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Dipyridylketone binding and subsequent C–C bond insertion reactions at cyclopentadienylrhodium

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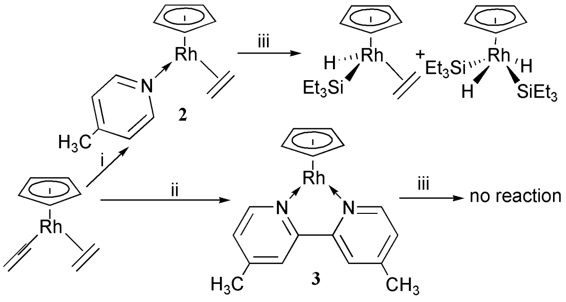
UV irradiation of a solution of (η^5-C_5H_5)bis(ethene)rhodium in the presence of 2,2′-dipyridylketone yields (η^5-C_5H_5)Rh(κ^2-*N*, *O*-2,2′-dipyridylketone) which inserts ethene to yield a bicyclic oxametallacyclopentane.

The photochemical ejection of ethene from (η^5-C_5H_5)Rh(C_2H_4)(L) where L = C_2H_4, PPh_3, PMe_3 or CO provides a route to the unsaturated metal centre (η^5-C_5H_5)Rh(L). These fragments have been shown to activate Si–H and C–H bonds[1] and coordinate two electron donor ligands such as acetonitrile[2] and arenes.[3] Upon prolonged photolysis, the elimination of the second ethene ligand from (η^5-C_5H_5)Rh(C_2H_4)$_2$ normally allows the generation of disubstitution products. The binding of hard nitrogen donors influences the reactivity of late transition metal centres dramatically. For example, Brookhart has shown that suitable complexes of diimine ligands polymerise ethylene and α-olefins,[4] while Tilset has demonstrated that benzene and methane C–H activation can be achieved under unusually mild conditions.[5] Here we describe how photolysis of (η^5-C_5H_5)Rh(C_2H_4)$_2$ **1** with nitrogen donors provides new routes to complexes with N and O ligands. One of these exhibits the rare mononuclear κ^2-*N*,*O* coordination mode of 2,2′-dipyridylketone and is activated towards ethene cycloaddition.

Photolysis of **1** (λ > 290 nm) in C_6D_6 with 4-methylpyridine affords the monosubstituted complex (η^5-C_5H_5)Rh(C_2H_4)(η^1-*N*-4-methylpyridine) **2** according to multinuclear NMR spectroscopy.† Upon prolonged photolysis no evidence for the double substitution product (η^5-C_5H_5)Rh(η^1-*N*-4-methylpyridine)$_2$ was obtained. However, with 4,4′-dimethyl-2,2′-bipyridyl, the double substitution product (η^5-C_5H_5)Rh(κ^2-*N*-*N*-4,4′-dimethyl-2,2′-bipyridyl) **3** was the only new species observed at 295 K (Scheme 1). Related complexes involving (η^5-C_5Me_5)M where M = Co, Ir and Rh have been reported.[6–8] In order to test the ability of these complexes to act as thermal sources of (η^5-C_5H_5)Rh(C_2H_4) and (η^5-C_5H_5)Rh respectively, their reactivity towards Et_3SiH was studied. For **2**, the reaction proved to be unselective yielding both mono- and disubstitution products while for **3** no reaction occurred.

When **1** was photolysed in pentane with 2, 2′-dipyridylketone (DPK), a deep blue product, (η^5-C_5H_5)Rh(κ^2-*N*,*O*-DPK) **4** precipitated. Single crystals of **4** were obtained from toluene at 243 K and their structure determined by X-ray analysis at 150 K (Fig. 1). Ligand binding through both nitrogen and oxygen centres is evident with the C(7)–O(9) bond length of 1.304(3) Å suggesting the retention of significant CO double bond character. In the corresponding $^{13}C\{^1H\}$ NMR spectrum, the ketyl carbon appears as a singlet at δ 161.2 which is 30 ppm lower in chemical shift than for the free ligand. Evidence for nitrogen binding to the rhodium centre in solution comes from the observation of two naturally abundant ^{15}N signals, a rhodium coupled doublet at δ −129.4 (J_{RhN} = 33.6 Hz) and a singlet at δ −77.4 (Fig. 2). The free ligand appears at δ −57.0.

The reaction of **4** with Et_3SiH proceeds cleanly at 40 °C to yield the disubstitution product (η^5-C_5H_5)Rh(H)$_2$(SiEt$_3$)$_2$ (Scheme 2). However, when a solution of **4** is left under ethene, the colour changes from blue to orange overnight and **5** is



Scheme 1 (i) hν, 295 K, 4-Mepy, C_6D_6; (ii) hν, 295 K, 2,2′-Me$_2$bpy, C_6D_6; (iii) Et_3SiH, C_6D_6, 333 K.

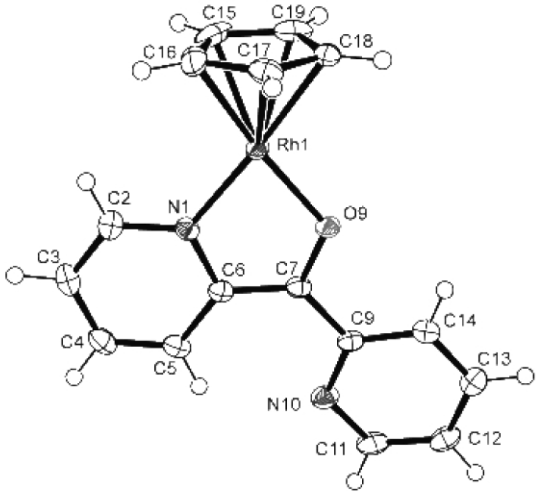


Fig. 1 ORTEP diagram of (η^5-C_5H_5)Rh(κ^2-*N*-*O*-DPK) **4**. Ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Rh(1)–O(9) 1.9816(16), Rh(1)–N(1) 1.9822(19), C(7)–O(9) 1.304(3), C(6)–C(7) 1.410(3), C(7)–C(9) 1.467(3), N(1)–C(6) 1.394(3), N(10)–C(9) 1.351(3), O(9)–Rh(1)–N(1) 78.38(7), Rh(1)–N(1)–C(6) 116.01(15).

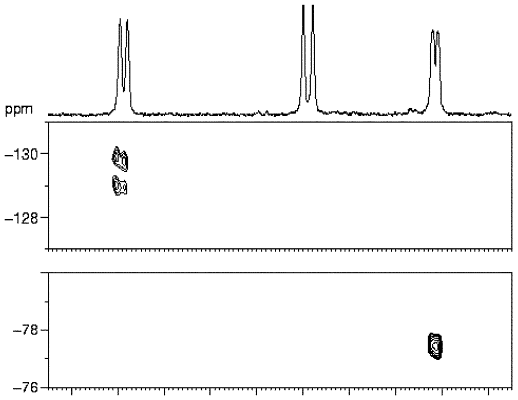


Fig. 2 2D HMQC ^1H-^{15}N spectrum showing connections between the α-pyridyl protons and the nitrogen centres of **4** in d_8-toluene.

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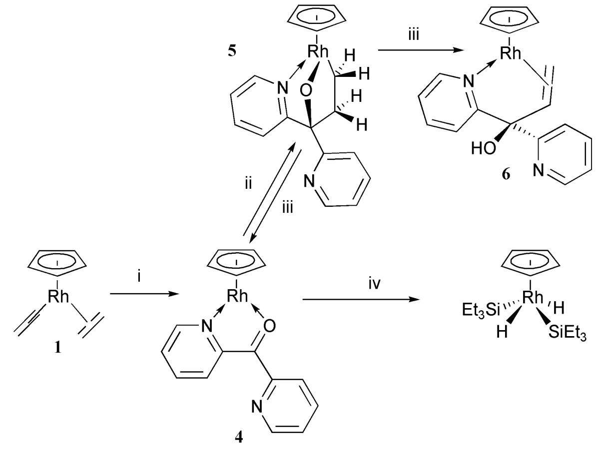

Scheme 2 (i) hν, DPK, 295 K; (ii) C_2H_4, 295 K; (iii) hν, C_6D_6, 295 K; (iv) Et_3SiH, 313 K.

formed while NMR spectroscopy showed **5** to contain a $RhCH_2CH_2$ unit, it was only unambiguously shown to correspond to a [2+2] cycloaddition product of ethene and **4** by X-ray crystallography (Fig. 3).‡ While one DPK nitrogen and the oxygen centre are still coordinated to the rhodium, as in **4**, there is an additional CH_2CH_2 bridge from rhodium to the ketyl carbon. In the ^1H NMR spectrum, this CH_2CH_2 bridge shows four diagnostic proton resonances at δ 4.10, 2.80, 2.40 and 1.92 that show cross peaks to each other in the corresponding COSY spectrum. The resonances at δ 4.1 and 1.92 are attached to one carbon centre, which yields a rhodium coupled ^{13}C signal at δ 14.6 (J_{RhC} = 22.3 Hz). The remaining pair of protons prove to be attached to another carbon which yields a singlet at δ 42.1 in the corresponding $^{13}C\{^1H\}$ NMR spectrum. The appearance of a ^{13}C resonance for the CO group in this species at δ 92.6 is consistent with the X-ray structure since the associated carbon centre is now saturated. Evidence for an N-bound pyridyl unit interacting with the rhodium(III) centre in **5** is evident as a ^{15}N signal at δ −102.7 with a RhN coupling of 19.8 Hz.

Complex **5** reacts further photochemically to form both **4** and a new species **6**; the product ratio is wavelength dependent. NMR data indicate that **6** contains both bound vinyl and N-bound pyridyl units *via* the observation of characteristic alkene signals at δ 3.84, δ 3.35 and δ 1.89 and ^{15}N signals at δ −132.3 (d, J_{RhN} = 22.8 Hz) and δ −86.0 (s). Complex **6** is assigned as the isomer of **5** formed through a hydrogen shift from carbon to oxygen. While the ^{15}N chemical shifts of the rhodium-bound pyridyl units in **4** and **6** are very similar, that of **5** is shifted by *ca*. 30 ppm to lower field. This is consistent with interaction with a more Lewis acidic site, implying a centre with a higher oxidation state. In contrast, the corresponding ^{103}Rh-^{15}N couplings are 22.8, 33.6 and 19.8 Hz for **6**, **4** and **5** respectively. The J_{RhN} values therefore do not appear to be a good indicator of oxidation state. We note, that the Rh–O and Rh–N bonds in **5** are longer than those in **4** by 0.073(2) and 0.061(3) Å respectively, a change that may be associated with the altered coordination geometry at rhodium.

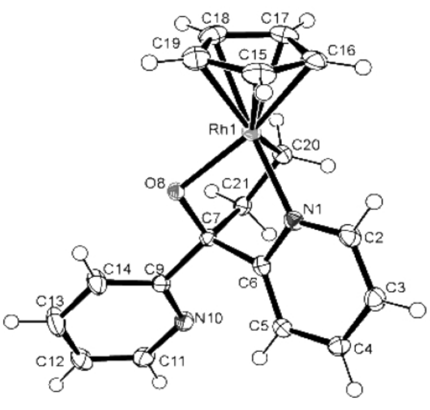

Fig. 3 ORTEP diagram of (η^5-C_5H_5)Rh(η^1-*N*,-C_5H_4N–C(η^1-*O*)(CH_2–CH_2)(C_5H_4N) **5**. Ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Rh(1)–O(8) 2.0417(14), Rh(1)–N(1) 2.0549(18), Rh(1)–C(20) 2.098(2), C(20)–C(21) 1.520(3), C(21)–C(7) 1.547(3), C(7)–O(8) 1.400(2), C(7)–C(6) 1.528(3), C(6)–N(1) 1.349(3), O(8)–Rh(1)–N(1) 77.90(6), O(8)–Rh(1)–C(20) 82.16(7), N(1)–Rh(1)–C(20) 79.97(8).

Here we have shown that (η^5-C_5H_5)Rh(C_2H_4)$_2$ reacts photochemically with a series of pyridine based nitrogen donors to yield both mono- and disubstitution products. With 2,2′-dipyridylketone, (η^5-C_5H_5)Rh(κ^2-*N*-*O*-DPK) is formed in which the ligand binds through both nitrogen and oxygen centres. There is evidence in the literature for DPK binding to a single metal centre in κ^2-*N*-*N* fashion,[9] but this is the first crystallographic evidence for a κ^2-*N*-*O* binding mode. Subsequent thermal reaction shows that coordinated DPK is activated towards attack by alkenes resulting in cycloaddition to form Rh–C and C–C bonds. The latter undergoes photochemical isomerisation from the oxametallacyclopentane to the hydroxy-metal(alkene). Natural abundance ^{15}N NMR spectroscopy is shown to be a tool for the identification of Rh–N bonds, although J_{RhN} values did not appear to be diagnostic of the oxidation state of rhodium in the way as J_{RhP} values.

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Notes and references

† ^1H NMR data for **2–7**; spectra were recorded in C_6D_6 at 400.13 MHz **2**, ^1H δ 1.61 (s, 3H, Me), 1.72 (br, 2H, C_2H_4), 3.35 (br, 2H, C_2H_4), δ 5.18 (s, 5H, C_5H_5), 6.05 (d, 2H, J_{HH} = 6 Hz), 8.44 (d, 2H, J_{HH} = 8 Hz). **3**, ^1H: δ 1.94 (s, 6H, Me), δ 5.17 (s, 5H, C_5H_5), δ 6.21 (d, 2H, J_{HH} = 6 Hz), δ 7.34 (s, 2H), δ 9.30 (d, 2H, J_{HH} = 6 Hz). **4**, ^1H: δ 4.86 (s, 5H, C_5H_5), δ 6.24 (m, 1H), δ 6.85 (m, 1H), δ 6.89 (m,1H), δ 7.22 (m, 1H), δ 8.42 (d, 1H, J_{HH} = 4.9 Hz), δ 8.74 (d, 1H), δ 9.07 (d, 1H, J_{HH} = 6.4 Hz), δ 10.72 (d,1H, J_{HH} = 9 Hz). **5**, ^1H: δ 1.92 (m, 1H, CH_2), δ 2.4 (m, 1H, CH_2), δ 2.8 (m, 1H, CH_2), δ 4.1 (m, 1H, CH_2), δ 5.00 (s, 5H, C_5H_5), δ 6.33 (m, 1H), δ 6.79 (ddd, 1H, J_{HH} = 7.45, 4.8 and 1.26 Hz), δ 6.91 (m, 1H), δ 7.35 (dd, 1H, J_{HH} = 7.7 and 1.9 Hz), δ 7.77 (d, 1H, J_{HH} = 7.7 Hz), δ 8.26 (d, 1H, J_{HH} = 5.5 Hz), δ 8.68 (d, 1H, J_{HH} = 3.9 Hz), δ 8.72 (d, 1H, J_{HH} = 7.9 Hz). **6**, ^1H: δ 1.98 (m, 1H, vinyl), δ 3.35 (m, 1H, vinyl), δ 3.83 (m, 1H, vinyl), δ 5.15 (s, 5H, C_5H_5), δ 6.01 (m, 1H), δ 6.70 (m, 1H), δ 6.71 (m, 1H), 6.96 (br, 1H, OH), δ 7.12 (d, 1H, J_{HH} = 8.05 Hz), δ 7.17 (m, 1H), δ 8.23 (d, 1H, J_{HH} = 5.5 Hz), δ 8.33 (d, 1H, J_{HH} = 5.4 Hz), δ 9.17 (d, 1H, J_{HH} = 7.9 Hz).

‡ Crystal data for **4**: $C_{16}H_{13}N_2ORh$, blue blocks, crystal dimensions 0.58 × 0.23 × 0.13 mm, monoclinic, $P2_1/n$, a = 12.0676(12), b = 5.5804(6), c = 19.407(2) Å, β = 100.5909(15)°, V = 1284.7(2) Å^3, Z = 4, μ(Mo-Kα) = 1.324 mm^{-1}, T 150(2) K; 7664 reflections measured, R(int) 0.0210. Crystal data for **5**: $C_{18}H_{17}N_2ORh$, orange blocks, crystal dimensions 0.34 × 0.31 × 0.31 mm, monoclinic, $P2_1/n$, a = 9.6828(13), b = 11.9109(16), c = 12.9438(17) Å, β = 97.842(2)°, V = 1478.9(3) Å^3, Z = 4, μ(Mo-Kα) = 1.157 mm^{-1}, T 150(2) K; 9196 reflections measured, R(int) 0.0231. CCDC 213069 and 213070. See http://www.rsc.org/suppdata/cc/b3/b306877c/ for crystallographic data in .cif or other electronic format.

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