
The oxadiazolyldiazenido(1-) ligand: a remarkably versatile platform for the synthesis of heteropolynuclear transition metal complexes

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ELECTRONIC SUPPLEMENTARY INFORMATION

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A. Representative experimental procedures and product characterisation data

Compound 2: *trans*-bis{bis(1,2-diphenylphosphino)ethane}(4-nitrophenyloxadiazolyldiazenido)bromotungsten: To a stirred solution of complex **1** (0.220 g, 0.167 mmol) in dichloromethane (20 mL), was added 4-nitrobenzoic hydrazide (0.138 g, 0.761 mmol) followed by triethylamine (0.5 mL). There was an immediate colour change from pale brown to dark purple and, after 4 h, the solution was washed with water (3 x 30 mL), dried over magnesium sulphate and filtered. Methanol (15 mL) was added and the solution was reduced to ca. 10 mL on a rotary evaporator. The resulting purple-black crystals were filtered off, washed with methanol and dried under vacuum, affording complex **2** (0.146 g, 68% yield). Complex **2** showed ^{1}H NMR resonances ($CDCl_3$) at δ 7.89 ppm (d, *J* = 8.3 Hz, H-*ortho* to NO_2), 6.96 - 7.34 (m, 40 H, PPh), 6.78 (d, *J* = 8.3 Hz, 2 H, (H-*meta* to NO_2), 2.91 (br s, 8 H, CH_2). IR (Nujol) 3055 ν(CH_{Ar}), 1494 (s, νC=N), 1328 (m, νNO_2). Anal. Calc. for $C_{60}H_{52}BrN_5O_3P_4W.CH_3OH$: C, 55.90; H, 4.31; N, 5.34%. Found: C, 56.22; H, 4.25; N, 5.41%.

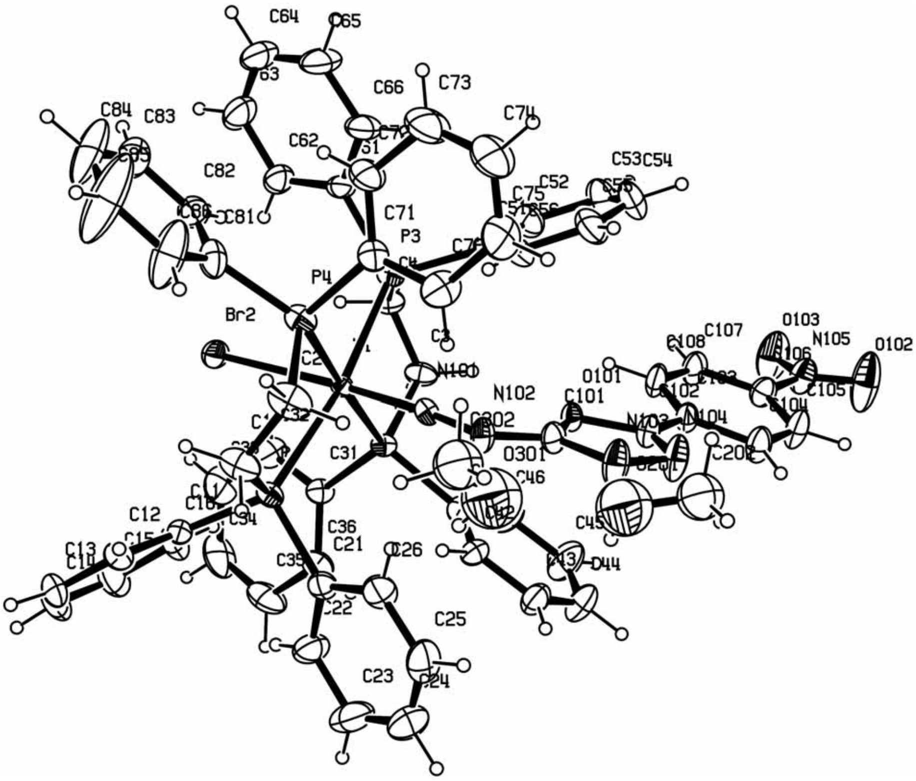
Compound 4: trans-bis{bis(1,2-diphenylphosphino)ethane}(4-pyridyloxadiazolyl-diazenido)bromotungsten: To a stirred solution of complex **1** (0.495 g, 0.376 mmol) in dichloromethane (20 mL), was added isonicotinic hydrazide (0.0523 g, 0.381 mmol) and triethylamine (1 mL). After 10 min a dark red-brown solution had formed, and after 24 h the solution was washed with water (3 x 20 mL), dried over magnesium sulfate and filtered. Methanol (15 mL) was added and the solution reduced in volume until crystallisation was complete. The brick-red crystalline solid was filtered off, washed with methanol, and dried under vacuum, affording complex **4** (0.251 g, 54% yield). Complex 4 showed ^{1}H NMR resonances ($CDCl_3$) at δ 8.29 ppm (d, *J* = 6.1 Hz, 2 H, ($N(\underline{CH})_2(CH)_2$), 7.00-7.47 (m, 40 H, PPh), 6.57 (d, *J* = 6.1 Hz, 2 H, ($N(CH)_2(\underline{CH})_2$), 2.90 (br s, 8 H, CH_2); ^{13}C ($CDCl_3$) δ (ppm) 127.52, 127.87, 129.39, 129.66, 131.46, 133.02, 135.18, 135.50, 135.67, 136.53, 136.84, 137.15 (Ar_{dppe}), 118.33, 133.57, 149.30 (pyridine), 155.23 and 160.36 (C-O-$\underline{C}$=N), 31.62, 31.47, 31.31 ppm (CH_2 of dppe); IR (Nujol) 3055 ν(CH_{Ar}), 1500/1542 (w, νC=N), 1572 (s, νC=N), 1605 (w, νC=C), 1248 cm^{-1} (w, νC-O). Anal. Calc. for $C_{59}H_{52}BrN_5OP_4W{\cdot}0.5CH_2Cl_2$: C, 55.95; H, 4.78; N, 5.48%. Found: C, 56.36; H, 4.72; N, 5.50%.

Compound 8: bis[(*trans*-bis{bis(1,2-diphenylphosphino)ethane}(4-pyridyloxadiazolyldiazenido)bromotungsten]bis(hexafluoroacetylacetonato)zinc(II): To a stirred solution of complex **4** (0.112 g, 0.091 mmol) in dichloromethane (15 mL), was added a solution of zinc(II) hexafluoroacetylacetonate dihydrate (0.0235 g, 0.046 mmol) in dichloromethane (5 mL). No immediate colour change was observed. After 48 h, the reddish-brown solution was treated with hexane (10 mL) and reduced in volume to ca. 5 mL on a rotary evaporator. The resulting orange-brown solid was filtered off, washed with hexane and dried under vacuum, affording complex **8** (0.109 g, 81% yield). Complex **8** showed ^{1}H NMR resonances ($CDCl_3$) at δ 8.23 (br d, *J* = 4.72 Hz, 4 H, $N(\underline{CH})_2(CH)_2$), 7.00-7.51 (m, 80 H, PPh), 6.50 (br s, 4 H, $N(CH)_2(\underline{CH})_2$), 6.00 (s, 2 H, $CF_3COC\underline{H}=C(O)CF_3$), 2.91 ppm (br s, 16 H, CH_2); ^{13}C ($CDCl_3$) δ (ppm) 128.01, 128.37, 129.96, 130.18, 133.30, 133.99 (Ar_{dppe}), 119.02, 149.23 (pyridine), 31.99 ppm (CH_2 of dppe); IR (Nujol) 3055 ν(CH_{Ar}), 1713 (w, νC=O), 1651 (m, νC=O), 1617 (w, νC=C), 1586 (w, νC=N), 1550 (w, νC=N), 1495 (br s, νC=N), 1256 (m, νC-O), 1200 and 1147 cm^{-1} (m, νC-F); Anal. Calc. for $C_{128}H_{106}Br_2F_{12}N_{10}O_6P_8ZnW_2 \cdot CH_2Cl_2$: C, 51.07; H, 3.59; N, 4.62%. Found: C, 50.88; H, 3.49; N, 4.47%.

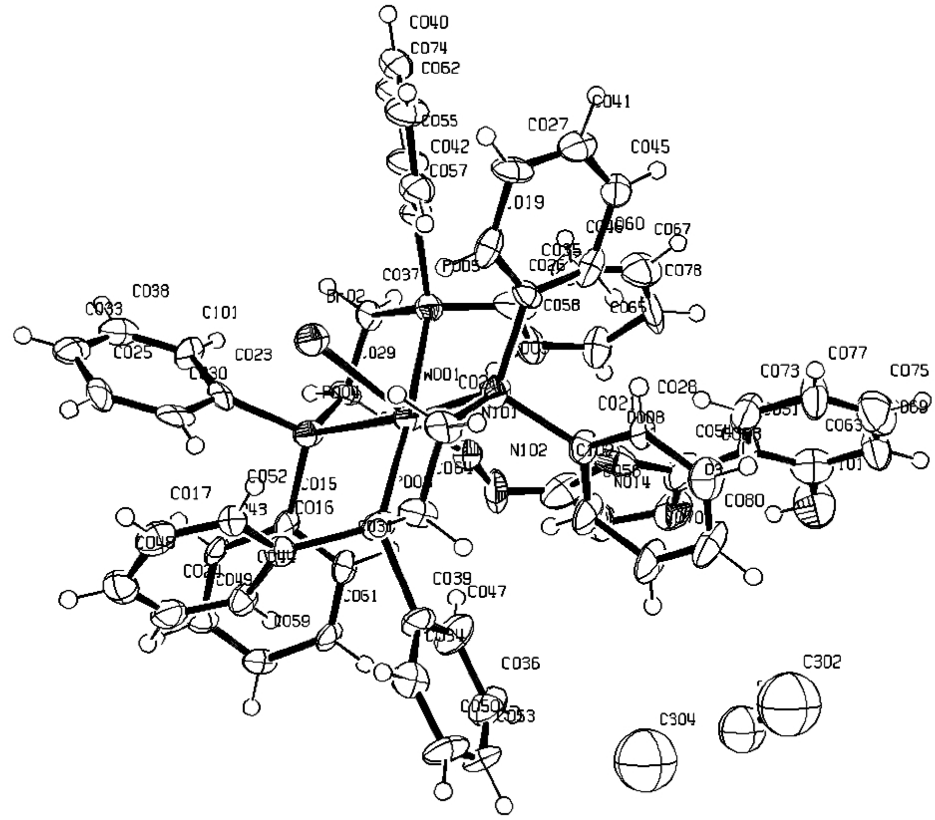
Compound 9: bis(*trans*-bis{bis(1,2-diphenylphosphino)ethane}(4-pyridyloxadiazolyldiazenido)bromotungsten)tetra-acetatodirhodium(II): To a stirred solution of complex **4** (0.098 g, 0.079 mmol) in dichloromethane (15 mL), was added dirhodium tetra-acetate dihydrate (0.018 g, 0.039 mmol). After 24 h, the deep red-brown solution was treated with methanol (15 mL) and reduced in volume until crystallisation was complete. The dark brick-red crystalline solid was filtered off, washed with methanol, and dried under vacuum, affording the tetranuclear complex **9** (0.085 g, 74% yield.) Complex **9** showed ^{1}H NMR resonances ($CDCl_3$) at δ 9.09 (d, *J* = 5.5 Hz, 4 H, ($N(\underline{CH})_2(CH)_2$)), 7.04-7.44 (m, 80 H, Ar_{dppe} and 4 H, $N(CH)_2(\underline{CH})_2$), 2.90 (br s, 16 H, CH_2), 1.93 ppm (s, 12 H, $(O_2C\underline{CH_3})_4$); ^{13}C ($CDCl_3$) δ (ppm) 127.52, 128.06, 129.32, 129.82, 133.28, 133.57, 136.44 (C Ph of dppe), 191.77 (C $(O_2\underline{C}CH_3)_4$), 119.66, 132.52, 150.51 (pyridine), 155.27 (C O-$\underline{C}$=N), 31.68 (CH_2 of dppe), 24.00 ppm (C $(O_2C\underline{C}H_3)_4$); IR (Nujol) 3055 ν(CH_{Ar}), 1591 (s, νC=O), 1497 (s, νC=N), 1244 cm^{-1} (w, νC-O). Anal. Calc. for $C_{126}H_{116}Br_2N_{10}O_9P_8Rh_2W_2 \cdot CH_2Cl_2$: C, 50.90; H, 3.97; N, 4.67%. Found: C, 50.81; H, 3.89; N, 4.55%.

B. Supplementary figures (SF1 to SF5), showing the molecular structures of compounds 2, 5, 6, 9 and 10, with atom numbering.

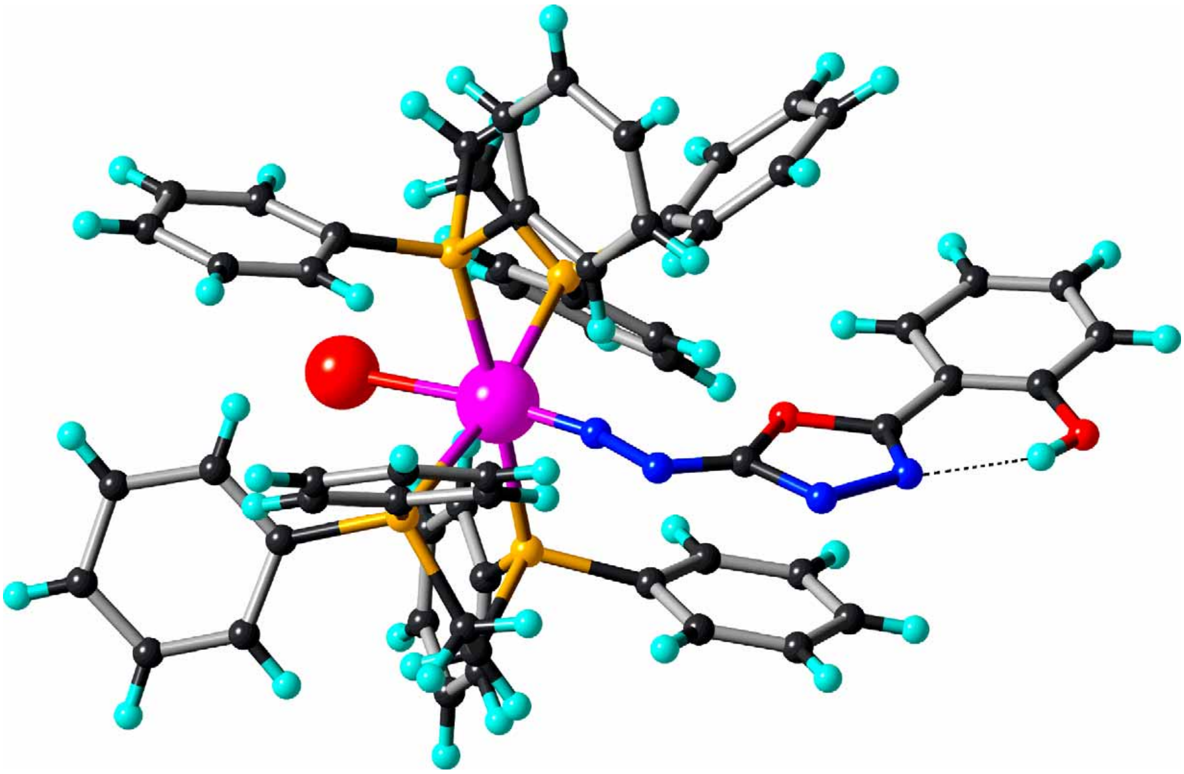
SF1: Complex 2



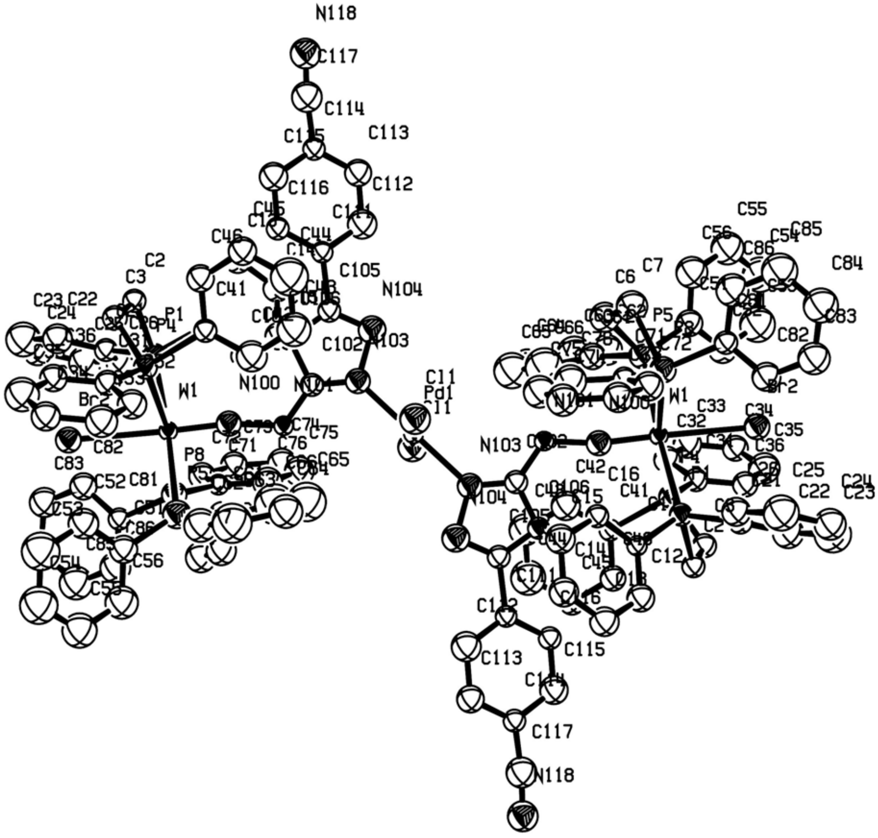
SF2a: Complex 5 (ellipsoids)



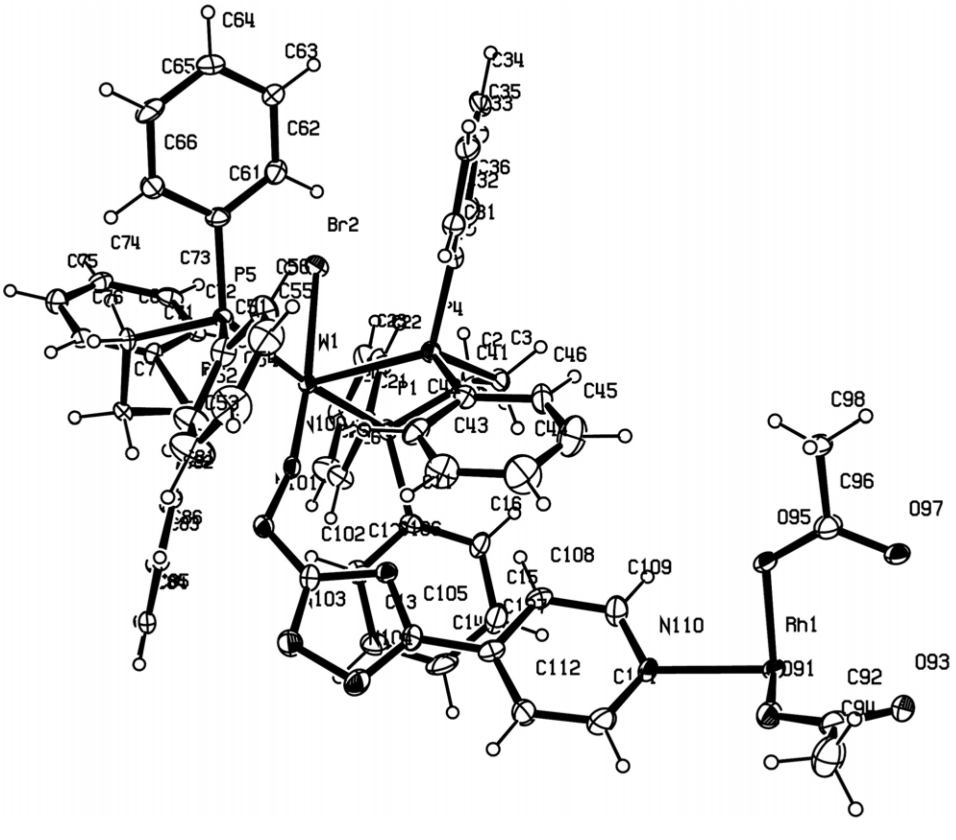
SF2b: Complex 5 (ball and stick)



SF3: Complex 6



SF4: Complex 9 (half of centrosymmetric molecule)



SF5: Complex 10