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Note

Oxidative addition of asparagusic acid based disulfides to Pt^0

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ABSTRACT

$[Pt(PPh_3)_4]$ reacts smoothly and swiftly at room temperature with asparagusic acid and with selected amide and ester derivatives of this cyclic disulfide to afford Pt^{II} dithiolate chelates of the type *cis*-$[Pt\{CRR'(CH_2S)_2\}(PPh_3)_2]$. The crystal structures of three such products are reported.

1. Introduction

The peculiar reactivity of the disulfide moiety plays a key role in biology and biochemistry [1], medicinal chemistry [2], organic synthesis and catalysis [3], coordination chemistry [4] and materials science [5]. The most favourable R_2S_2 conformation exhibits a C–S–S–C torsion angle close to 90° [6]. Strong deviations from this ideal value, caused for example by steric hindrance or ring closure, drastically increase the reactivity of the S–S bond. In fact, small C–S–S–C torsion angles correlate with elongated S–S bonds, which is primarily due to sulfur lone pair repulsion [7]. Not surprisingly, disulfides with strained, elongated S–S bonds undergo faster thiol/disulfide exchange [8]. They exhibit a higher electron affinity and are therefore easier to reduce than unstrained analogues [9]. The oxidative addition of S–S bonds to low-valent precious metal centres is an important aspect of disulfide redox chemistry and a key issue in such diverse areas as, for example, transition metal catalysis, medicinal chemistry involving *cis*-platin, and self-assembled monolayers on gold, platinum and related metals. During the oxidative addition process, the S–S bond is reductively cleaved and two metal–thiolate bonds are formed. The oxidative addition of disulfides to low-valent platinum is of particular current interest [10].

2. Results and discussion

During the course of our investigations concerning the use of asparagusic acid based 1,2-dithiolane derivatives for the fabrication of self-assembled monolayers [11], we have turned our attention to the oxidative addition of their S–S bond to zero-valent precious metal, which constitutes the crucial step of their chemisorption on such substrates. We have studied this step in molecular coordination chemistry by reactions of the platinum(0) complex $[Pt(PPh_3)_4]$ with asparagusic acid (**1**), its synthetic precursor *cyclo*-$S_2C_3H_5$-4,4-$(COOEt)_2$ (**2**) and the azobenzene-functionalised compounds **3**–**5** (Scheme 1). The reaction of the cyclic four-membered disulfide bis(trifluoromethyl)-1,2-dithiethene with $[Pt(PPh_3)_3]$, which was described by Davison et al. in 1964, appears to be the first example of an oxidative addition of a disulfide to zero-valent platinum [12]. The first report concerning an analogous reaction of a 1,2-dithiolane derivative was published in 1994 by Weigand et al. [13].

The reactions were performed on an NMR tube scale and were conveniently monitored by ^{31}P NMR spectroscopy. They proved to proceed smoothly and swiftly at room temperature over the course of several hours in C_6D_6 solvent, affording the platinacycles **6**–**10** in essentially quantitative yield. No side reactions were observed even with of the iodo-substituted derivative **5**, where in principle also activation of the C–I bond seemed possible. The bond dissociation energy of the C–I bond of iodobenzene has a value of 67.2 kcal/mol [14], which is ca. 7 kcal/mol lower than the S–S bond dissociation energy of unstrained open-chain aliphatic disulfides [15], but ca. 20 kcal/mol higher than the S–S bond dissociation energy in the strained 1,2-dithiolane derivatives [16]. We note that only a single example of a related asparagusic acid based metallacyclic complex has been reported to date, viz. the nickel(II) chelate [Ni(dppe)(aspOH)] [aspOH = $CH(CH_2S)_2COOH$] [17], which contains the same chelate ligand as complex **6**. The NMR spectroscopic characterisation of complexes **6**–**10** turned out to be straightforward. The ^{31}P NMR signal was observed close to 20 ppm in each

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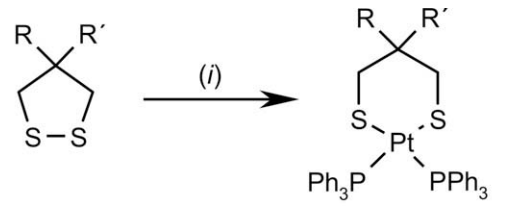

	R	R´
1, 6	H	COOH
2, 7	COOEt	COOEt
3, 8	H	C(O)NH-*p*-C_6H_4-N=N-Ph
4, 9	H	C(O)O-*p*-C_6H_4-N=N-Ph
5, 10	H	C(O)O-*p*-C_6H_4-N=N-*p*-C_6H_4-I

Scheme 1. Reagent and conditions: (i) [$Pt(PPh_3)_4$] (1 equiv.), benzene, room temp., 12 h.

case, exhibiting the expected ^{195}Pt satellites with $^1J_{Pt-P}$ values in the range between 2830 and 2878 Hz. The corresponding ^{195}Pt NMR signal appears as a doublet with a chemical shift value in the range between −4700 and −4612 ppm. These NMR spectroscopic values are in accord with data obtained for closely related six-membered platinacycles [13,18]. The crystal structures of **7** (Fig. 1), **8** (Fig. 2) and **9** (Fig. 3) were determined by single-crystal X-ray diffraction.

Bond parameters compare well with those of closely related compounds [19]. In each case the Pt^{II} atom resides in a slightly distorted square-planar coordination environment (sum of angles ca. 360°). The P–Pt–P and S–Pt–S bond angles are close to 98° and 91°, respectively. The Pt–P bond lengths have a value of ca. 2.29 Å and are indistinguishable within experimental error. The Pt–S bond lengths are only marginally longer (average value ca. 2.34 Å). The intramolecular S···S distances are ca. 3.35 Å, which is less than the sum of the estimated traditional van der Waals radii and very similar to the value of the intermolecular S···S contact observed for asparagusic acid (vide supra) and the closest intramolecular S···S

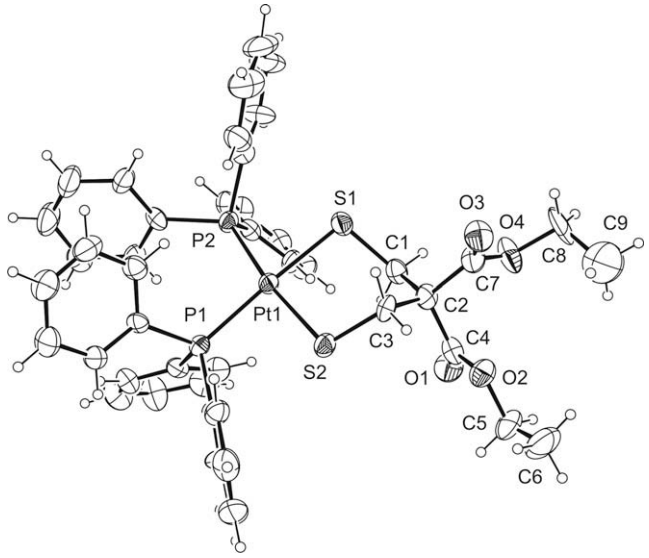

Fig. 1. Molecular structure of **7** in the crystal. Only one of the two individual molecules present in the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): C1–C2 1.523(13), C2–C3 1.538(16), C1–S1 1.851(12), C3–S2 1.780(11), P1–Pt1 2.287(3), P2–Pt1 2.294(3) S1–Pt1 2.348(3), S2–Pt1 2.341(3); P1–Pt1–P2 100.44(11), P1–Pt1–S2 87.54(11), P2–Pt1–S1 81.58(11), S1–Pt1–S2 90.29(11).

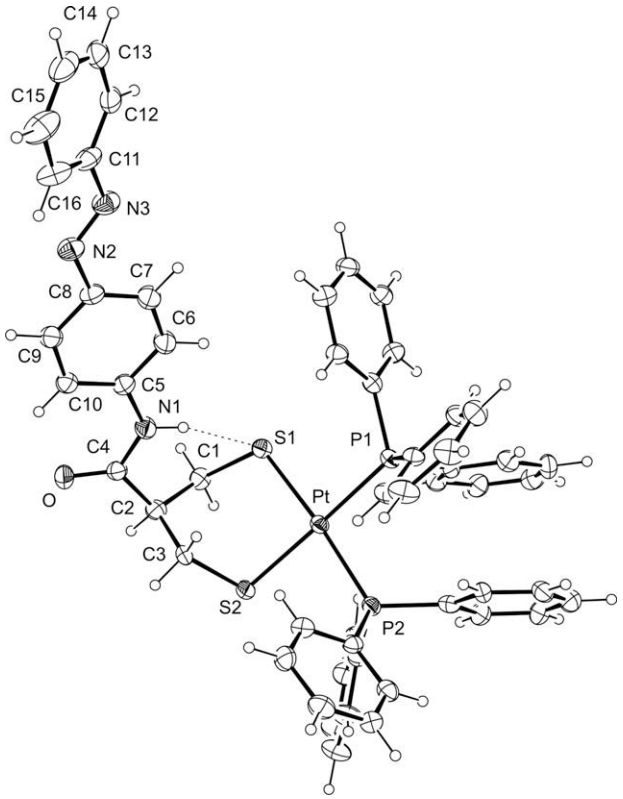

Fig. 2. Molecular structure of **8** in the crystal. The intramolecular hydrogen bond is indicated by a dotted line. Selected bond lengths (Å) and angles (°): C1–C2 1.541(10), C2–C3 1.545(9), C1–S1 1.823(7), C3–S2 1.805(6), P1–Pt 2.2904(16), P2–Pt 2.2909(16) S1–Pt 2.3355(17), S2–Pt 2.3585(16); P1–Pt–P2 97.65(6), P1–Pt–S1 88.01(6), P2–Pt–S2 83.38(6), S1–Pt–S2 91.08(6).

contact in *cyclo*-S_8 [20]. The intricate nature of chalcogen···chalcogen interactions was recently analysed by high-level quantum-chemical methods and is still a matter of current debate [21]. It has been pointed out that, owing to the non-spherical electron density distribution around divalent sulfur, the effective size of divalent sulfur in S···S contacts is a function of the orientation of the substituents**,** with the shortest contacts occurring when the substituents are coplanar. In this case a lower limit of 2.9 Å has been rationalised for intramolecular contacts [22]. The amide derivative **8** exhibits an intramolecular N–H···S interaction, whose parameters (H···S 2.41 Å, N···S 3.14 Å, N–H···S 141.8°) are indicative of a comparatively strong hydrogen bond according to commonly accepted criteria [23]. We note that intramolecular N–H···S hydrogen bonds are relevant for the conformation of peptides based on the conformationally restricted cystin analogue 4-aminoasparagusic acid [24].

3. Conclusion

The present study has shown that [$Pt(PPh_3)_4$] reacts smoothly and swiftly at room temperature with asparagusic acid and with selected amide and ester derivatives of this cyclic disulfide to afford Pt^{II} dithiolate chelates of the type *cis*-[$Pt\{CRR'(CH_2S)_2\}(PPh_3)_2$]. The ease of this oxidative addition reaction is related to the presence of a five-membered ring, whose S–S bond is elongated in comparison to standard acyclic disulfides.

4. Experimental

Synthetic work was routinely performed under an atmosphere of dry nitrogen by using standard Schlenk techniques or a conven-

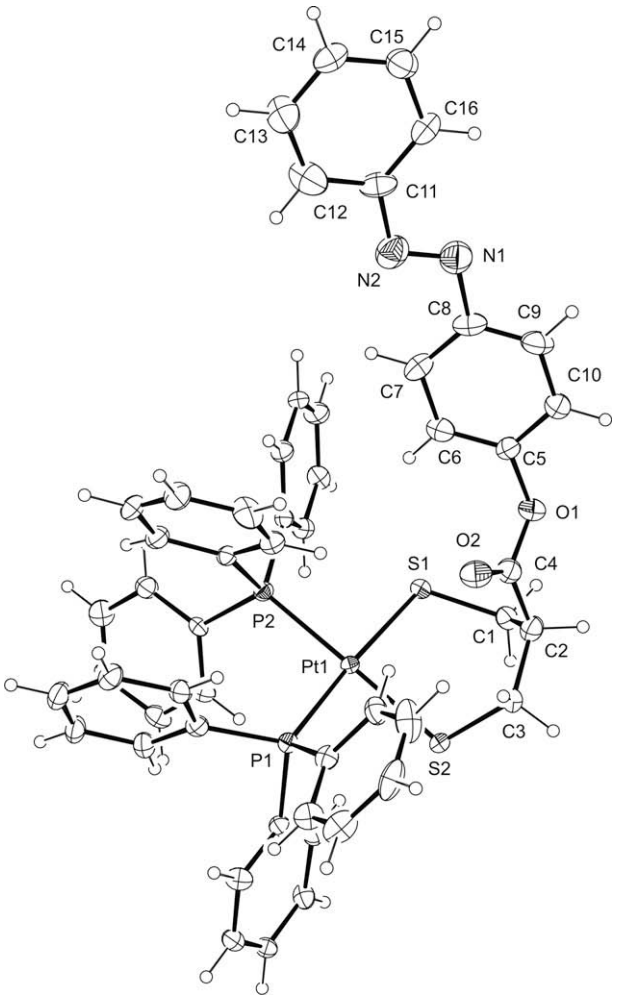

Fig. 3. Molecular structure of **9** in the crystal. Selected bond lengths (Å) and angles (°): C1–C2 1.532(12), C2–C3 1.551(10), C1–S1 1.812(9), C3–S2 1.815(9), P1–Pt1 2.297(2), P2–Pt1 2.287(2) S1–Pt1 2.326(2), S2–Pt1 2.348(2); P1–Pt1–P2 97.55(8), P1–Pt1–S2 84.47(8), P2–Pt1–S1 87.25(8), S1–Pt1–S2 91.14(8).

tional glovebox. Solvents were appropriately dried and purified. Asparagusic acid [25], diethyl-1,2-dithiolane-4,4-dicarboxylate (**2**) [26] and asparagusic acid derivatives **3**–**5** [11] were prepared by published procedures. All other chemicals were procured from standard commercial sources and used as received. NMR spectra were recorded with a Varian Unity INOVA 500 spectrometer operating at 500.13 MHz for ^{1}H. ^{195}Pt NMR spectra were recorded directly and referenced to external $K_2[PtCl_4]$ in D_2O (δ −1623 ppm) [27]. MALDI mass spectra were obtained with a BiFlex IV instrument (Bruker Daltonics, Bremen, Germany). ESI mass spectra were obtained with a Finnigan LCQ Deca instrument (ThermoQuest, San José, USA). High-resolution ESI mass spectra were obtained with micrOTOF instrument (Bruker Daltonics, Bremen, Germany) utilising an Apollo™ ion funnel ESI ion source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). Elemental analyses were carried out by the microanalytical laboratory of the University of Halle-Wittenberg, Germany.

4.1. General procedure for the preparation of the Pt complexes **6**–**10**

An NMR tube was charged with $[Pt(PPh_3)_4]$ (50 mg, 0.04 mmol). The complex was dissolved in a minimal amount of C_6D_6. A solution of one equivalent of the respective dithiolane derivative in C_6D_6 (ca. 2 mL) was added. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, which indicated an essentially quantitative yield after ca. 6 h in each case. After 12 h the reaction mixture was layered with *n*-hexane (2 mL). The crystals which formed during the course of several hours to days were isolated by filtration after 3 days and dried in vacuo.

4.1.1. Complex **6**

Asparagusic acid (**1**) (6 mg, 0.04 mmol) was used as starting material. The product was obtained as a light yellow solid, which precipitated almost immediately upon mixing of the two solutions. Layering with *n*-hexane was therefore not necessary in this case. Yield 21 mg (61%). ^{1}H NMR ($CDCl_3$): δ 3.34 (m, 1H, aliphatic CH), 3.54 (m, 2H, CH_2), 3.67 (m, 2H, CH_2), 7.08 (m, 12H, Ph), 7.23 (m, 6H, Ph), 7.37 (m, 12H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.8, 46.7, 127.5, 130.1, 130.2, 134.6, 177.5. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 17.3. ^{195}Pt NMR ($CDCl_3$): δ −4661 (d, $^{1}J_{Pt-P}$ 2878 Hz). HRMS/ESI(+): *m*/*z* 870.1366 $[M+H]^+$, calc. for $[C_{40}H_{37}O_2P_2PtS_2]^+$ 870.1352. Anal. Calc. for $C_{40}H_{36}O_2P_2PtS_2$ (869.1): C, 55.23; H, 4.14; S, 7.36. Found: C, 55.76; H, 4.40; S, 7.74%.

4.1.2. Complex **7**

Diethyl-1,2-dithiolane-4,4-dicarboxylate (**2**) (10 mg, 0.04 mmol) was used as starting material. The product was obtained as yellow needles. Yield 23 mg (59%). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, ^{3}J 7.3 Hz, Me), 3.43 (m, 4H, CH_2), 4.23 (q, ^{3}J 7.3 Hz, 4H, CH_2Me), 7.12 (m, 12H, Ph), 7.22 (m, 6H, Ph), 7.39 (m, 12 H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.3. ^{195}Pt NMR ($CDCl_3$): δ −4692 (d, $^{1}J_{Pt-P}$ 2836 Hz). HRMS/ESI(+): *m*/*z* 970.1876 $[M+H]^+$, calc. for $[C_{45}H_{45}O_2P_2PtS_2]^+$ 970.1877. Anal. Calc. for $C_{45}H_{44}O_2P_2PtS_2$ (969.1): C, 55.72; H, 4.54; S, 6.60. Found: C, 54.76; H, 4.85; S, 6.68%.

4.1.3. Complex **8**

The amide derivative **3** (13 mg, 0.04 mmol) was used as starting material. Owing to its low solubility, a suspension in C_6D_6 was used. The reaction mixture cleared up gradually over the course of several hours and eventually became a solution. The product was obtained as red needles. Yield 30 mg (57%). ^{1}H NMR ($CDCl_3$): δ 3.16 (m, 1H, aliphatic CH), 3.30 (m, 2H, CH_2), 3.52 (m, 2H, CH_2), 7.18 (m, 12H, aromatic CH), 7.30 (m, 6H, aromatic CH), 7.42 (m, 2H, aromatic CH), 7.46 (m, 12H, aromatic CH), 7.50 (m, 3H, aromatic CH), 7.85 (m, 4H, aromatic CH), 10.08 (m, 1H, NH). ^{31}P{^{1}H} NMR (C_6D_6): δ 23.3. ^{195}Pt NMR (C_6D_6): δ −4612 (d, $^{1}J_{Pt-P}$ 2838 Hz). HRMS/MALDI(+): *m*/*z* 1049.2207 $[M+H]^+$, calc. for $[C_{52}H_{46}N_3OP_2PtS_2]^+$ 1049.2200. Anal. Calc. for $C_{52}H_{45}N_3OP_2PtS_2$ (1048.2): C, 61.79; H, 4.86; N, 3.73; S, 5.68. Found: C, 61.71; H, 5.36; N, 3.79; S, 5.59%.

4.1.4. Complex **9**

The ester derivative **4** (13 mg, 0.04 mol) was used as starting material. The product was obtained as red needles. Yield 15 mg (36%). ^{1}H NMR ($CDCl_3$): δ 3.58 (m, 1H, aliphatic CH), 3.70 (m, 2H, CH_2), 3.88 (m, 2H, CH_2), 6.88–7.22 (m, 35H, aromatic CH), 7.87 (m, 2H, aromatic CH), 8.02 (m, 2H, aromatic CH). ^{31}P{^{1}H} NMR (C_6D_6): δ 25.5. ^{195}Pt NMR (C_6D_6): δ −4700 (d, $^{1}J_{Pt-P}$ 2830 Hz). HRMS/MALDI(+): *m*/*z* 1049.1919 $[M]^+$, calc. for $[C_{52}H_{44}N_2O_2P_2PtS_2]^+$ 1049.1858. Anal. Calc. for $C_{52}H_{44}N_2O_2P_2PtS_2$ (1049.2): C, 59.47; H, 4.19; N, 2.67. Found: C, 59.64; H, 4.26; N, 1.92%.

4.1.5. Complex **10**

The ester derivative **5** (17 mg, 0.04 mmol) was used as starting material. The product was obtained as an orange, microcrystalline solid. Yield 19 mg (41%). ^{1}H NMR ($CDCl_3$): δ 3.50 (m, 1H, aliphatic CH), 3.65 (m, 2H, CH_2), 3.80 (m, 2H, CH_2), 6.82–7.19 (m, 34H, aromatic CH), 7.84 (m, 4H, aromatic CH). ^{31}P{^{1}H} NMR (C_6D_6): δ 25.5. ^{195}Pt NMR (C_6D_6): δ −4699 (d, $^{1}J_{Pt-P}$ 2832 Hz). HRMS/ESI(+): *m*/*z*

1176.1004 $[M+H]^+$, calc. for $[C_{52}H_{44}N_2IO_2P_2PtS_2]^+$ 1176.1006. Anal. Calc. for $C_{52}H_{43}N_2IO_2P_2PtS_2$ (1175.1): C, 53.06; H, 3.66; N, 2.38; S, 5.45. Found: C, 53.19; H, 4.10; N, 2.49; S, 4.83%.

4.2. X-ray crystallography

For each data collection a single-crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo Kα radiation ($\lambda = 0.71073$ Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red [28]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL97) [29]. All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2-fold isotropic displacement parameters, except for H58 in **8**, which was refined freely with an isotopic displacement parameter. Graphical representations were made using ORTEP-3 win [30].

4.2.1. Crystal structure determination of 7·0.5C_6H_6

$C_{96}H_{94}O_8P_4Pt_2S_2$, $M = 2018.01$, monoclinic, $a = 21.7209(16)$, $b = 15.7228(7)$, $c = 29.671(2)$ Å, $\beta = 118.562(5)^\circ$, $U = 8899.9(10)$ Å^3, $T = 298(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, 59 875 reflections measured, 16 484 unique ($R_{int} = 0.1619$) which were used in all calculations. The final $wR(F^2)$ was 0.0837 (all data), the final $R_1(F)$ was 0.0540 [$I > 2\sigma(I)$]. Owing to the poor diffraction behaviour of the single-crystal, the quality of the crystal structure determination is affected by the low number of observed reflections (refl. obs./refl. msrd. 7063/16 064, resulting in an unusually high R_factor_all). It was further compromised by a disorder of the ethyl groups at O4 and O8, which is not resolvable.

4.2.2. Crystal structure determination of 8·C_6H_6

$C_{58}H_{51}N_3OP_2PtS_2$, $M = 1127.17$, monoclinic, $a = 19.2645(14)$, $b = 14.7195(9)$, $c = 19.8911(19)$ Å, $\beta = 116.214(7)^\circ$, $U = 5060.3(7)$ Å^3, $T = 153(2)$ K, space group $P2_1/n$ (no. 14), $Z = 4$, 19 815 reflections measured, 8517 unique ($R_{int} = 0.0656$) which were used in all calculations. The final $wR(F^2)$ was 0.0908 (all data), the final $R_1(F)$ was 0.0397 [$I > 2\sigma(I)$].

4.2.3. Crystal structure determination of 9·C_6H_6

$C_{58}H_{50}N_2O_2P_2PtS_2$, $M = 1128.15$, triclinic, $a = 11.3328(10)$, $b = 14.7162(13)$, $c = 15.1442(13)$ Å, $\alpha = 98.983(7)$, $\beta = 92.568(7)$, $\gamma = 99.832(7)^\circ$, $U = 2451.4(4)$ Å^3, $T = 153(2)$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, 15 978 reflections measured, 8122 unique ($R_{int} = 0.0749$) which were used in all calculations. The final $wR(F^2)$ was 0.0800 (all data), the final $R_1(F)$ was 0.0435 [$I > 2\sigma(I)$].

5. Supplementary material

CCDC 723722, 723723 and 723725 contain the supplementary crystallographic data for **9**·C_6H_6, **8**·C_6H_6 and **7**·0.5C_6H_6. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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