Synthesis and reactivity of novel cyclometallated complexes derived from [C,N,O] terdentate ligands. Crystal structure of [Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)C_6H_4]$}$(PPh_3)$]

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Treatment of the Schiff base ligands 2,3,4-$(MeO)_3C_6H_2C(H)=N[2-(OH)C_6H_4]$, **a**, and 2,3,4-$(MeO)_3C_6H_2$-$C(H)=N[2-(OH)$-4-$MeC_6H_4]$, **b**, with palladium(II) acetate in toluene gave the cyclometallated complexes [Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)C_6H_4]$}]$_n$, **1a**, and [Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)$-4-$MeC_6H_4]$}]$_n$, **1b**, respectively, as air stable solids, with the [C,N,O] ligand terdentate after deprotonation of the –OH group. Reaction of the cyclometallated complexes with triphenylphosphine gave the mononuclear species [Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)C_6H_4]$}$(PPh_3)$], **2a**, and [Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)$-4-$MeC_6H_4]$}-(PPh_3)], **2b**, with cleavage of the polynuclear structure. The molecular structure of **2a** has been determined by X-ray crystallography. Treatment of **1a** and **1b** with the diphosphines dppm, dppp, dppb, dpppe and dppf in a 1 : 2 molar ratio afforded the dinuclear cyclometallated complexes [(Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)C_6H_4]$})$_2${μ-$PPh_2(CH_2)_nPPh_2$}] (**3a**: $n = 1$; **4a**: $n = 3$; **5a**: $n = 4$; **6a**: $n = 5$), [(Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)C_6H_4]$})$_2$(μ-$PPh_2C_5H_4FeC_5H_4PPh_2$)], **7a**, [(Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)$-4-$MeC_6H_4]$})$_2${μ-$PPh_2(CH_2)_nPPh_2$}] (**3b**: $n = 3$; **4b**: $n = 4$) and [(Pd{2,3,4-$(MeO)_3C_6HC(H)=N[2-(O)$-4-$MeC_6H_4]$})$_2$(μ-$PPh_2C_5H_4FeC_5H_4PPh_2$)], **5b**, as air stable solids. Treatment of **1a** and **1b** with an excess of mono- or diphosphine did not produce cleavage of the Pd–$O_{chelating}$ bond.

Introduction

Cyclometallated compounds have been extensively surveyed[1–5] and they exhibit a good number of applications which extend from organic and organometallic compounds, to metal mesogenic species and catalytic materials,[6–14] as well as promoting unusual coordination environments.[15]

In the past, we have been interested in palladium(II) and platinum(II) cyclometallated complexes derived from [C,N,X] (X = N, O, S) terdentate ligands.[16–21] Those derived from semicarbazones reacted readily with palladium(II) salts to give cyclometallated complexes with the [C,N,O] ligand terdentate, yielding mononuclear species.[16,17] Also, reactions of *o*-hydroxyazobenzenes with palladium(II) salts to give mononuclear [C,N,O][22] or dinuclear [C,N][23] cyclometallated complexes have been reported. In the case of the terdentate [C,N,S] thiosemicarbazones, **I** (Fig. 1), the corresponding palladium(II) and platinum(II) derivatives show tetranuclear structures, with an eight membered Pd_4S_4 core,[24,25] as opposed to the mononuclear semicarbazone analogues. Similar tetranuclear complexes have also been reported by Navarro-Ranninger *et al.*;[26] and Kawamoto *et al.* have reported the synthesis of tetranuclear cluster complexes derived from benzothiazolines **II** (Fig. 1).[27,28] In order to attain neutrality, the ligand is usually deprotonated in the complex at the hydrazinic or the benzothiazoline nitrogen atom. Even in cases where there is no metal–carbon bond formation, the tetranuclear structure is reached only after deprotonation, as has been reported for a coordination compound derived from an [N,N,S] terdentate ligand, **III** (Fig. 1);[29] whereas deprotonation was not observed in the semicarbazone complexes.

Therefore, in view of these results, we reasoned that using the phenol derivatives 2,3,4-$(MeO)_3C_6H_2C(H)=N[2$-

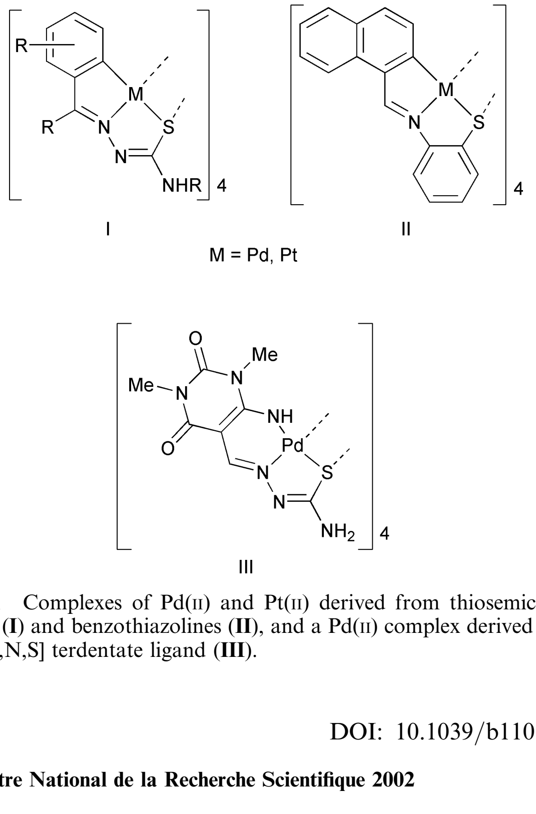

Fig. 1 Complexes of Pd(II) and Pt(II) derived from thiosemicarbazones (**I**) and benzothiazolines (**II**), and a Pd(II) complex derived from an [N,N,S] terdentate ligand (**III**).

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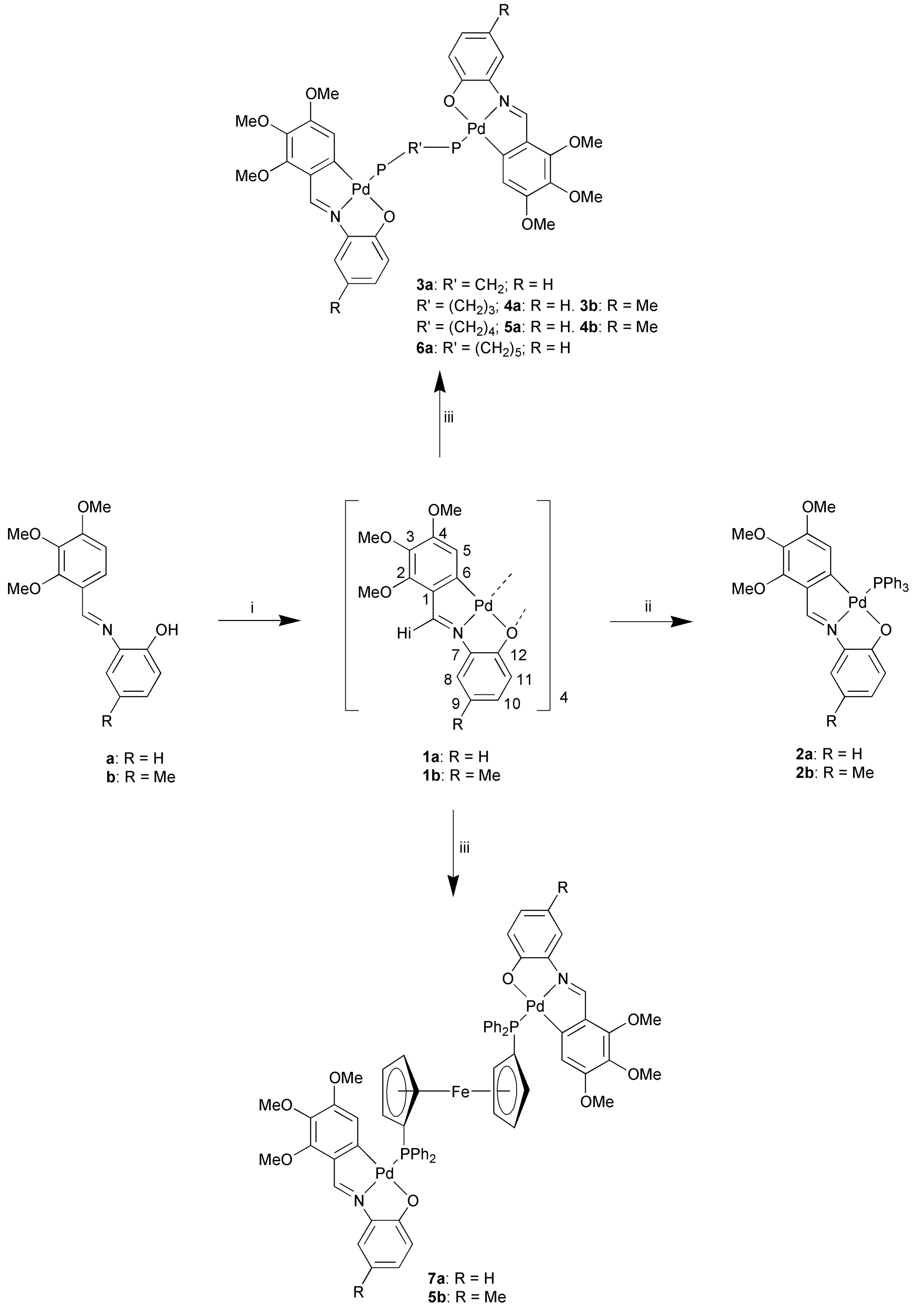
$(OH)C_6H_4]$ and $2,3,4\text{-}(MeO)_3C_6H_2C(H){=}N[2\text{-}(OH)\text{-}4\text{-}MeC_6H_4]$ we would be able to synthesize tetranuclear cyclometallated palladium(II) compounds with [C,N,O] terdentate ligands, hitherto unknown, with deprotonation of the –OH group. Consequently, we prepared the Schiff base ligands **a** and **b** by reaction of 2,3,4-trimethoxybenzaldehyde and 2-aminophenol or 2-amino-3-methylphenol, respectively, and treated them with palladium(II) acetate, upon which we obtained cyclometallated compounds with [C,N,O] terdentate ligands, **1a** and **1b**, and the results are reported herein. However, although the spectroscopic and FAB mass data point to a tetranuclear structure, we tentatively propose a polynuclear composition for **1a** and **1b** until additional data, such as X-ray diffraction analysis, is possible. Nevertheless, the reactivity of complexes **1a** and **1b** towards tertiary phosphines suggests that the P–$O_{chelating}$ bond is unexpectedly strong, in contrast to earlier results with semicarbazones. The X-ray diffraction structure of one of these complexes is also presented.

Results and discussion

For the convenience of the reader, the compounds and reactions are shown in Scheme 1. The compounds described in this



Scheme 1 (i) $Pd(AcO)_2$ (toluene); (ii) PPh_3 (acetone); (iii) diphosphine (acetone).

paper were characterized by elemental analysis (C, H, N) and by IR spectroscopy (data in the Experimental section) and by ^{1}H, ^{31}P-{^{1}H} (see Table 1) and, in part, ^{13}C-{^{1}H} NMR spectroscopy and FAB mass spectrometry (Experimental section).

Reaction of the Schiff base ligands **a** and **b** with palladium(II) acetate in toluene at 60 °C gave the complexes [Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)C_6H_4]$}]$_n$, **1a** and [{Pd[2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)\text{-}4\text{-}MeC_6H_3]$}]$_n$, **1b**, respectively, as air stable solids which were fully characterized. The IR spectra showed a shift of the ν(C=N) stretch toward lower wavenumbers as compared to the free ligand, due to N-coordination of the imine,[30,31] and the absence of the ν(O–H) band [present in the spectra of the free ligands at 3428 (**a**) and 3450 cm^{-1} (**b**)], in accordance with loss of the –OH proton. The absence of ν(COO) bands in the IR spectra precludes the formulation of compounds **1a** and **1b** as typical dinuclear species with bridging acetate ligands, as obtained previously when using palladium(II) acetate as the metal salt.[32]

In the ^{1}H NMR spectra, all the resonances were high-field shifted as compared to the uncoordinated ligand (see Table 1) and they were in agreement with metallation of the ligand with coordination of the palladium atom *via* the imine nitrogen atom. The most noticeable shifts concern the HC=N and H^5 resonances, *ca.* 1.5 and 1.1 ppm, respectively (Table 1), which are usually in the range 0.5–1.0 ppm; the low δ values in these cases are due to the structure of the complexes (a fragment is depicted in Fig. 2) which puts the HC=N and H^5 protons in the proximity of the shielding area of the phenyl rings of a neighbouring metallated ligand (a similar situation has been reported by us in the structurally related thiosemicarbazone derivatives, where a tetranuclear structure was confirmed by X-ray diffraction analysis[24,25]).

Deprotonation of the –OH group was confirmed by the absence of OH resonances in the ^{1}H NMR spectra. Likewise, no signals could be assigned to the acetate methyl groups, showing these ligands were not present in the coordination sphere of palladium.

The ^{13}C-{^{1}H} spectra of the complexes showed signals assigned to the C6, C=N, and C1 carbons, shifted to higher frequency, confirming that metallation had occurred.[24,25] However, the shift of the C=N carbon resonance was less than the expected, *ca.* 15 ppm. The resonance assigned to the C–O carbon was shifted to higher frequency by *ca.* 15 ppm upon Pd–O bond formation.

The FAB mass spectra of **1a** and **1b** showed clusters of peaks, centred at 1566 and 1623 amu, which correspond to [M]$^+$ and [MH]$^+$, respectively. Although the isotopic pattern is in good agreement with a tetramer, it could also be due to a tetranuclear fragment of a larger polynuclear species.

Reactivity of the complexes

Treatment of the cyclometallated complexes with triphenylphosphine gave the mononuclear species [Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)C_6H_4]$}$(PPh_3)$], **2a**, and [Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)\text{-}4\text{-}MeC_6H_3]$}$(PPh_3)$], **2b**, in which the polynuclear structure has been opened due to P–O$_{\text{bridging}}$ bond cleavage. Whereas in the synthesis of compound **2a** a 1 : 4 complex : phosphine molar ratio was used, the preparation of **2b** required excess triphenylphosphine and the final product was isolated by column chromatography. In both cases, the Pd–O$_{\text{chelating}}$ bond remained, as shown by the spectroscopic data (see Experimental and Table 1). The strength of the Pd–O$_{\text{chelating}}$ bond was tested by treating **1a** and **1b** with a large excess of phosphine, which only yielded complexes **2a** and **2b**, as well as unreacted phosphine. This behaviour contrasts with the facile breakage of the palladium–oxygen bond observed by us in semicarbazone compounds.[16, 17]

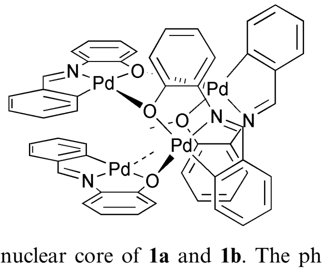


Fig. 2 The tetranuclear core of **1a** and **1b**. The phenyl substituents have been omitted for clarity.

The ^{1}H NMR spectra of **2a** and **2b** showed resonances due to the H^5 and HC=N protons coupled to the ^{31}P nucleus of the phosphine ligand (*ca.* 4 and 10 Hz, respectively), and in the ^{31}P-{^{1}H} spectra the phosphorus resonances were singlets at δ *ca.* 34; these findings are in agreement with a phosphorus *trans* to nitrogen arrangement.[33–36] The HC=N proton resonances at δ 8.17 (**2a**) and 8.12 (**2b**) showed smaller low-field shifts than in compounds **1a** and **1b**, in agreement with the opening of the polynuclear structure. However, the H^5 resonances at δ 5.51 (**2a**) and 5.50 (**2b**) showed greater shifts than in **1a** and **1b** due to shielding by the phosphine phenyl rings, as we have observed before in related complexes;[24,25] this shielding also affects the C4-MeO proton signals, which are also moved to lower frequency upon phosphine coordination to the metal. The FAB mass spectrum of **2a** showed the cluster of peaks at 653 amu characteristic of the [M]$^+$ fragment.

Reaction of the cyclometallated tetramers with the diphosphines dppm, dppp, dppb, dpppe and dppf in a 1 : 2 molar ratio gave the dinuclear cyclometallated complexes [(Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)C_6H_4]$})$_2${μ-$PPh_2(CH_2)_n$-$PPh_2$}] (**3a**: $n = 1$; **4a**: $n = 3$; **5a**: $n = 4$; **6a**: $n = 5$), [(Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)C_6H_4]$})$_2$(μ-$PPh_2C_5H_4FeC_5H_4PPh_2$)], **7a**, [(Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)\text{-}4\text{-}MeC_6H_4]$})$_2${μ-$PPh_2(CH_2)_nPPh_2$}] (**3b**: $n = 3$; **4b**: $n = 4$) and [(Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)\text{-}4\text{-}MeC_6H_4]$})$_2$(μ-$PPh_2C_5H_4FeC_5$-$H_4PPh_2$)], **5b**, as air stable solids, which were fully characterized (see Experimental section and Table 1). The IR and ^{1}H NMR spectra of the complexes showed similar features for the cyclometallated moiety as those of the parent mononuclear compounds (see Table 1). Only one singlet for the two equivalent nuclei was observed in each ^{31}P-{^{1}H} NMR spectrum, in accordance with the centrosymmetric nature of the dinuclear complexes. The FAB mass spectra of the dinuclear complexes showed sets of peaks corresponding to the [M]$^+$ or [MH]$^+$ ions.

The strength of the Pd–O$_{\text{chelating}}$ bond was confirmed by the reaction of **1a** and **1b** with a large excess of diphosphine. As we[16,17] and others[37] have shown before, in complexes with Pd–O bonds, the use of tertiary diphosphines in the appropriate molar ratio yields species with the phosphine chelated to the metal center through both phosphorus atoms, with cleavage of the Pd–O bond; the stability of the compound being enhanced by the chelate effect of the bidentate phosphine. However, in the present case, even the use of strong chelating phosphines such as dppm did not split the Pd–O bond, and the oxygen atom was coordinated to the metal in all cases.

Crystal structure of [Pd{2,3,4-$(MeO)_3C_6HC(H){=}N[2\text{-}(O)C_6H_4]$}$(PPh_3)$], 2a

Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The molecular structure is illustrated in Fig. 3.

The crystal structure comprises one molecule of **2a** per asymmetric unit. The palladium(II) atom is bonded to the aryl carbon C(1), the imine nitrogen N(1) and the oxygen O(1) of the Schiff base ligand and to a phosphorus atom of the triphenylphosphine ligand, P(1).

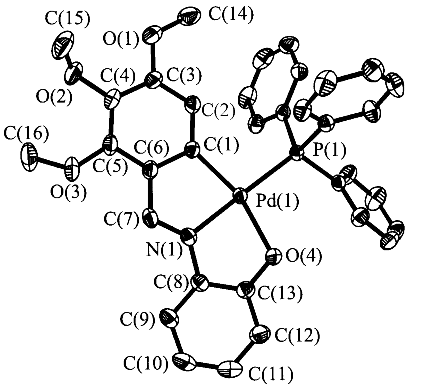


Fig. 3 Molecular structure of [Pd{2,3,4-$(MeO)_3C_6HC(H)$=N[2-$(O)C_6H_4$]}(PPh_3)], **2a**. Ellipsoids drawn at 40%. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.012(2), Pd(1)–C(1) 2.021(3), Pd(1)–O(4) 2.098(2), Pd(1)–P(1) 2.2624(8), C(1)–C(6) 1.426(4), C(6)–C(7) 1.446(5), N(1)–C(7) 1.278(4), N(1)–C(8) 1.414(4), C(8)–C(13) 1.415(4), O(4)–C(13) 1.321(4); N(1)–Pd(1)–C(1) 81.75(11), N(1)–Pd(1)–O(4) 80.90(9), C(1)–Pd(1)–O(4) 162.65(10), N(1)–Pd(1)–P(1) 177.35(7), C(1)–Pd(1)–P(1) 99.44(9), O(4)–Pd(1)–P(1) 97.91(6).

The Pd–N(1) bond distance of 2.012(2) Å is within the value expected based on the sum of the covalent radii[38] for palladium (1.31 Å) and sp^2 nitrogen (0.7 Å) and similar to other distances reported previously.[16,17,39] The Pd–C(1) [2.021(3) Å] and Pd(1)–P(1) [2.2624(8) Å] bond distances, somewhat shorter than the predicted values,[38] are within the range found earlier for related complexes.[16,17] The Pd–O(1) bond distance [2.098(2) Å] is longer than the predicted value of 1.97 Å, but analogous to Pd–O bond distances reported in the literatue,[40–42] and reflects the *trans* influence of the aryl carbon atom. The sum of the angles about the palladium atom is *ca.* 360° (359.99°), with the only noteworthy deviations being the somewhat reduced N(1)–Pd(1)–C(1) and N(1)–Pd(1)–O(1) bond angles of 81.75(11) and 80.90(9)°, respectively, as a consequence of chelation.

A characteristic of the coordinated ligand is the shortening of the O(4)–C(13) bond distance as compared to values reported previously for uncoordinated phenols[43] [1.321(4) *vs.* 1.411(5) Å in *N*-(2-hydroxyphenyl)-2-hydroxyaniline].

Experimental

General procedures

Solvents were purified by standard methods.[44] Chemicals were reagent grade. The phosphines PPh_3, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2P(CH_2)_5PPh_2$ (dpppe) and $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Model 1108 elemental analyzer. IR spectra were recorded from Nujol mulls or KBr discs on Perkin-Elmer 1330 and Mattson spectrophotometers. NMR spectra were obtained from $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, $^{13}C-\{^1H\}$) or 85% H_3PO_4 ($^{31}P-\{^1H\}$) and were recorded on a Bruker AC-200F spectrometer. All chemical shifts are reported downfield from the standards. The FAB mass spectra were recorded using a Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Syntheses

Preparation of 2,3,4-$(MeO)_3C_6H_2C(H)$=N[2-$(OH)C_6H_4$] (a). 2,3,4-$(MeO)_3C_6H_2C(=O)H$ (0.683 g, 3.48 mmol) was added to a solution of 2-aminophenol (0.380 g, 3.48 mmol) in 50 cm^3 of dry chloroform. The solution was heated under reflux in a Dean–Stark apparatus for 4 h. After cooling to room temperature, the chloroform was removed to give a brown solid. Yield 89%. IR (cm^{-1}): ν(O–H) 3428s; ν(C=N) 1612sh, m.$^{13}C-\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ 152.8 (C=N); 122.6 (C1); 156.8, 154.7, 141.8 (C2, C3, C4); 107.9 (C5); 122.5 (C6); 136.4 (C7); 116.0 (C8); 120.0 (C9); 128.3 (C10); 114.7 (C11); 152.1 (C12); 62.1, 60.9, 56.1 (OCH_3).

2,3,4-$(MeO)_3C_6H_2C(H)$=N[2-(OH)-4-MeC_6H_3] (b). Schiff base **b** was prepared similarly and obtained as a brown solid. Yield 97%. IR (cm^{-1}): ν(O–H), 3450s cm^{-1}; ν(C=N), 1612sh, m cm^{-1}. $^{13}C-\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ 152.5 (C=N); 122.7 (C1); 156.7, 154.7, 141.8 (C2, C3, C4); 107.9 (C5);122.5 (C6); 136.1 (C7); 116.5 (C8); 129.2 (C9); 128.8 (C10); 114.4 (C11); 149.9 (C12); 62.1, 60.9, 56.1 (OCH_3).

Preparation of [Pd{2,3,4-$(MeO)_3C_6HC(H)$=N[2-(O)-C_6H_4)]}]$_n$ (1a). A pressure tube containing 2,3,4-$(MeO)_3C_6H_2C(H)=NC_6H_4OH$ (0.652 g, 2.26 mmol), palladium acetate (0.510 g, 22.7 mmol) and 20 cm^3 of dry toluene was sealed under argon. The resulting mixture was heated at 60 °C for 24 h. After cooling to room temperature, the solution was filtered through Celite to remove the small amount of black palladium formed. The solvent was removed under vacuum to give a red oil, which was chromatographed on a column packed with silica gel. Elution with dichloromethane–ethanol (0.4%) afforded a red oil after solvent removal, which was recrystallized from dichloromethane–hexane to give the desired product as a red solid. Yield 83%. Anal. found: C, 48.5; H, 3.8; N, 3.4; $C_{64}H_{60}N_4O_{16}Pd_4$ (based on a tetranuclear fragment) requires C, 49.1; H, 3.8; N, 3.6%. IR (cm^{-1}): ν(C=N), 1589sh, m. $^{13}C-\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ 155.0 (C=N);137.1, 136.8, 134.9 (C1, C3, C7); 155.3, 152.6, 151.0 (C2, C4, C6); 111.2 (C5); 116.9 (C8); 123.5 (C9); 128.9 (C10); 114.4 (C11); 167.3 (C12); 61.7, 60.6, 55.8 (OCH_3). FAB-MS: *m/z* 1566 $[M]^+$; 391 $[M/4]^+$.

[Pd{2,3,4-$(MeO)_3C_6HC(H)$=N[2-(O)-4-MeC_6H_3)]}]$_n$ (1b). Compound **1b** was prepared similarly and obtained as a red solid. Yield 80%. Anal. found: C, 50.4; H, 4.2; N, 3.3; $C_{68}H_{68}N_4O_{16}Pd_4$ (based on a tetranuclear fragment) requires C, 50.3; H, 4.2; N, 3.4%. IR (cm^{-1}): ν(C=N), 1572s. $^{13}C-\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ 154.3 (C=N); 137.2, 136.4, 135.0 (C1, C3, C7); 155.1, 152.6, 151.9 (C2, C4, C6); 111.1 (C5); 123.1 (C8); 126.0 (C9); 129.8 (C10); 114.6 (C11); 165.3 (C12); 61.6, 60.8, 55.5 (OCH_3). FAB-MS: *m/z* 1623 $[MH]^+$; 406 $[(M/4)H]^+$.

Preparation of [Pd{2,3,4-$(MeO)_3C_6HC(H)$=N[2-$(O)C_6H_4$]}-(PPh_3)] (2a). PPh_3 (16 mg, 0.061 mmol) was added to a suspension of **1a** (24 mg, 0.015 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the solvent removed to give a violet solid which was recrystallized from acetone–hexane. Yield 67%. Anal. found: C, 62.1; H, 4.5; N, 2.0; $C_{34}H_{30}NO_4PPd$ requires C, 62.4; H, 4.6; N, 2.1%. IR (cm^{-1}): ν(C=N), 1571s. FAB-MS: *m/z* 653 $[M]^+$.

Compounds **3a**–**7a** were obtained following a similar procedure, but using a 1 : 2 complex **1a** : diphosphine molar ratio, and obtained as red (**3a**, **5a**) or violet (**4a**, **6a**, **7a**) solids.

[{Pd{2,3,4-$(MeO)_3C_6HC(H)$=N[2-$(O)C_6H_4$]}}$_2$(μ-PPh_2CH_2-PPh_2)] (3a). Yield 94%. Anal. found: C, 58.1; H, 4.4; N, 2.3; $C_{57}H_{52}N_2O_8P_2Pd_2$ requires C, 58.6; H, 4.5; N, 2.4%. IR (cm^{-1}): ν(C=N), 1573s. $^{13}C-\{^1H\}$ NMR (50.28 MHz, $CDCl_3$): δ 153.3 (d, C=N, J_{CP} = 4.2); 139.4, 137.7, 136.5 (d, C1, C3, C7, J_{CP} = 2.1); 154.3 (d, J_{CP} = 3.5), 153.7 (d, J_{CP} = 7.8), 152.3 (C2, C4, C6); 117.3 (d, C5, J_{CP} = 8.5); 115.6 (C8); 120.9 (C9); 130.6 (C10); 113.6 (C11); 172.3 (d, C12, J_{CP} = 3.5); 3.5); 61.7, 60.6, 55.2 (OCH_3); P-phenyl: 135.4 [d, C_o,

Table 1 ^{31}P[a] and ^{1}H[b]-NMR data for all the compounds

	^{31}P	Aromatic	Others
a		7.90 [d, 1H, H^{6}, 8.8[c]]	8.98 [s, 1H, H[d]]
		6.78 [d, 1H, H^{5}, 8.8[c]]	8.76 [s, 1H, –OH[e]]
		7.30 [dd, 1H, H^{8}, 7.8[c], 1.5[f]]	4.00 [s, 3H, OMe]
		6.91 [dt, 1H, H^{9}, 7.8[c], 1.5[f]]	3.93 [s, 3H, OMe]
		7.18 [dt, 1H, H^{10}, 7.8[c], 1.5[f]]	3.91 [s, 3H, OMe]
		7.01 [dd, 1H, H^{11}, 7.8[c], 1.5[f]]	
1a		5.67 [s, 1H, H^{5}]	7.57 [s, 1H, H[d]]
		6.62 [dd, 1H, H^{8}, 7.6[c], 1.5[f]]	4.02 [s, 3H, OMe]
		6.37 [dt, 1H, H^{9}, 7.5[c], 1.5[f]]	3.82 [s, 3H, OMe]
		6.91 [dt, 1H, H^{10}, 7.5[c], 1.5[f]]	3.51 [s, 3H, OMe]
		7.44 [d, 1H, H^{11}, 7.6[c], 1.5[f]]	
2a	34.3	5.51 [d, 1H, H^{5}, 3.9[g]]	8.17 [d, 1H, H[d], 10.2[g]]
		7.11 [dd, 1H, H^{8}, 7.6[c], 1.5[f]]	3.96 [s, 3H, OMe]
		6.37 [t, 1H, H^{9}, 7.3[c]]	3.73 [s, 3H, OMe]
		6.91 [td, 1H, H^{10}, 7.8[c], 1.5[d]]	2.92 [s, 3H, OMe]
		6.52 [dd 1H, H^{11}, 7.6[c], 0.9[f]]	
3a[d]	26.1	5.39 [d, 1H, H^{5}, 3.9[g]]	8.11 [d, 1H, H[d], 10.2[g]]
		7.10 [dd, 1H, H^{8}, 7.6[c], 1.5[d]]	3.93 [s, 3H, OMe]
		6.41 [t, 1H, H^{9}, 7.6[c]]	3.69 [s, 3H, OMe]
		6.98 [td, 1H, H^{10}, 7.8[c], 1.5[f]]	2.90 [s, 3H, OMe[h]]
		6.52 [dd 1H, H^{11}, 7.6[c], 1.5[f]]	
4a	27.7	5.45 [d, 1H, H^{5}, 3.9[g]]	8.12 [d, 1H, H[d], 10.7[g]]
		7.13 [dd, 1H, H^{8}, 7.6[c], 1.5[f]]	3.93 [s, 3H, OMe]
		6.41 [t, 1H, H^{9}, 7.6[c]]	3.64 [s, 3H, OMe]
		6.95 [td, 1H, H^{10}, 7.8[c], 1.5[f]]	2.96 [s, 3H, OMe[h]]
		6.55 [dd 1H, H^{11}, 7.6[c], 0.9[f]]	
5a	29.9	5.51 [d, 1H, H^{5}, 3.9[g]]	8.11 [d, 1H, H[d], 10.7[g]]
		7.09 [d, 1H, H^{8}, 7.6[c]]	3.92 [s, 3H, OMe]
		6.86 [t, 1H, H^{10}, 7.8[c]]	3.70 [s, 3H, OMe]
		6.34 [m, 2H, H^{9}, H^{11}]	2.98 [s, 3H, OMe[h]]
6a	29.8	5.49 [d, 1H, H^{5}, 3.9[g]]	8.12 [d, 1H, H[d], 10.3[g]]
		7.10 [dd, 1H, H^{8}, 7.8[c], 1.5[f]]	3.93 [s, 3H, OMe]
		6.36 [t, 1H, H^{9}, 7.6[c]]	3.69 [s, 3H, OMe]
		6.88 [td, 1H, H^{10}, 7.6[c], 1.5[f]]	2.98 [s, 3H, OMe[h]]
		6.44 [dd 1H, H^{11}, 7.6[c], 1.2[f]]	
7a[i]	24.5	5.44 [d, 1H, H^{5}, 4.4[g]]	8.16 [d, 1H, H[d], 10.8[g]]
		7.14 [dd, 1H, H^{8}, 7.6[c], 1.5[f]]	3.96 [s, 3H, OMe]
		6.36 [t, 1H, H^{9}, 7.6[c]]	3.73 [s, 3H, OMe]
		6.95 [td, 1H, H^{10}, 7.6[c], 1.5[f]]	2.88 [s, 3H, OMe[h]]
		6.57 [dd 1H, H^{11}, 7.6[c]]	
b		7.90 [d, 1H, H^{5}, 8.8[c]]	8.95 [s, 1H, H[f]]
		6.79 [d, 1H, H^{6}, 8.8[c]]	8.65 [s, 1H, –OH[e]]
		7.10 [s, 1H, H^{8}]	4.02 [s, 3H, OMe]
		7.00 [dd, 1H, H^{10}, 8.3[c], 1.5[f]]	3.94 [s, 3H, OMe]
		6.89 [d, 1H, H^{11}, 8.3[c]]	3.92 [s, 3H, OMe]
			2.33 [s, 3H, Me]
1b		5.67 [s, 1H, H^{5}]	7.49 [s, 1H, H[d]]
		6.41 [d, 1H, H^{8}, 1.5[f]]	4.00 [s, 3H, OMe]
		6.72 [dd, 1H, H^{10}, 8.3[c], 1.5[f]]	3.83 [s, 3H, OMe]
		7.34 [d, 1H, H^{11}, 8.3[c]]	3.48 [s, 3H, OMe]
			2.11 [s, 3H, Me]
2b	34.1	5.50 [d, 1H, H^{5}, 3.9[g]]	8.12 [d, 1H, H[d], 10.7[g]]
		6.89 [s, 1H, H^{8}]	3.96 [s, 3H, OMe]
		6.72 [dd, 1H, H^{10}, 8.3[c], 2.2[f]]	3.72 [s, 3H, OMe]
		6.42 [d, 1H, H^{11}, 8.3[c]]	2.92 [s, 3H, OMe[h]]
			2.17 [s, 3H, Me]
3b	27.6	5.94 [s, 1H, H^{5}, 4[g]]	8.07 [d, 1H, H[d], 10.7[g]]
		6.91 [s, 1H, H^{8},]	3.93 [s, 3H, OMe]
		6.78 [d, 1H, H^{10}, 7.8[c]]	3.64 [s, 3H, OMe]
		6.46 [d, 1H, H^{11}, 7.8[c]]	2.96 [s, 3H, OMe[h]]
			2.21 [s, 3H, Me]
4b	29.8	5.50 [s, 1H, H^{5}, 4[g]]	8.07 [d, 1H, H[d], 10.7[g]]
		6.88 [s, 1H, H^{8},]	3.93 [s, 3H, OMe]
		6.69 [dd, 1H, H^{10}, 8.3[c], 1.5[f]]	3.70 [s, 3H, OMe]
		6.27 [d, 1H, H^{11}, 8.3[c]]	2.98 [s, 3H, OMe[h]]
			2.18 [s, 3H, Me]

Table 1 (continued)

^{31}P		Aromatic	Others
5b^{i}	24.4	5.44 [s, 1H, H^{5}, 4.0^{g}]	8.11 [d, 1H, H^{d}, 11.2^{g}]
		6.93 [s, 1H, H^{8}]	3.96 [s, 3H, OMe]
		6.77 [dd, 1H, H^{10}, 8.3^{c}, 2.0^{f}]	3.73 [s, 3H, OMe]
		6.48 [d, 1H, H^{11}, 8.3^{c}]	2.88 [s, 3H, OMe^{h}]
			2.19 [s, 3H, Me]

[a] In $CDCl_3$, unless otherwise stated. Measured at 80.9 MHz (*ca.* ±20 °C); chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. [b] In $CDCl_3$. Measured at 200 MHz (*ca.* ±20 °C); chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$. Coupling constants in Hz. s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt, doublet of triplets; m, multiplet; br, broad. [c] $^{3}J_{HH}$/Hz. [d] PCH_2P δ_H 4.1. [e] Resonance taken from a spectrum recorded in DMSO-d^{6}. [f] $^{4}J_{HH}$/Hz. [g] J_{PH}/Hz. [h] C4-(OMe). [i] $CH_{Ferrocene}$: δ_H 5.26 [br, 2H], 4.25 [br, 2H] for compound **7a**; δ_H 5.43 [br, 2H], 4.24 [br, 2H] for compound **5b**.

J_{CP} = 14.2]; 128.2 [d, C_m, J_{CP} = 10.6]; 131.0 (C_p); 129.4 [d, C_i, J_{CP} = 46.1 Hz]. FAB-MS: *m/z* 1168 [MH]$^+$; 882 [M − L]$^+$, 776 [M − L − Pd]$^+$.

[(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]})$_2$(μ-PPh$_2$(CH$_2$)$_3$-PPh$_2$)] (4a). Yield 92%. Anal. found: C, 59.5; H, 4.6; N, 2.1; $C_{59}H_{56}N_2O_8P_2Pd_2$ requires C, 59.3; H, 4.7; N, 2.3%. IR (cm^{-1}): ν(C=N), 1572s. FAB-MS: *m/z* 1197 [MH]$^+$; 776 [M − L − Pd]$^+$; 391 [M − L − Pd − dppp]$^+$.

[(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]})$_2$(μ-PPh$_2$(CH$_2$)$_4$-PPh$_2$)] (5a). Yield 68%. Anal. found: C, 59.6; H, 4.8; N, 2.2; $C_{60}H_{58}N_2O_8P_2Pd_2$ requires C, 59.6; H, 4.8; N, 2.3%. IR (cm^{-1}): ν(C=N), 1573s. ^{13}C-{^{1}H} NMR (50.28 MHz, $CDCl_3$): δ 153.4 (d, C=N, J_{CP} = 4.2); 139.7, 137.8, 135.9 (d, C1, C3, C7, J_{CP} = 2.1); 154.4 (d, J_{CP} = 3.5), 153.2 (d, J_{CP} = 8.5), 152.5 (C2, C4, C6); 117.3 (d, C5, J_{CP} = 9.2); 115.5 (C8); 121.1 (C9); 130.6 (C10); 113.5 (C11); 173.3 (d, C12, J_{CP} = 3.5); 3.5); 61.7, 60.6, 55.2 (OCH_3); P-phenyl: 134.0 (d, C_o, J_{CP} = 12.1); 128.6 (d, C_m, J_{CP} = 10.6); 130.9 (d, C_p, J_{CP} = 2.1); 130.2 (d, C_i, J_{CP} = 44.7); P(CH$_2$)$_4$P: 27.1 (d, P*C*H$_2$CH$_2$–, J_{CP} = 28.4); 26.0 (d, PCH$_2$*C*H$_2$–, J_{CP} = 14.9 Hz). FAB-MS: *m/z* 1210 [M]$^+$.

[(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]})$_2$(μ-PPh$_2$(CH$_2$)$_5$-PPh$_2$)] (6a). Yield 57%. Anal. found: C, 60.2; H, 4.8; N, 2.1; $C_{61}H_{60}N_2O_8P_2Pd_2$ requires C, 59.9; H, 4.9; N, 2.3%. IR (cm^{-1}): ν(C=N), 1571s. FAB-MS: *m/z* 1225 [MH]$^+$; 391 [M − L − Pd − dppp]$^+$.

[(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]})$_2$(μ-PPh$_2$C$_5$H$_4$-FeC$_5$H$_4$PPh$_2$)] (7a). Yield 34%. Anal. found: C, 59.6; H, 4.3; N, 2.1; $C_{66}H_{58}N_2O_8P_2FePd_2$ requires C, 59.2; H, 4.4; N, 2.1%. IR (cm^{-1}): ν(C=N), 1573s. FAB-MS: *m/z* 1332 [M]$^+$; 944 [M − L − Pd]$^+$; 696 [M − L − Pd − P(C$_6$H$_5$)$_2$ − C$_5$H$_4$)]$^+$.

Preparation of [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-4-MeC$_6$H$_3$]}(PPh$_3$)] (2b). A large excess of PPh$_3$ (25 mg, 0.095 mmol) was added to a suspension of **1b** (19 mg, 0.012 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 24 h. The solvent was removed under vacuum to give a violet oil, which was chromatographed on a column packed with silica gel. Elution with dichloromethane afforded a violet oil after solvent removal, which was recrystallized from dichloromethane–hexane to give the desired product as a violet solid. Yield 80%. Anal. found: C, 62.7; H, 4.8; N, 2.0; $C_{35}H_{32}NO_4PPd$ requires C, 62.9; H, 4.8; N, 2.1%. IR (cm^{-1}): ν(C=N), 1572s.

[(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-4-MeC$_6$H$_3$]})$_2$(μ-PPh$_2$-(CH$_2$)$_3$PPh$_2$)] (3b). Compound **3b** was obtained following a similar procedure as violet solid, but using a 1 : 2 complex **1b** : diphosphine molar ratio. Yield 36%. Anal. found: C, 60.0; H, 4.7; N, 2.1; $C_{61}H_{60}N_2O_8P_2Pd_2$ requires C, 59.9; H, 4.9; N, 2.3%. IR (cm^{-1}): ν(C=N), 1572s. FAB-MS: *m/z* 1225 [M]$^+$; 813 [MH − L − Pd]$^+$; 638 [M − L − Pd − P(C$_6$H$_5$)$_2$]$^+$; 406 [MH − L − Pd − dppp]$^+$.

Preparation of [(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-4-MeC$_6$H$_3$]})$_2$(μ-PPh$_2$(CH$_2$)$_4$PPh$_2$)] (4b). PPh$_2$(CH$_2$)$_4$PPh$_2$ (9 mg, 0.021 mmol) was added to a suspension of **1b** (17.2 mg, 0.042 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 12 h and the solvent removed to give a violet solid which was recrystallized from dichloromethane–hexane. Yield 34%. Anal. found: C, 59.8; H, 4.9; N, 2.2; $C_{62}H_{62}N_2O_8P_2Pd_2$ requires C, 60.1; H, 5.0; N, 2.3%. IR (cm^{-1}): ν(C=N), 1572s. FAB-MS: *m/z* 1238 [M]$^+$; 832 [MH − L − Pd]$^+$; 647 [M − L − Pd − P(C$_6$H$_5$)$_2$]$^+$.

[(Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-4-MeC$_6$H$_3$]})$_2$(μ-PPh$_2$-C$_5$H$_4$FeC$_5$H$_4$PPh$_2$)] (5b). Compound **5b** was prepared similarly and obtained as a violet solid. Yield 14%. Anal. found: C, 59.0; H, 4.4; N, 2.1; $C_{68}H_{62}N_2O_8P_2FePd_2$ requires C, 59.3; H, 4.4; N, 2.1%. IR (cm^{-1}): ν(C=N), 1571s. FAB-MS: *m/z* 1366 [M]$^+$; 944 [MH − L − Pd]$^+$; 710 [M − L − Pd − P(C$_6$H$_5$)$_2$ − C$_5$H$_4$]$^+$; 654 [M − L − Pd − P(C$_6$H$_5$)$_2$ − C$_5$H$_4$ − Fe]$^+$.

Single-crystal X-ray diffraction analysis

Three-dimensional, room temperature X-ray data were collected in the range $3.0 < 2\theta < 56.6°$ on a Siemens SMART CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in ω. Of the 20437 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption using a semi-empirical correction based on symmetry-equivalent and repeated reflections (max, min transmissions 0.87, 0.71), 4859 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$ The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0401$ ($wR_2 = 0.0922$ for all 7230 unique data), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.688 and 0.439 e Å^{-3}. The structure solution and refinement were carried out using the program package SHELX-97.[45]

Crystal data: $C_{34}H_{30}NO_4Pd$, $M = 653.96$, monoclinic, $a = 27.408(1)$, $b = 12.013(1)$ $c = 18.325(1)$ Å, $\beta = 103.171(8)°$, $U = 5875.0(5)$ Å^3, $Z = 8$, $D_c = 1.479$ g cm^{-3}, space group $C2/c$ (no. 15), μ(Mo-Kα) = 0.726 mm^{-1}, $T = 273$ K.

CCDC reference number 177246. See http://www.rsc.org/suppdata/nj/b1/b110197h/ for crystallographic data in CIF or other electronic format.

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