N)L]$ (**III**) in refluxing toluene affords, after workup, red/brown prisms of $[W(\eta\text{-}C_5Me_5)Cl_3\{m\text{-}(O_2C)C_6H_4(\mu_3\text{-}N)L\}]$ (**2**) in ca. 30% isolated yield. The IR spectrum of **2** is similar to that of **1** [ν(N−H) 3364; ν(C−N) 1259, and ν(C−O) 1690 and 1594 cm^{-1}], while the EPR spectrum (MeCN, 298 K) is sharp with $g = 2.008$. Confirmation of the nature of the ligand is provided by a crystallographic study. Suitable crystals of **1·MeCN** and **2·3MeCN** were grown from saturated solutions of acetonitrile on prolonged standing at ambient temperature. Diagrams of **1** and **2** are shown in Figures 1 and 2, respectively, with selected bond lengths and angles given in each caption. Crystallographic data appear in Table 1.

The coordination geometry at each tungsten center is best described as pseudo-octahedral with a *mer* arrangement of chlorines; an oxygen atom of the *syn* carboxylate is *trans* to the centroid of the C_5Me_5 ligand. For **1**, the W−C distances (range 2.370(8)−2.442(7) Å) are consistent with a slightly slipped but still η^5 group in which the C_5Me_5 ring carbons are planar within ±0.019(5) Å.[10] The C_5Me_5 methyl groups are all bent away from the W atom relative to the C(1)−C(5) ring, with C(8) and C(10) displaced furthest at ca. 0.25 Å compared to C(6), C(7), and C(9) at ca. 0.09 Å. The W to ring centroid distance is 2.071(4) Å. In the case of **2**, the C_5Me_5 ring is better described as a slipped η^3-Cp* group (range of W−C distances: 2.309(14)−2.418(15) Å). The five ring carbons are co-planar within ±0.012(9) Å (the W to ring centroid distance is 2.040(6) Å), while the methyl groups bend away from W relative to the C(1)−C(5) ring by 0.017, 0.240, 0.079, 0.170, and 0.166 Å for C(6)−C(10), respectively. The ligand fragment **II** is sterically related to Troger's base (see **I**).† However, in contrast to the latter, where a bridging carbon spans two nitrogen atoms, in **1**, N(1) is the bridgehead atom and spans the carbons C(18) and C(25) to form two six-membered rings, each adopting a partial boat conformation with a pronounced "stern" atom N(1); the out of plane fold angles for N(1) about the C(18)−C(25) vector are 121.4° relative to C(18)−N(2)−C(27)−C(26)−C(25) and 129.3° relative to C(18)−C(19)−C(24)−N(3)−C(25). The two ring C−N bonds have clearly lost their double bond character [N(3)−C(25) 1.452(9), N(2)−C(18) 1.478(8) Å]. Both N(2) and

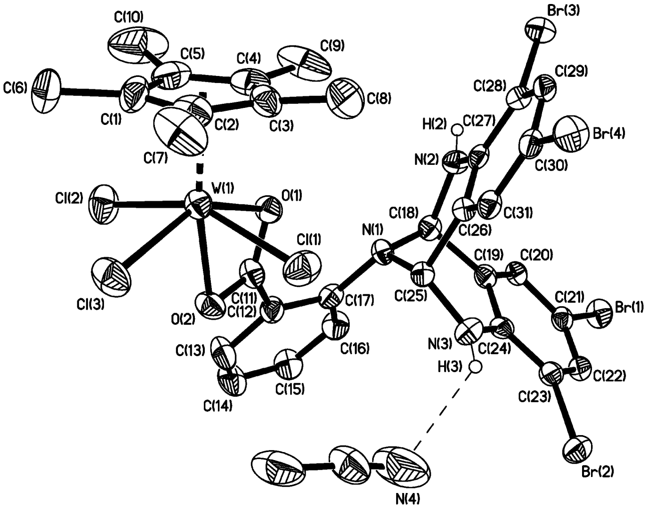


Figure 1. Molecular structure of **1** (30% probability ellipsoids). Selected bond lengths (Å) and angles (°): W(1)−O(1) 2.140(4), W(1)−Cl(1) 2.429(3), W(1)−Cl(2) 2.437(3), W(1)−Cl(3) 2.379(2); Cl(1)−W(1)−Cl(2) 151.09(8), W(1)−O(1)−C(11) 92.8(4), W(1)−O(2)−C(11) 91.1(4), O(1)−C(11)−O(2) 115.3(6), C(18)−N(1)−C(25) 107.6(5), C(17)−N(1)−C(18) 118.1(5), N(2)−C(18)−C(19) 111.7(5).

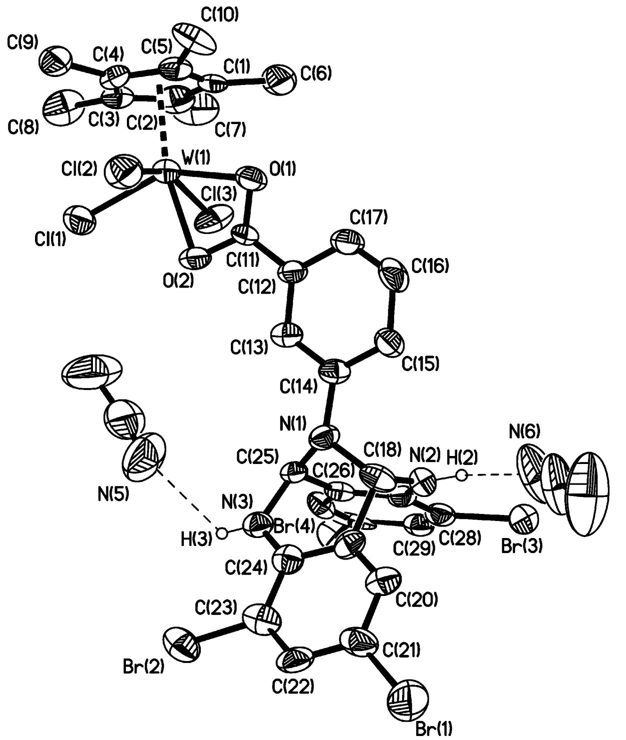


Figure 2. Molecular structure of **2** (30% probability ellipsoids). One acetonitrile molecule not H-bonded omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)−O(1) 2.130(9), W(1)−Cl(1) 2.352(4), W(1)−Cl(2) 2.400(4), W(1)−Cl(3) 2.374(4); Cl(1)−W(1)−Cl(2) 86.29(19), W(1)−O(1)−C(11) 94.0(8), W(1)−O(2)−C(11) 90.6(8), O(1)−C(11)−O(2) 115.7(13), C(18)−N(1)−C(25) 106.0(10), N(2)−C(18)−C(19) 113.4(11).

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[10] For other Cp*−W bond lengths, see for example: Redshaw, C.; Gibson, V. C.; Clegg, W.; Edwards, A. J.; Miles, B. *J. Chem. Soc., Dalton Trans.* **1997**, 3343.

Table 1. Crystallographic and Data Processing Parameters for 1·MeCN and 2·3MeCN[a]

complex	**1·MeCN**	**2·3MeCN**
formula	$C_{33}H_{30}Br_4Cl_3N_4O_2W$	$C_{37}H_{36}Br_4Cl_3N_6O_2W$
M	1124.45	1206.56
crystal size (mm^3)	0.18 × 0.15 × 0.06	0.10 × 0.08 × 0.03
temperature (K)	293(2)	293(2)
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	8.709(5)	15.137(3)
b (Å)	39.323(6)	15.119(3)
c (Å)	10.903(3)	19.620(4)
α (°)	90	90
β (°)	91.19(4)	107.10(3)
γ (°)	90	90
U (Å^3)	3733(2)	4291.7(15)
Z	4	4
D_c (Mg m^{-3})	2.001	1.867
F(000)	2148	2324
μ(Mo K$_\alpha$) (mm^{-1})	7.626	6.642
reflns collected	12539	12722
independent reflns	6470	6812
R_{int}	0.0702	0.0434
restraints/parameters	0/429	102/480
final R indices ($I > 2\sigma(I)$)	0.0413	0.0716
wR for all data	0.1067	0.2223
goodness of fit on F^2 (all data)	0.951	0.998
largest difference peak	±1.168	±2.193

[a] Data in common: graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit $= [\sum(F_o^2 - F_c^2)2/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

N(3) are protonated, with N(3) involved in H-bonding to a solvent (MeCN) molecule, while the geometry at the amine nitrogen N(1) is best described as pyramidal. For **2**, the out of plane fold angles for the "capping atom" N(1) about the C(18)−C(25) vector are 128.7° relative to C(18)−N(2)−C(27)−C(26)−C(25) and 120.4° relative to C(18)−C(19)−C(24)−N(3)−C(25). Both N(2) and N(3) are involved in H-bonding to solvent (MeCN) molecules.

The use of our new bulky ligands in both early and late transition metal systems, and the catalytic application thereof, is currently under investigation.

Experimental Section

General. All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox unless stated otherwise. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the School of Chemical Sciences at UEA. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz (^{1}H); chemical shifts are referenced to the residual protio impurity of the deuterated solvent. EPR spectra were recorded on a Varian E-12 (X-band) spectrometer. IR spectra (nujol mulls, KBr windows) were recorded on either Perkin-Elmer 577 or 457 grating spectrophotometers. The complex [W(η-C_5Me_5)Cl_4] was prepared as described in the literature.[7] All other chemicals were obtained commercially and used as received unless stated otherwise.

The ligands **II** and **III** were prepared in air by standard condensation procedures (see below) and used in situ. The free ligands are readily isolated as yellow solids in near-quantitative yields. Ligand **II** is sparingly soluble in acetone from which it can be recrystallized by slow evaporation. For **II**: $^1/_2$ acetone: Found C, 38.7; H, 2.1; N, 6.0%. $C_{22}H_{13}N_3O_2Br_4$ requires C, 38.3; H, 2.0; N, 6.4%. Mp: 175 °C. IR: 3461w, 3380w, 3361w, 3337w, 1706s, 1674s, 1605s, 1588s, 1549s, 1313s, 1296s, 1244s, 1201s, 1176s, 1158s, 1105s, 1053m, 1009w, 970w, 951m, 854m, 812m, 748s, 722s, 683w. ^{1}H NMR (acetone-d_6): δ 7.92 (dd, 1H, $^3J = 8.0$ Hz, $^4J = 1.8$ Hz, aryl*H*), 7.49 (m, 2H, aryl*H*), 7.44 (m, 2H, aryl*H*), 7.36 (tm, 1H, $^3J = 6.8$ Hz, aryl*H*), 7.20 (tm, 1H, $^3J = 7.8$ Hz, aryl*H*), 6.93 (dd, 1H, $^3J = 8.2$ Hz, $^4J = 1.1$ Hz, aryl*H*), 6.61 (d, slightly broad, 2H, $^3J_{NHCH} = 3.7$ Hz, N*H*), 5.80 (d, 2H, $^3J = 3.7$ Hz, CH_2), CO_2H not observed. MS (EI): 660 (M + H)$^+$.

For **III**: Found C, 38.7; H, 2.1; N, 6.0%. $C_{21}H_{13}N_3O_2Br_4$ requires C, 38.3; H, 2.0; N, 6.4%. Mp: 230 °C. IR: 3376m, 1798s, 1616s, 1602s, 1576s, 1531s, 1405s, 1286s, 1259m, 1220w, 1191m, 1150w, 1102w, 1074w, 986w, 943w, 890m, 870m, 820w, 807w, 788w, 754m, 734m, 703w, 678m, 668w, 576w, 548w. MS (ES): 660 (M + H)$^+$, 616 (MH$^+$ − CO_2). The poor solubility of ligand **III** precluded the attainment of meaningful NMR data.

Preparation of [W(η-C_5Me_5)Cl_3{*o*-(O_2C)C_6H_4(μ_3-N)L}] (1). 2-Amino-3,5-dibromobenzaldehyde (2.00 g, 7.17 mmol) and *o*-anthranilic acid (0.98 g, 7.18 mmol) were combined in ethanol (30 mL), and a few drops of formic acid were added. After refluxing for 12 h, the solution was concentrated to ca. 20 mL and left to stand at ambient temperature for 3−4 days. The yellow crystalline mass was isolated by filtration and was dried in vacuo. This solid (1.0 g, 1.52 mmol) was then transferred to a Schlenk flask containing [W(η-C_5Me_5)Cl_4] (0.70 g, 1.52 mmol) and toluene (30 mL), and the system was refluxed for 12 h. Following removal of volatiles, the residue was extracted into warm acetonitrile (30 mL) and left to stand at ambient temperature to form large brown/red prisms of **1**. Yield: 0.9 g, 52.7%. Mp: 210 °C. Found: C, 36.2; H, 2.5; N, 5.0%. $WBr_4Cl_3O_2N_3C_{31}H_{27}$·1$^1/_2$MeCN requires C, 35.7; H, 2.8; N, 5.5%. MS (FAB): 1084 (M$^+$). IR: 3321w, 2393w, 2358w, 2247w, 1697w, 1594m, 1577w, 1311m, 1295m, 1259s, 1207m, 1165s, 1096s, 1052s, 1019s, 967m, 889w, 864m, 812m, 719w, 658w. EPR (MeCN, 298 K): g 1.897.

Preparation of [W(η-C_5Me_5)Cl_3{*m*-(O_2C)C_6H_4(μ_3-N)L}] (2). Procedure is the same as for **1**, but using 2-amino-3,5-dibromobenzaldehyde (1.00 g, 3.57 mmol), *m*-anthranilic acid (0.49 g, 3.57 mmol), and [W(η-C_5Me_5)Cl_4] (0.50 g, 1.08 mmol), affording **2** as orange/brown crystals in 29.8% yield (0.36 g). Mp: 215 °C. Found: C, 36.1; H, 2.7; N, 6.0%. $WBr_4Cl_3O_2N_3C_{31}H_{27}$·2MeCN requires C, 36.1; H, 2.9; N, 6.0%. MS (FAB): 1084 (M$^+$), 1048.5 (M$^+$ − Cl). IR: 3364bw, 2247w, 1700w, 1680w, 1594m, 1586m, 1531w, 1310m, 1259s, 1222m, 1165s, 1130s, 1095bm, 1027s, 976m, 932w, 869m, 804m, 735m, 668w. EPR (MeCN, 298 K): g 2.008.

Crystallography. Measurements for 2-amino-3,5-dibromobenzaldehyde were made on a Bruker AXS SMART 1000 CCD area detector diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å).[11] Narrow-frame exposures (0.3° in ω) were employed. Cell parameters were refined from all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. Measurements for **1·MeCN** and **2·3MeCN** were made on a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating anode X-ray source (Mo Kα radiation) and graphite monochromator.[12] Using 4° oscillations, 46 exposures of 15 min each were made. No

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[11] SMART and SAINT software for CCD diffractometers; Bruker AXS Inc.: Madison, WI, 2001.

[12] Otwinowski, Z.; Minor, W. Processing of X-ray diffraction data collected in the oscillation mode. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York; Vol. 276; Macromolecular Crystallography, Part A, pp 307−326.

absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values for all unique data.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in a riding model with U_{iso} set to be 1.2 times (1.5 times for methyl-H) U_{eq} for the carrier atom. Further details are presented in Table 1.

Acknowledgment. We thank the University of East Anglia for support. We also thank the National Mass Spectrometry Service Centre, Swansea, U.K.

Supporting Information Available: Crystallographic data in CIF or other electronic format and X-ray structure of 2-amino-3,5-dibromobenzaldehyde. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Sheldrick, G. M. *SHELXL* user manual, version 6.10; Bruker AXS Inc.: Madison, WI, 2000.