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Formation of novel diaza-metallacycles by insertion of tungsten(II) aryloxides into aromatic diazine rings

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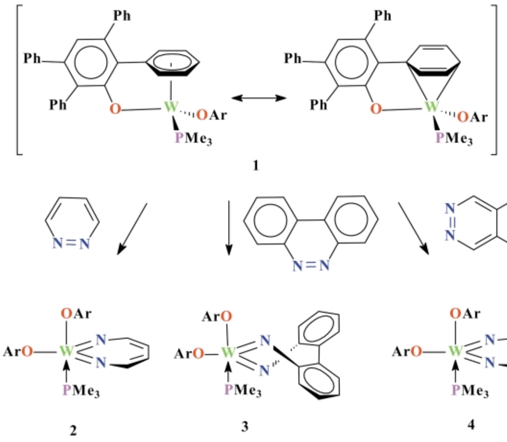
The tungsten(II) aryloxide [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(PMe$_3$)] (1) (OC$_6$HPh$_4$-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide) cleanly inserts into the aromatic diazine rings of pyridazine, benzo[*c*]cinnoline and phthalazine.

The chemistry of early transition metal imido compounds continues to be an area of intense research.[1] Interest has focused both upon the intrinsic reactivity of the metal imido function as well as its important role as an ancillary ligand.[2] We have previously shown that tungsten(II) aryloxides containing chelated *ortho*-phenylphenoxides, *e.g.* **1**, can activate a variety of X=Y double bonds including the four electron reduction of *trans*-diazines to produce bis(imido) derivatives.[3] We wish to report here the application of this reactivity to the production of a series of novel diaza-metallacycles.[4,5]

Hydrocarbon solutions of the deep green tungsten(II) aryloxide **1** react rapidly (assessed *via* color change and ^{1}H NMR spectroscopy) with pyridazine, benzo[*c*]cinnoline and phthalazine to form a series of seven membered ring compounds (Scheme 1). ^{1}H and ^{31}P NMR spectra show all reactions to be quantitative in yield.† This spectroscopic data is also consistent with the presence of a virtual mirror plane passing through the diaza-metallacycle ring of **2** and **4**.

Structural studies (Fig. 1–3)‡ show all three compounds to possess geometries about the metal best described as trigonal bipyrimidal with an axial aryloxide and PMe$_3$ group. Both 2,3,5,6-tetraphenylphenoxide ligands are terminal, non-chelating.

Of particular interest are the structural parameters for the three seven-membered rings which lie in the equatorial plane. It can be seen that complete rupture of the initial N=N bond has occurred. In compounds **2** and **4** the metallacycle rings are planar while in **3** the ring is slightly puckered due (Fig. 2) to a twisting of the two aryl rings {torsion angle = 31.2(6)°}. The metallacycle rings can be represented as two different resonance forms (**A** and **B** in Fig. 4) in which the formal oxidation states of the tungsten are +6 and +4, respectively.[6] The structural parameters for compounds **2** and **3** are more consistent with a 2,7-diazatungstacyclohepta-1,3,5,7-tetraene resonance form with two tungsten–imido bonds. However there appears to be a small contribution of a 2,7-diazatungstacyclohepta-2,4,6-triene resonance form for **4**, driven undoubtedly by the fused aromatic ring in the backbone. All compounds display sharp, non-contacted NMR resonances consistent with a d^0-W(IV) metal center being present.[7]



Scheme 1 Synthesis of **2**, **3** and **4** from **1**.

There is NMR evidence in solution for compound **4** undergoing further reaction with phthalazine. It appears that the

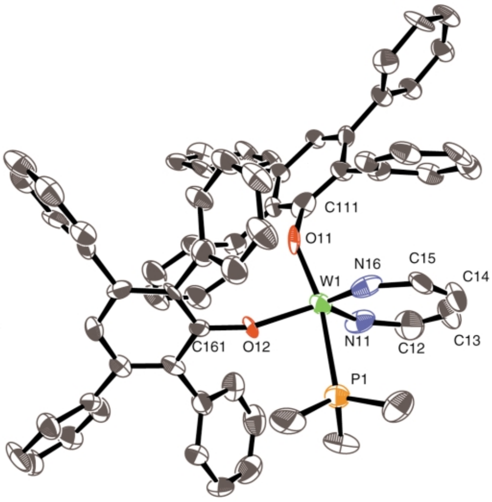


Fig. 1 Selected bond distances (Å) and angles (°) for **2**: W(1)–N(11) 1.740(7), W(1)–N(16) 1.744(7), W(1)–P(1) 2.580(2), W(1)–O(11) 1.961(6), W(1)–O(12) 1.970(6), N(11)–W(1)–N(16) 101.0(4), O(11)–W(1)–O(12) 88.8(2), O(12)–W(1)–P(1) 79.2(2), O(11)–W(1)–P(1) 168.0(2).

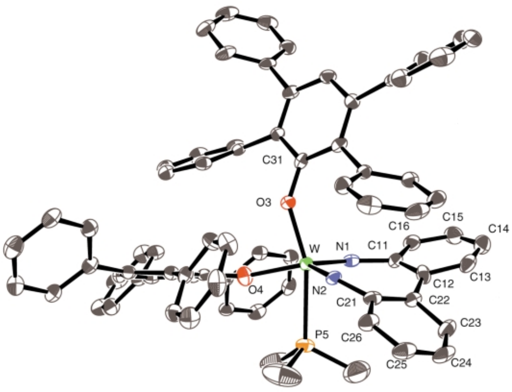


Fig. 2 Selected bond distances (Å) and angles (°) for **3**: W–N(1) 1.753(4), W–N(2) 1.751(4), W–P(5) 2.566(1), W–O(3) 1.991(3), W–O(4) 1.987(3), N(1)–W–N(2) 97.9(2), O(3)–W–O(4) 85.8(1), O(4)–W–P(5) 76.71(9), O(3)–W–P(5) 162.52(9).

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† Electronic supplementary information (ESI) available: synthesis of compounds **1–4**. See http://www.rsc.org/suppdata/cc/b2/b207805h/

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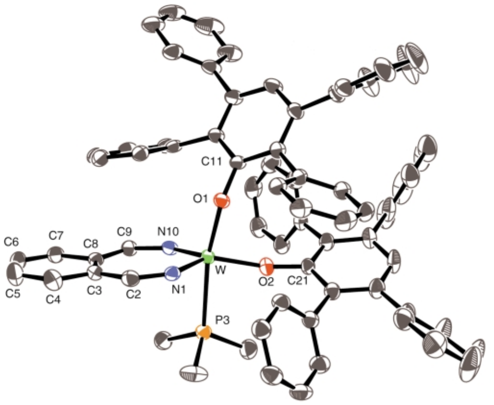

Fig. 3 Selected bond distances (Å) and angles (°) for **4**: W–N(1) 1.797(3), W–N(10) 1.791(3), W–P(3) 2.565(1), W–O(1) 1.982(2), W–O(2) 1.959(2), N(1)–W–N(10) 98.7(1), O(1)–W–O(2) 91.3(1), O(2)–W–P(3) 80.07(8), O(1)–W–P(3) 168.90(7).

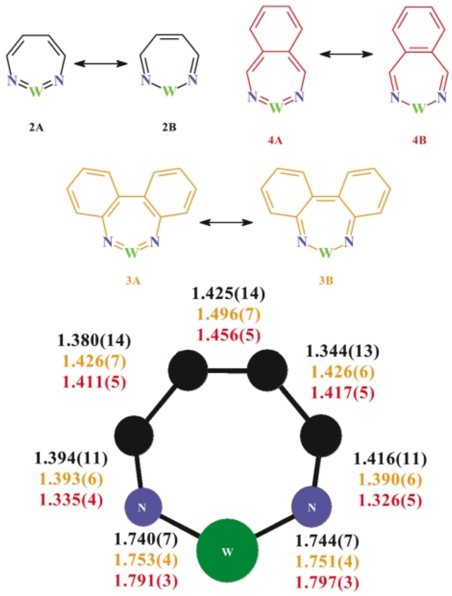

Fig. 4 Possible resonance contributions and structural parameters for the diaza-metallacycle rings in **2**, **3** and **4**.

excess phthalazine can compete with the PMe_3 for coordination to the metal. Furthermore variable temperature NMR studies of this reactivity indicate that phthalazine exchange can occur within this new molecule. Hence there is preliminary evidence that in this case the rupture of the N=N bond may be reversible on the NMR timescale. Further labelling and mechanistic studies of the reactivity of these new metallacycles are planned.

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Notes and references

‡ *Selected spectroscopic data*. For **1**: ^{1}H NMR (C_6D_6, 30 °C): δ 7.00–8.00 (m, 37H, aromatics); 3.45, 2.94, 1.94, 1.52, 1.19 (m, 5H, η^6-C_6H_5); 0.96 (d, 9H, PMe_3). ^{31}P NMR (C_6D_6, 30 °C): δ 31.6 [$^1J(^{183}W-^{31}P)$ = 372 Hz]. For **2**: ^{1}H NMR (C_6D_6, 25 °C): δ 7.54 (dd, 2H, *H*C–N), 7.24–6.97 (m, 42H, aromatics), 5.83 (dd, 2H, NHC = C*H*–), −0.25 (d, 9H, P*Me*$_3$, $^2J(^{31}P-^1H)$ = 8.4 Hz). ^{31}P NMR (C_6D_6, 25 °C): δ −11.0 (br. PMe_3). For **3**: ^{1}H NMR (C_6D_6, 25 °C): δ 8.53 (s, 2H, *H*C–N), 6.94–7.30 (m, 46H, aromatics), 6.5–6.65 (m, 2H, aromatics), −0.58 (d, 9H, PMe_3, $^2J(^{31}P-^1H)$ = 8.1 Hz). ^{31}P NMR (C_7D_8, −30 °C): δ −17.7 [$^1J(^{183}W-^{31}P)$ = 296 Hz]. For **4**: ^{1}H NMR (C_7D_8, −50 °C): δ 8.63 (d, 2H, aromatic), 7.72–6.73 (m, 44H, aromatics), 6.55 (d, 2H, aromatics), −0.58 (d, 9H, PMe_3, $^2J(^{31}P-^1H)$ = 9.8 Hz). ^{31}P NMR (C_7D_8, −50 °C): δ −0.5 [$^1J(^{183}W-^{31}P)$ = 338 Hz].

Crystal data: For **2***$2C_6H_6$ at 150 K: $WPO_2N_2C_{67}H_{55}$, $M = 1291.25$, space group $P2_1/c$ (No. 14), $a = 24.8331(5)$, $b = 11.5704(3)$, $c = 44.5364(12)$ Å, $\beta = 101.3130(8)°$, $V = 12548.0(10)$ Å^3, $d_{calc} = 1.367$ g cm^{-3}, $Z = 8$. Of the 16755 unique reflections collected ($5 \leq \theta \leq 22°$) with Mo-K$_\alpha$ ($\lambda = 0.71073$ Å), the 16755 with $F_o^2 > 2.0\,\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R = 0.051$ and $R_W = 0.084$. CCDC 191649. For **3***C_6H_6 at 150K: $WPO_2N_2C_{75}H_{59}$, $M = 1235.04$, space group $P2_1/n$ (No. 14), $a = 12.2150(2)$, $b = 32.4594(5)$, $c = 17.0957(2)$ Å, $\beta = 93.0186(9)°$, $V = 6768.9(3)$ Å^3, $d_{calc} = 1.365$ g cm^{-3}, $Z = 4$. Of the 11445 unique reflection collected ($5 \leq \theta \leq 30°$) with Mo-K$_\alpha$ ($\lambda = 0.71073$ Å), the 11445 with $F_o^2 > 2.0\,\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.042$ and $R_W(F_o^2) = 0.089$. CCDC 191650. For **4** at 150 K: $WPO_2N_2C_{71}H_{57}$, $M = 1185.08$, space group $P1$ (No. 2), $a = 11.32550(10)$, $b = 16.3547(3)$, $c = 18.3239(3)$ Å, $\alpha = 70.6136(7)$, $\beta = 73.1055(6)$, $\gamma = 71.1026(11)°$, $V = 2964.61(10)$ Å^3, $d_{calc} = 1.327$ g cm^{-3}, $Z = 2$. Of the 13873 unique reflections collected ($5 \leq \theta \leq 27°$) with Mo-K$_\alpha$ ($\lambda = 0.71073$ Å), the 13868 with $F_o^2 > 2.0\,\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R = 0.038$ and $R_W = 0.085$. CCDC 191651. See http://www.rsc.org/suppdata/cc/b2/b207805h/ for electronic files in .cif or other electronic format.

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