Activation of metal-bound η^5 -C₅Me₅ groups to Diels–Alder addition of 3O_2 and other dienophiles[†]

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Received (in Cambridge, UK) 20th October 2008, Accepted 24th December 2008 First published as an Advance Article on the web 27th January 2009 DOI: 10.1039/b818537a

Pt(η^5 -C₅Me₅)(PR₃)I (PR₃ = PPh₃, PPhCy₂, PPhMe^tBu) reacts with ³O₂ to form the metal-bound endoperoxide Pt(η^1 , η^2 -C₅Me₅O₂)(PR₃)I; analogous reactions of Pt(η^5 -C₅Me₅)(PPh₃)I with a variety of other dienophiles to form Pt(η^1 , η^2 -C₅Me₅CH₂CHR)(PPh₃)I (R = C(O)H, CO₂Me, C(O)Et) in which the metal is *anti* to the incoming dienophile are indicative of direct Diels–Alder addition to the η^5 -C₅Me₅ ring.

Although Diels-Alder [4 + 2] cycloadditions to metal-bound η^1 -cyclopentadienyl rings are not uncommon and have been utilised in the synthesis of substituted norbornenes and norbornadienes,¹ formal Diels-Alder [4 + 2] cycloadditions to metal-bound η^5 -cyclopentadienyl rings are rare and are only found when the dienophile is an electron deficient alkyne, the classic case being the addition of dimethylacetylene dicarboxylate to nickelocene.² In all examples, however, the double bond originating from the dienophile ends up bound to the metal in the final metal-bound η^1, η^2 -norbornadiene and a mechanism involving a metal mediated condensation of an η^{1} -cyclopentadienyl intermediate that also contains the metalbound alkyne is thought to be operative. This is unfortunate because direct Diels–Alder addition to an η^5 -ring would offer an inherently face-selective methodology.³ Herein we describe this specific reactivity of a platinum-bound η^5 -pentamethylcyclopentadienyl ring to a variety of dienophiles including dioxygen.

Whereas solutions of $Pt(\eta^5-C_5Me_5)(CO)I$ in aerated $CDCl_3$ are stable for several hours as might be expected for a Pt(II)complex, the corresponding solutions of $Pt(\eta^5-C_5Me_5)(PR_3)I$ (R = aryl, alkyl), **1**, rapidly change from an initial green colour to pale yellow over a few minutes. The NMR spectra of these pale yellow solutions revealed that the fivefold degeneracy of the cyclopentadienyl ring had been broken with the new, quantitatively generated species exhibiting a 1:2:2ratio of both the ring carbon and ring methyl resonances, further reduced to 1:(1:1):(1:1) when the phosphine contained three differing R groups. Particularly distinctive were the unique methyl resonance in the ¹H NMR spectra (~0.3 ppm, ²J_{PtH} = ~60 Hz) and the unique ring carbon in the ¹³C{¹H} NMR spectra (~40 ppm), which exhibited a platinum carbon constant characteristic of a σ -bound carbon (~500 Hz). Although these parameters are indicative of $\eta^5 \rightarrow \eta^1$ ring slippage, the magnitudes of the platinum and phosphorus coupling constants to the remaining pentamethyl-cyclopentadienyl resonances were inconsistent with a ring slipped product.⁴ Furthermore, the long-term stability of solutions of Pt(η^5 -C₅Me₅)(PPh₃)I under anaerobic conditions suggested to us that the new products arose from aerial oxidation.

On a preparative scale, stirred green solutions of $Pt(\eta^5-C_5Me_5)(PR_3)I$ (PR₃ = PPh₃, 1a, PPhCy₂, 1b, PMe^tBuPh, 1c)§ in open vessels completely react at room temperature over 2–3 h affording, on work-up, pale yellow complexes, 2, with identical NMR spectroscopic properties to the species formed *in situ*.¶ It was found that the same reaction takes place in the dark with no diminution in rate and also in the presence of



Fig. 1 An ORTEP diagram of the molecular structure of **2b** showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (°). Pt–I 2.6913(17), Pt–C2 2.08(2), Pt–P 2.286(5), Pt–(midpt)C4/C5 2.129, C4–C5 1.41(3), O1–O2 1.52(3), C2–Pt–P 105.6(5), C2–Pt–I 158.0(5), P–Pt–I 96.33(14), I–Pt–(midpt)C4/C5 97.86, C2–Pt–(midpt)C4/C5 60.19.

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[†] Electronic supplementary information (ESI) available: Full synthetic procedures, analytical and spectroscopic data for complexes **2** and **3** as well as CIF files for complexes **2b** and **3c**. CCDC 706170 and 706171. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b818537a

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radical scavengers as well as in the solid state, albeit over several weeks.

The structure of **2b** was subsequently identified by X-ray crystallography (Fig. 1) as a metal-bound endoperoxide arising from dioxygen addition to the pentamethylcyclopentadienyl ring, $Pt(\eta^1, \eta^2-C_5Me_5O_2)(PPh_3)I$ **2b** (Scheme 1).|| The dioxygen has essentially undergone Diels–Alder addition to the ring on the opposite face to the metal forming an endoperoxide group coordinated to the metal *via* a σ and a π bond with a "bite" of 60.2° resulting in a platinum atom in a distorted square planar environment. The iodide is *trans* to the σ -bound carbon of the endoperoxide group. The O–O distance 1.52(3) Å is within the range expected for a cyclic peroxide linkage.⁶

The endoperoxides **2** are light sensitive and decompose over several days. The only platinum species we have been able to identify after decomposition are the known halo phosphine complexes *trans*-[Pt₂(PR₃)₄I₂] and *trans*-[Pt(PR₃)₂I₂].⁷ As yet, the fate of the organic fragment is unknown.

There are only sporadic reports of reactions of metal-bound carbocyclic ligands with dioxygen. The radicals $Co(n^5-C_5H_5)_2$ and $Fe(\eta^5-C_6H_6)(\eta^5-C_5H_5)$ react with O₂ to form dimeric complexes containing bridging peroxo bridges between the C_5H_5 and C_6H_6 rings, respectively.⁸ [Rh(η^4 -diphenylfulvene)₂]⁺ reacts with O2 generating a bis-cyclopentadienyl cation with a peroxide bridge between the exocyclic carbons of the diphenyl substituent,9 while an iridium metallabenzene undergoes 1,4-addition of O₂ across the ring generating a bicyclic peroxide.¹⁰ Insertion into metal alkyl and metal hydrogen bonds generating linear peroxides is also well established.¹¹ In other examples, reaction with oxygen leads to oxygen atom transfer¹² or deprotonation of the carbocyclic ring.¹³ Pentamethylcyclopentadiene itself reacts with O₂ to form a pyrylium salt via the intermediacy of a peroxide arising from O₂ insertion into the ring C-H bond,¹⁴ whereas with singlet oxygen an endoperoxide is formed.¹⁵

Diels–Alder addition of dioxygen to an η^5 -bound cyclopentadienyl group is unprecedented, but the reaction is analogous to Diels–Alder addition of singlet dioxygen to cyclopentadienes. Diels–Alder addition of triplet dioxygen, although formally spin forbidden, is known to occur for several diene systems, particularly those in which there is a degree of ring strain, and is thought to follow a radical pathway.¹⁶ The degenerate "diene" and "allyl-ene" distortions of the ring in d⁸-M(η^5 -C₅R₅)L₂ systems are well established¹⁷ and it is possible that on platinum the distortion has become sufficiently diene-like, with a corresponding inherently high degree of ring strain, that the ring is now susceptible to spontaneous oxidation through the established radical pathway.

In support of this, we have found that the platinum-bound η^5 -pentamethylcyclopentadienyl ring will undergo Diels–Alder



addition to a variety of other standard dienophiles (Scheme 2). For example, hexane solutions of $Pt(\eta^5-C_5Me_5)(PPh_3)I$ react with acrolein, methyl acrylate or ethyl vinyl ketone at elevated temperatures over 1-2 days to afford $Pt(\eta^{1}, \eta^{2}-C_{5}Me_{5}CH_{2}CHR)(PPh_{3})I (R = C(O)H, 3a, R =$ CO_2Me , **3b**, R = C(O)Et, **3c**) in essentially quantitative yields. These show similar NMR spectroscopic features to the endoperoxides, with additional resonances attributable to the fragment arising from the dienophile.** In all cases, both exo and endo isomers were formed; however, only with the less sterically demanding acrolein were significant quantities $(\sim 15\%)$ of the exo isomer generated. The endo-ethyl vinyl ketone derivative, 3c, (Fig. 2) was also characterised by X-ray crystallography.^{††} The structure and structural parameters are very similar to those of **2b** with the peroxide linkage replaced by the endo-CH₂CHC(O)Et group.

It is difficult to envisage how the *anti* stereochemistry (with respect to the metal) found for the bicyclic ring in the crystal structures of **2b** and **3c** can be generated other than by direct [4 + 2] addition as a metal templated addition would generate



Fig. 2 An ORTEP diagram of the molecular structure of 3c showing 50% probability thermal ellipsoids. Selected bond distances (in Å) and angles (°). Pt–I 2.6969(9), Pt–C2 2.105(8), Pt–P 2.262(2), Pt–(midpt)C4/C5 2.164, C2–Pt–P 102.0(2), C2–Pt–I 159.6(2), P–Pt–I 98.01(6), I–Pt–(midpt)C4/C5 98.80, C2–Pt–(midpt)C4/C5 60.83.

a norbene fragment with the corresponding *syn* stereochemistry. Such a fragment would be unable to coordinate to the metal in the manner found. By contrast, reaction of nickelocene with the activated alkenes methylketene or tetrafluoroethylene results in [2 + 2] cycloaddition not [4 + 2] cycloaddition.¹⁸ The reactivity found for these platinum systems suggests that group 10 metal mediated addition may provide a solution to the long sought goal of facial selectivity in Diels–Alder addition reactions to cyclic systems.

Notes and references

§ The species 1 were obtained from the hexane mediated reaction of $Pt(\eta^5-C_5Me_5)(CO)I$ with the appropriate phosphine. $Pt(\eta^5-C_5Me_5)(CO)I$ was prepared by reaction of $Pt_2(\eta^5-C_5Me_5)_2(CO)_2$ with I_2 at -116 °C (ether slush).⁵

¶ Spectroscopic data for **2b**: ¹H NMR (CD₂Cl₂) δ 7.5–7.4 (m 5H, Ph), 2.8–1.0 (m 22H, Cy), 1.97 (d, 6H, Me, $J_{PH} = 3.0$ Hz, $J_{PtH} = 27.7$ Hz), 1.34 (s, 6H, Me), 0.39 (d, 3H, Me, $J_{PH} = 0.9$ Hz, $J_{PtH} = 61.5$ Hz); selected ¹³C{¹H} (CD₂Cl₂) δ 113.2 (d, 2C, =CMe, $J_{PC} = 13$ Hz, $J_{PtC} = 78$ Hz), 95.9 (d, 2C, C(O)Me, $J_{PC} = 4$ Hz, $J_{PtC} = 69$ Hz), 42.0 (s, 1C, CMe, $J_{PtC} = 503$ Hz), 13.3 (br s, 2C, Me, $J_{PtC} = 11$ Hz), 10.7 (s, 2C, Me, $J_{PtC} = 17$ Hz), 9.1 (s, 1C, Me, $J_{PC} = 4$ Hz); ¹⁹⁵Pt{¹H} (C₆D₆, $\Xi = 21.4$), δ 444 (d, $J_{PtP} = 4461$ Hz); ³¹P{¹H}(C₆D₆) δ 28.3 (s, $J_{PtP} = 4459$ Hz).

|| Crystal data for **2b**: C₂₈H₄₂IO₂PPt, M = 763.58, monoclinic, a = 9.954(3), b = 11.961(4), c = 12.053(5) Å, $\beta = 93.41(3)^\circ$, U = 1432.5(8) Å³, T = 203(2) K, space group $P2_1$, Z = 2, 3645 reflections measured, 3455 unique ($R_{int} = 0.0480$); reflections with $I > 2\sigma(I) = 2440$, $R_1 = 0.063$ ($I > 2\sigma(I)$), w $R_2 = 0.142$ (all data), GOF = 1.039. ** Spectroscopic data for **3b** (major isomer): selected ¹H NMR (C_6D_6) δ 1.98 (d, 3H, Me, $J_{PH} = 3.3$ Hz, $J_{PtH} = 30.8$ Hz) 1.81 (d, 3H, Me, $J_{PH} = 3.2$ Hz, $J_{PtH} = 36.6$ Hz), 1.47 (s, 3H, Me), 1.33 (s, 3H, Me), -0.19 (d, 3H, Me, $J_{PH} = 1.3$ Hz, $J_{PtH} = 64.0$ Hz); selected ¹³C{¹H} (CD₂Cl₂) δ 173.4 (s, 1C, C(O)), 113.8 (d, 1C, =CMe, $J_{PC} = 15$ Hz, $J_{PtC} = 68$ Hz), 110.0 (d, 1C, CMe, $J_{PC} = 13$ Hz, $J_{PtC} = 73$ Hz), 67.4 (s, 1C, CMe, $J_{PtC} = 84$ Hz), 63.2 (s, 1C, CMe), 39.9 (s, 1C, CH₂, $J_{PtC} = 111$ Hz), 51.2 (s, 1C, CO₂Me), 39.9 (s, 1C, CH₂, $J_{PtC} = 17$ Hz), 15.2 (s, 1C, Me, $J_{PtC} = 17$ Hz), 14.4 (s, 1C, Me, $J_{PC} = 32$ Hz), 13.5 (d, 1C, Me, $J_{PtC} = 34$ Hz), 14.7 (C₆D₆, $\Xi = 21.4$), δ 719 (d, $J_{PtP} = 4587$ Hz); ³¹P{¹H}(C₆D₆) δ 19.9 (s, $J_{PtP} = 4588$ Hz).

†† Crystal data for **3c**: $C_{28}H_{42}IO_2PPt$, M = 803.59, a = 9.490(3), b = 15.263(4), c = 21.282(7) Å, $\beta = 92.55(2)^{\circ}$, U = 3079.5(15) Å³, T = 293(2) K, space group monoclinic, $P2_1/c$, Z = 4, 7499 reflections measured, 7094 unique ($R_{int} = 0.0314$); reflections with $I > 2\sigma(I) = 4258$, $R_1 = 0.049$ ($I > 2\sigma(I)$), w $R_2 = 0.115$ (all data), GOF = 1.053.

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