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Flexible κ^4-PNN`O-tetradentate ligands: synthesis, complexation and structural studies

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Experimental Section

Materials. Reactions were carried out under aerobic conditions. All chemicals and solvents were obtained from commercial suppliers and used without further purification. Compounds **1b**, **1c**, **2b** and **2c** were prepared according to a literature procedure used for **1a** and **2a**.[1]

Instrumentation. FT–IR spectra were recorded as pressed KBr pellets over the range 4000–400 cm^{-1} using a Perkin-Elmer system 2000 FT spectrometer. ^1H NMR NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) reported relative to external TMS. All NMR spectra were recorded in $(CD_3)_2SO$ solutions at *ca.* 298 K. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Compounds **1b, 1c** and **2c** were analysed by low-resolution EI and CI (positive ion mode only) using CH_2Cl_2/CH_3OH as the solvent.

Preparation of *1,4*-(OH)C_6H_4{NHC(O)CH_2NHCO_2Bz} (1c). To a THF (120 ml) solution of carbobenzyloxyglycine (5.027 g, 0.024 mol) was added, in quick succession, 4-hydroxyaniline (2.618 g, 0.024 mol) and dicyclohexylcarbodiimide (5.295 g, 0.026 mol). The solution was stirred for *ca.* 4 h during which time a white solid formed. The solid was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The THF solvent was replaced by ethyl acetate (100 ml) and petroleum ether (b.p 40–60 °C, 100 ml) to afford **1c** which was collected by suction filtration and dried *in vacuo*. Yield: 4.827 g, 67%. Selected data: ^1H [$(CD_3)_2SO$]: 9.74 (s, 1H), 9.24 (s, 1H), 7.57–7.31 (m, 8H), 6.72 (d, 2H), 5.07 (s, 2H), 3.78 (d, 2H) ppm. FT–IR: 3332, 1693, 1669 cm^{-1}. EI–MS: *m/z* 301 [M^++H]. Anal. (%) Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.38; N, 9.33. Found: C, 64.03; H, 5.65; N, 9.69. Similarly, compound **1b** was prepared (80%). Selected data: ^1H {$(CD_3)_2SO$}: 9.57 (s, 1H), 7.75–7.13 (m, 10H), 5.47 (m, 1H), 5.07 (s, 2H), 4.50 (d, 2H), 3.81 (d, 2H) ppm. FT–IR: 3374, 3297, 1707, 1693, 1673 cm^{-1}. EI–MS: *m/z* 314 [M^+]. Anal. (%) Calcd. for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.78; N, 8.91. Found: C, 65.02; H, 5.73; N, 8.82. Compound **1a** has previously been reported.[1]

Preparation of *1,4*-(OH)C_6H_4{NHC(O)CH_2NH_2} (2c). A mixture of **1c** (1.025 g, 3.41 mmol), Pd (10% on C) (0.264 g), EtOH (50 ml) and cyclohexene (2.5 ml) was refluxed for 15 min. After cooling, the mixture was filtered and the solution evaporated to dryness under reduced pressure to afford **2c**. Yield: 0.491 g, 87%. Selected data: ^1H [$(CD_3)_2SO$]: 9.55 (br, 1H), 8.31 (s, 1H), 7.39 (d, 2H), 6.69 (d, 2H), 3.20 (s, 2H) ppm. FT–IR: 3472, 3373, 3294, 2928, 1659 cm^{-1}. CI–MS: *m/z* 167 [M^+]. Anal. (%) Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.08; N, 16.86. Found: C, 57.95; H, 6.38; N, 16.67. Compound **2b** was prepared similarly. Selected data: ^1H {$(CD_3)_2SO$}: 8.02–7.04 (m, 4H), 5.40 (br, 1H), 4.52 (s, 2H), 3.27 (s, 2H). Compound **2a** has previously been reported.[1]

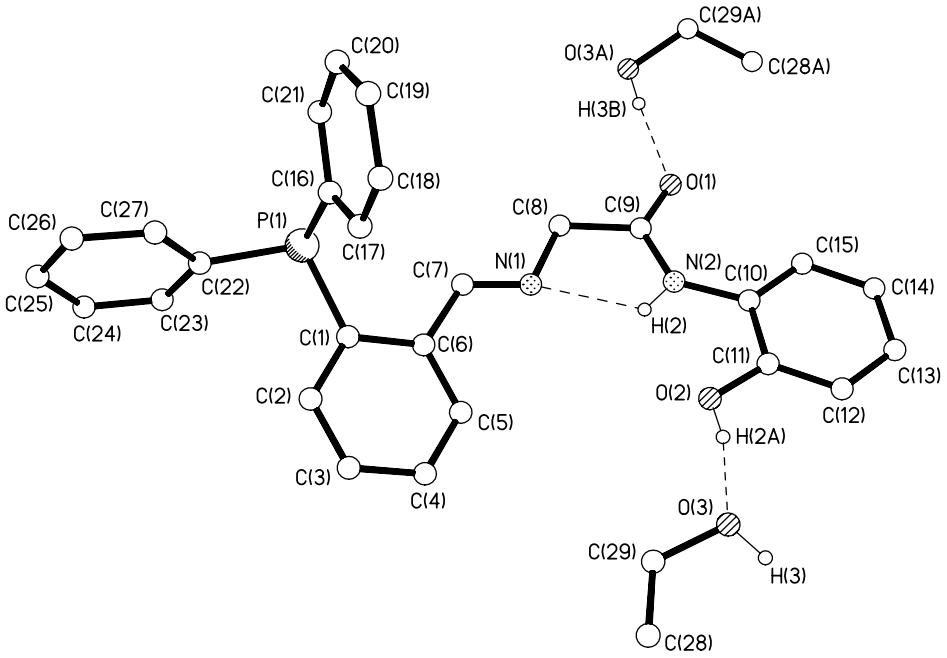
Reference

1. M. R. Bermejo, A. M. González, M. Fondo, A. García-Deibe, M. Maneiro, J. Sanmartín, O. L. Hoyos and M. Watkinson, *New J. Chem*., 2000, **24**, 235.

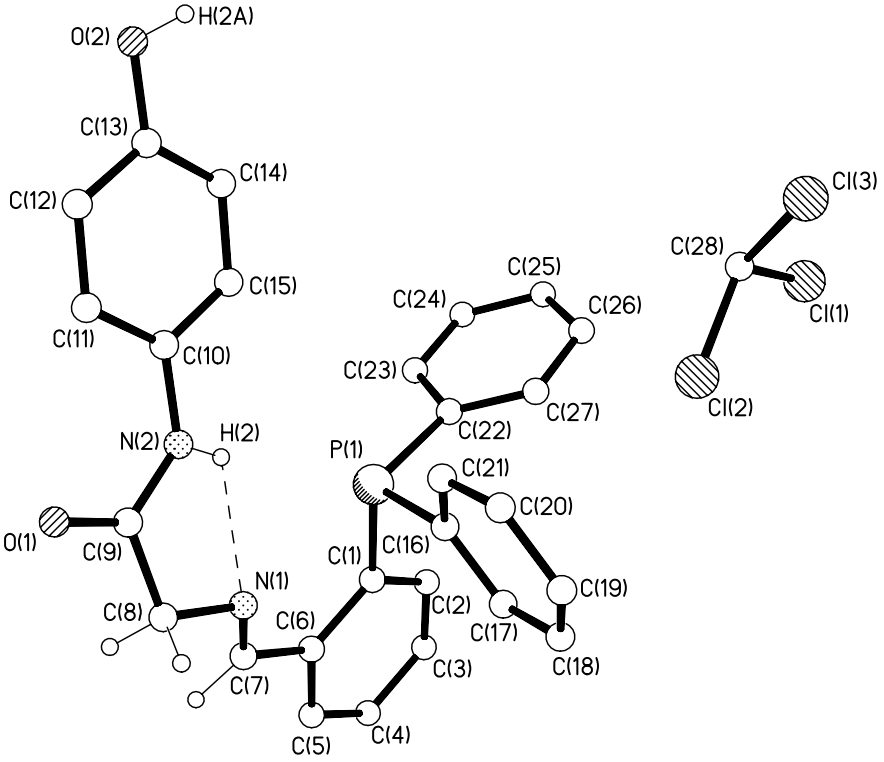
Additional Single Crystal X-ray Figures
Further figures for all crystallographically characterised compounds reported are included.

ESIFIG1 for **3a·HH·**EtOH showing the full atom numbering scheme.
ESIFIG2 for **3c·HH·**0.5$CHCl_3$ showing the full atom numbering scheme.
ESIFIG3 for **3c·HH·**0.5$CHCl_3$ showing the various H-bonding interactions.
ESIFIG4 for **4a** showing the full atom numbering scheme.
ESIFIG5 for **4a** showing the various H-bonding interactions.
ESIFIG6 for **7c·**CH_2Cl_2 showing the full atom numbering scheme.
ESIFIG7 for **7c·**CH_2Cl_2 showing the various H-bonding interactions.
ESIFIG8 for **8a·**$CHCl_3$ showing the full atom numbering scheme.
ESIFIG9 for **8b·**1.5C_7H_8 showing the full atom numbering scheme.
ESIFIG10 for **8d·**2C_7H_8 showing the full atom numbering scheme.
ESIFIG11 for **11a·**CH_3OH showing the full atom numbering scheme.
ESIFIG12 for **11b·**0.5$CHCl_3$·0.5Et_2O showing the full atom numbering scheme for both independent molecules.
ESIFIG13 for **11c** showing the full atom numbering scheme.
ESIFIG14 for **11d·**$CHCl_3$ showing the full atom numbering scheme.

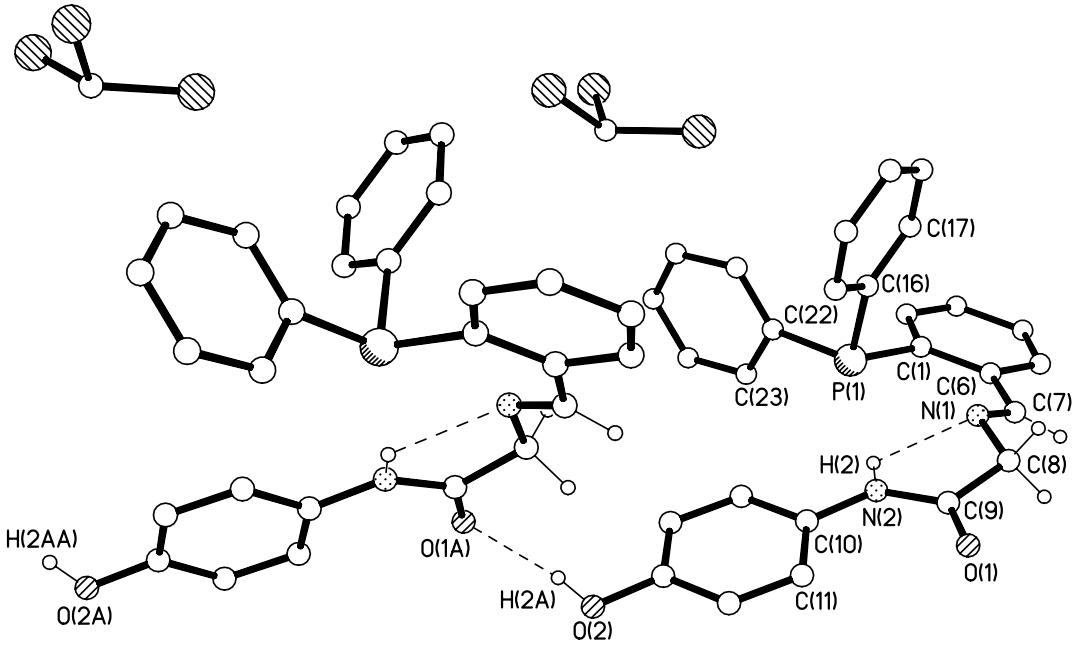
ESIFIG1 for **3a·HH·**EtOH showing the full atom numbering scheme.



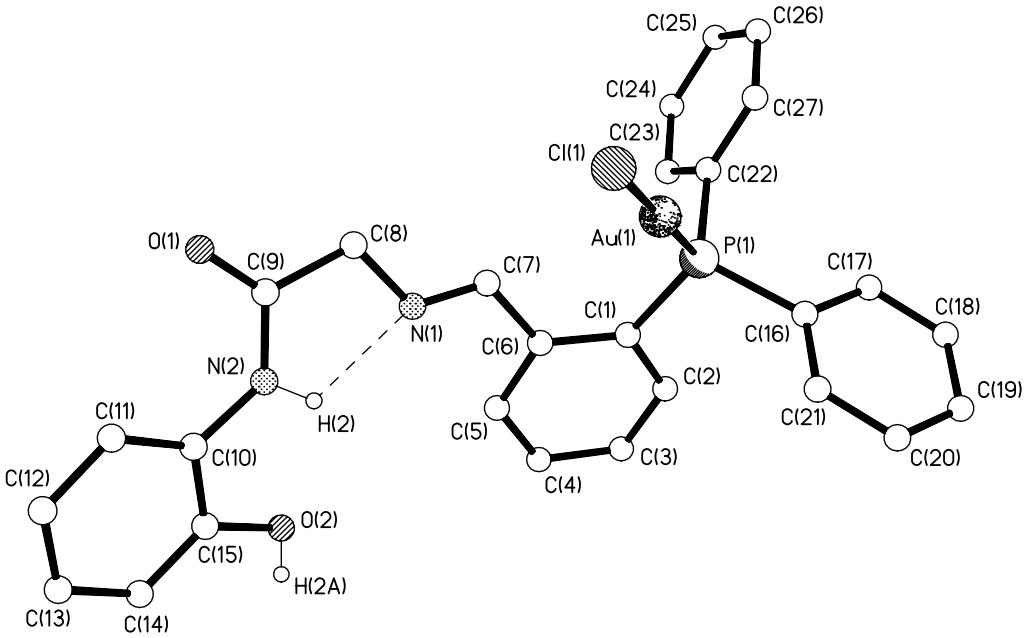
ESIFIG2 for **3c·HH**·0.5$CHCl_3$ showing the full atom numbering scheme.



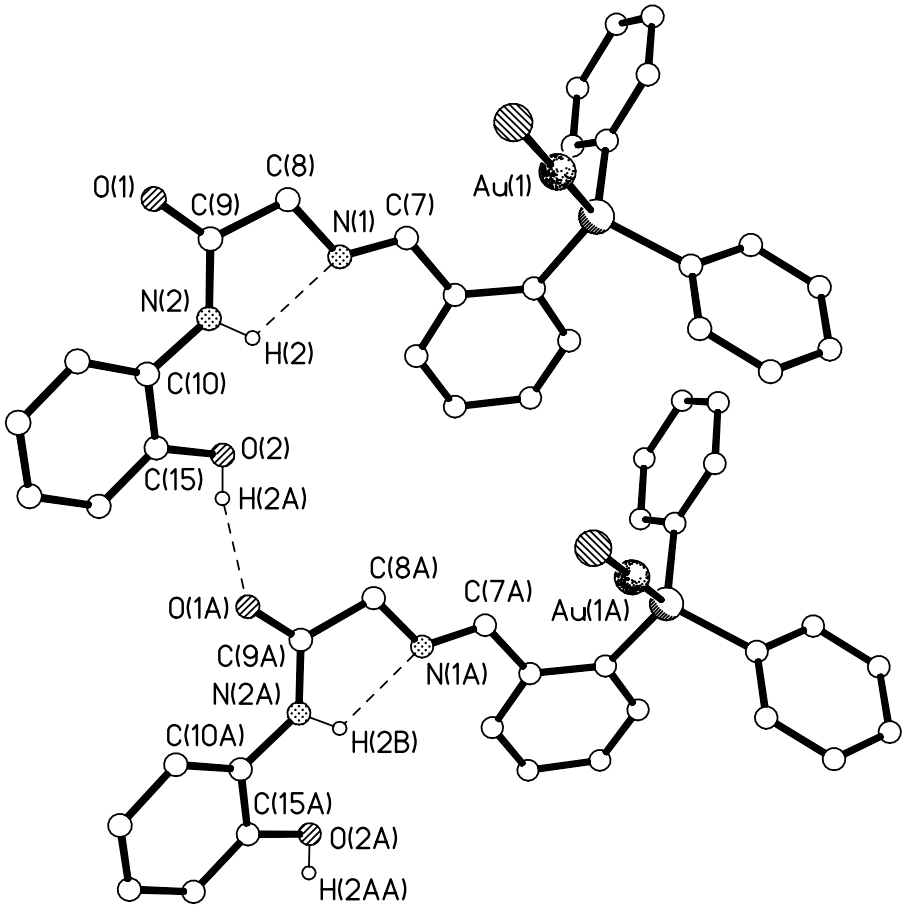
ESIFIG3 for **3c·HH**·0.5$CHCl_3$ showing the various H-bonding interactions.



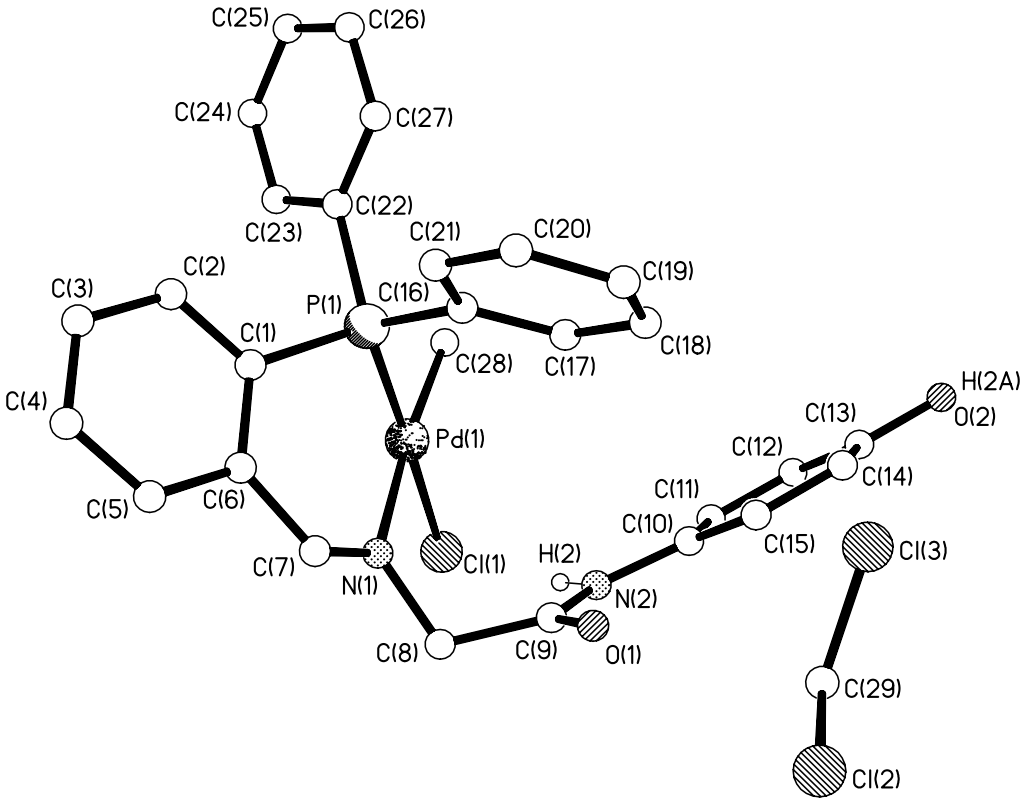
ESIFIG4 for **4a** showing the full atom numbering scheme.



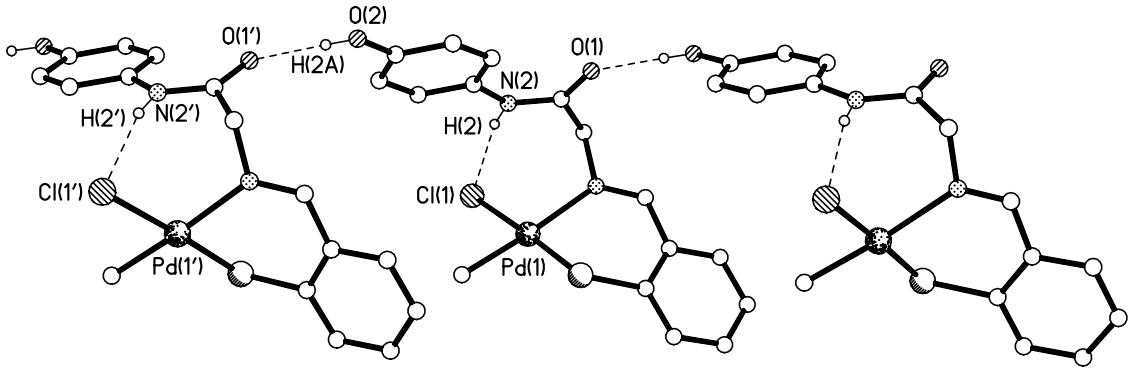
ESIFIG5 for **4a** showing the various H-bonding interactions.



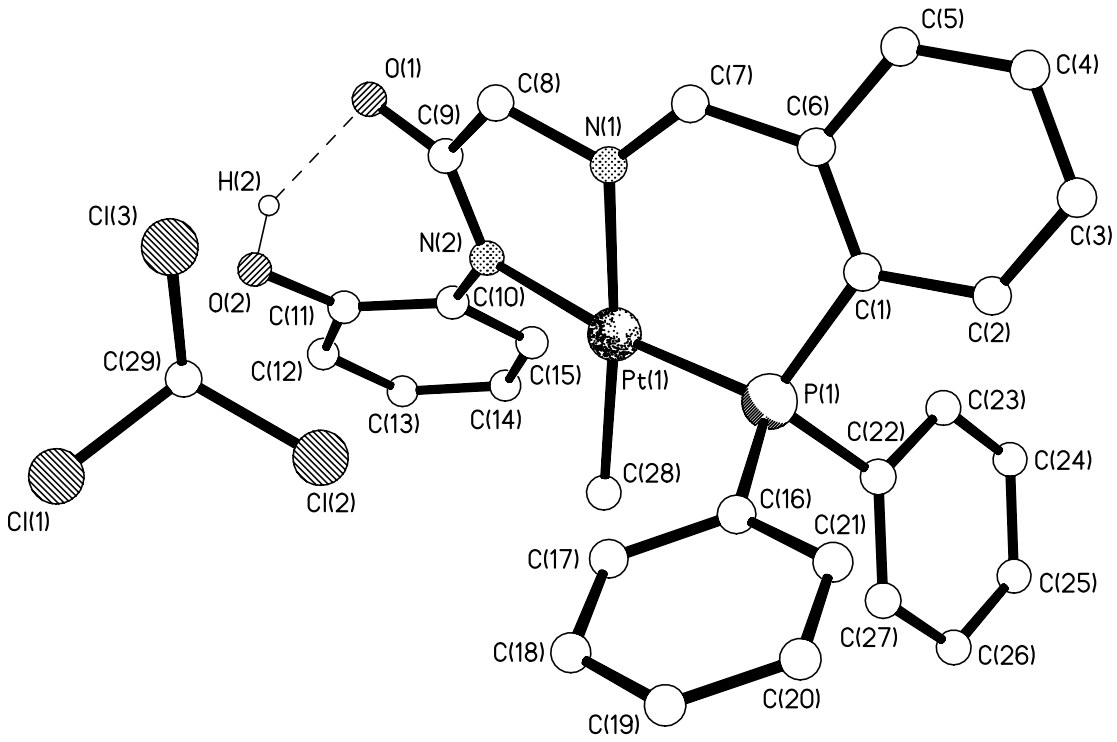
ESIFIG6 for **7c**·CH_2Cl_2 showing the full atom numbering scheme.



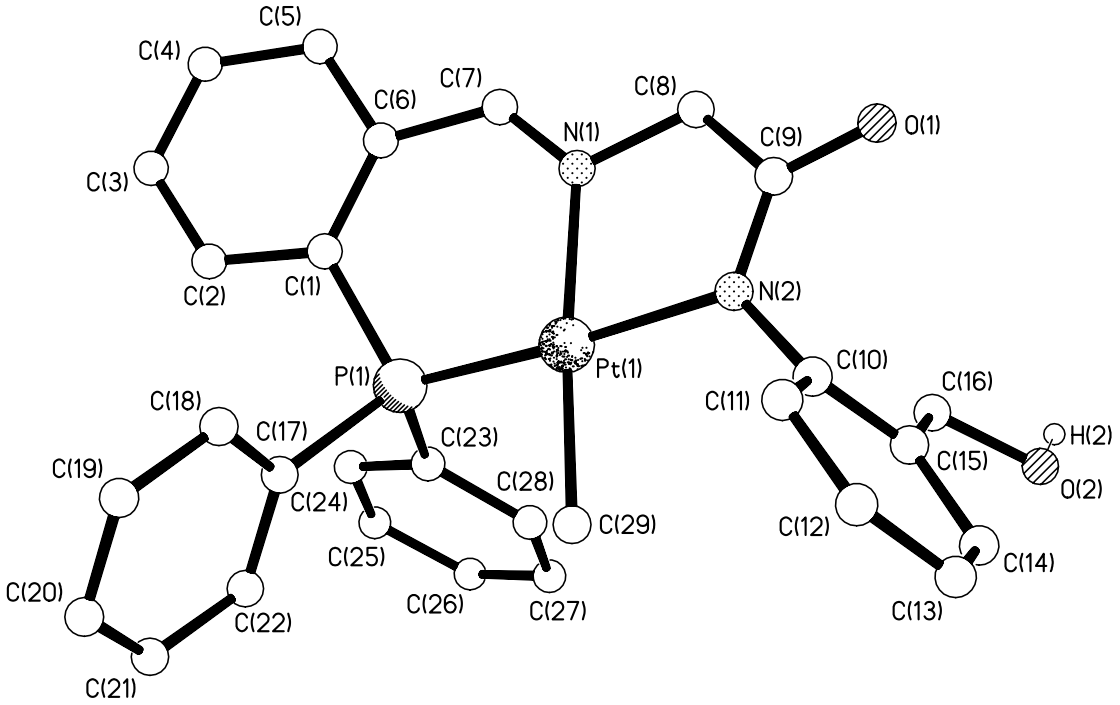
ESIFIG7 for **7c**·CH_2Cl_2 showing the various H-bonding interactions.



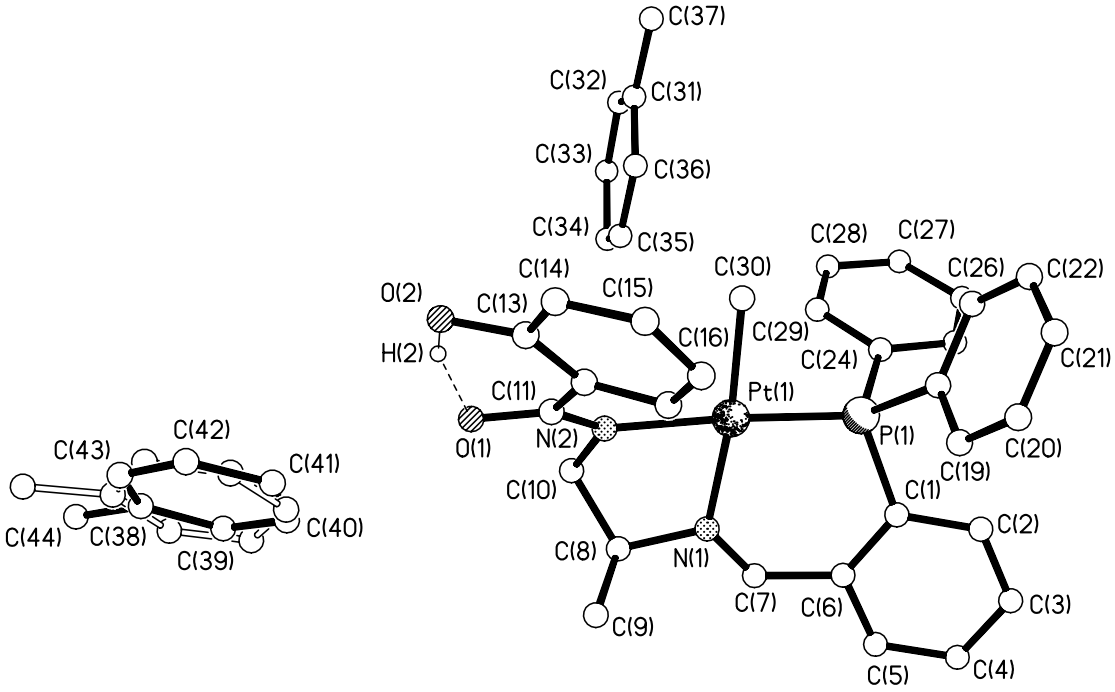
ESIFIG8 for **8a**·$CHCl_3$ showing the full atom numbering scheme.



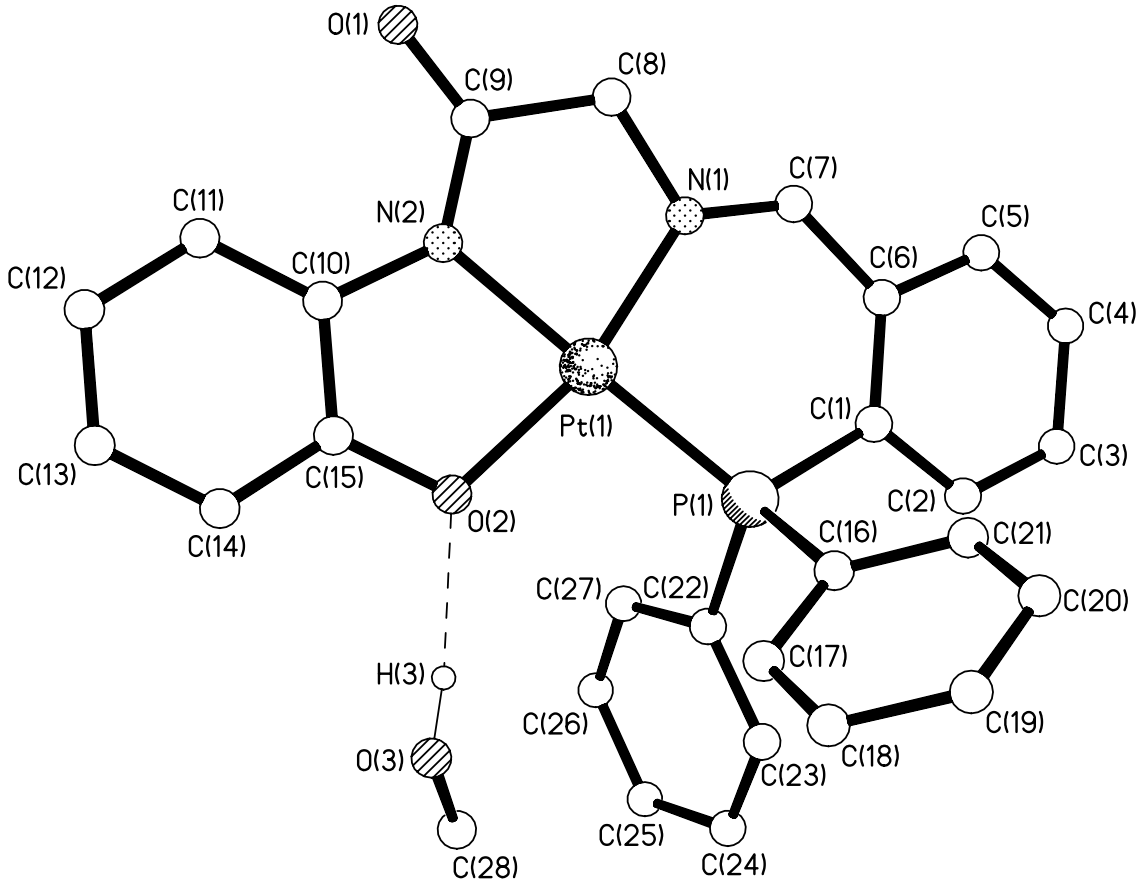
ESIFIG9 for **8b**·1.5C_7H_8 showing the full atom numbering scheme.



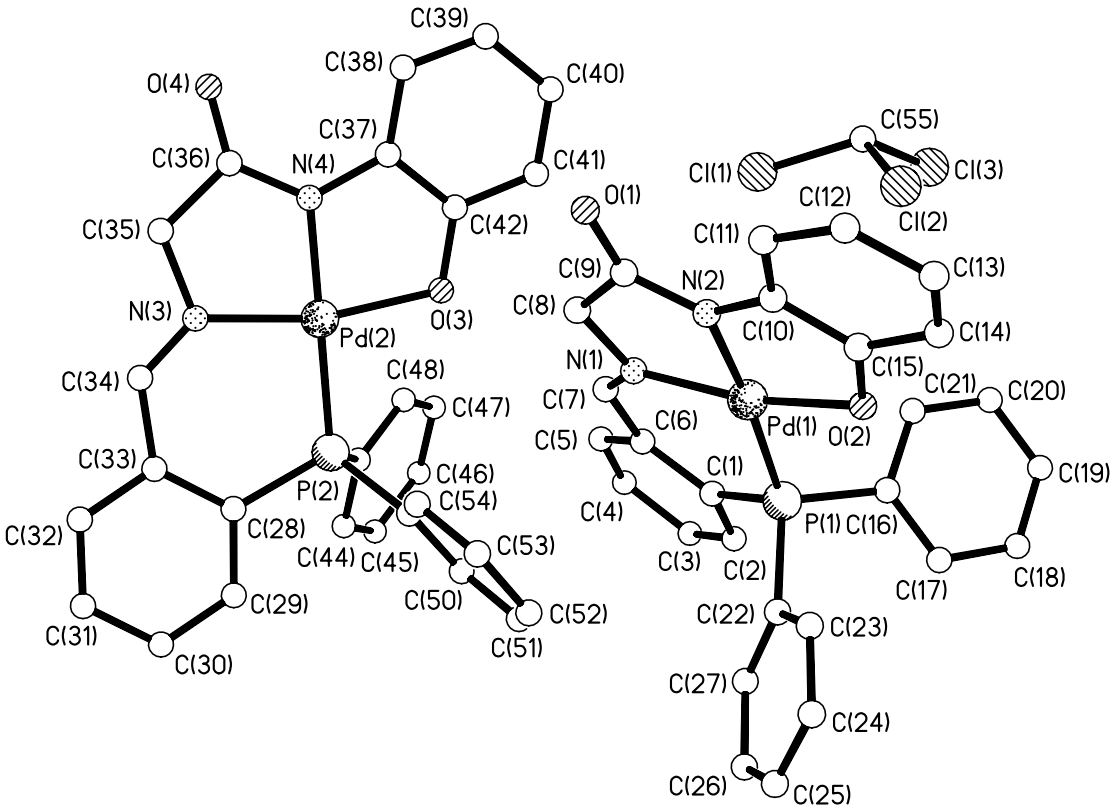
ESIFIG10 for **8d**·$2C_7H_8$ showing the full atom numbering scheme.



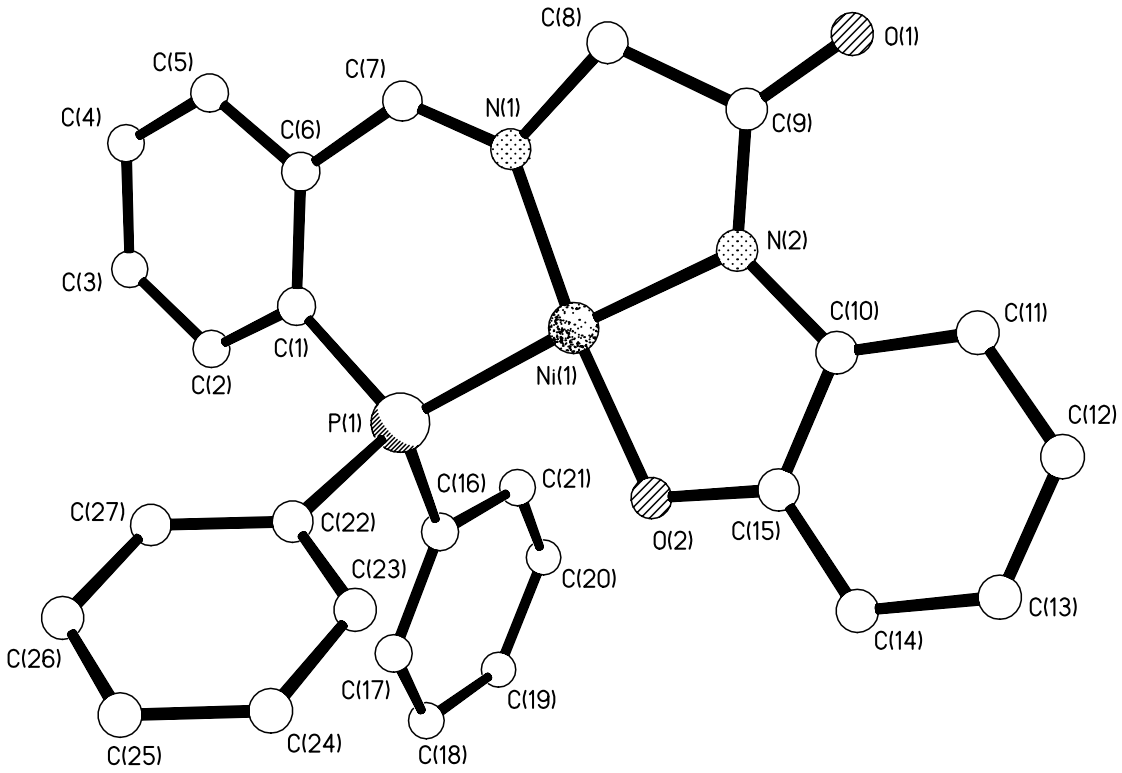
ESIFIG11 for **11a**·CH_3OH showing the full atom numbering scheme.



ESIFIG12 for **11b**·0.5$CHCl_3$·0.5Et_2O showing the full atom numbering scheme for both independent molecules.



ESIFIG13 for **11c** showing the full atom numbering scheme.



ESIFIG14 for **11d**·$CHCl_3$ showing the full atom numbering scheme.