Appendix A

Facial coordination of a pincer-like amido complex of platinum(IV) generated by photoisomerization[†]

[†] Adapted from Harkins, S. B.; Peters, J. C.; Facial coordination of a pincer-like amido complex of platinum(IV) generated by photoisomerization. *Inorg. Chem.*, to be submitted for publication.

Introduction

A growing number of mono-anionic chelating pincer-like amido ligands which contain a diaryl amide functionality {(LNL)$^-$} are currently being explored.[1,2,3,4,5] Prior to this manuscript, these metal complexes have been described exclusively with meridinal ligand coordination. Our group and others have described cationic Pt complexes supported by (LNL)$^-$ ligands that have been shown to mediate C-H bond activation of benzene.[b,d] It is well documented that Pt^{IV} intermediates are involved in the catalytic oxidation of alkanes in Shilov-like processes using Pt^{II} catalysts.[6,7] Although in related chelating nitrogen ligand complexes of Pt^{II}, oxidation to Pt^{IV} with alkyl halides is readily achieved, the discrete oxidative addition of a substrate to an {(LNL)Pt^{II}} complex has yet to be demonstrated.[8] This manuscript describes the oxidative addition of MeI and subsequent photoisomerization and protonation of (BQA)PtMe, **1a** {BQA = bis(8-quinolinyl)amine}.

We have previously reported the synthesis and characterization of **1a**, and its protonation with triflic acid to afford the neutral complex (BQA)Pt(OTf).[b] This triflato complex undergoes base-promoted C-H activation of benzene at 150 °C to generate (BQA)PtPh (**1b**) in high yield.[b] Subsequently, we have found that addition of a catalytic amount of $B(C_6F_5)_3$ (0.2 equivalents) to **1a** in benzene quantitatively generates **1b** in 5 h at 70 ºC. The focus of our current work has been to examine the intriguing behavior of (BQA)Pt^{IV} complexes, and we have been able to induce a facile ligand isomerization which affords an unprecedented *sp^3*-hybridized diarylamido moiety.

Results and Discussion

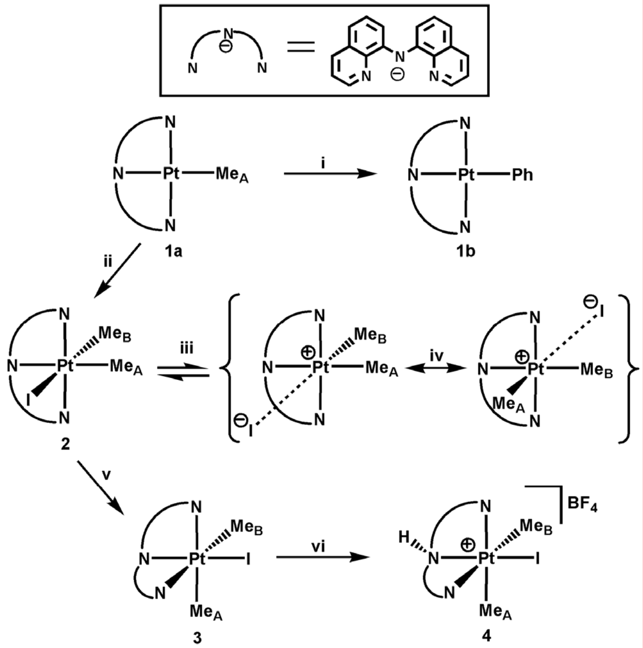

Figure 1: Synthesis of **1b**, **2**, **3**, and **4**. Conditions: (i) 0.2 equiv. $B(C_6F_5)_3$, C_6H_6, 5 h, 20 ºC; (ii) 10 equiv. MeI, acetone, 70 °C, 18 h; (iii) iodide dissociation; (iv) methyl scrambling; (v) acetone, 100 W incandescent light, 48 h; (vi) HBF_4 etherate, CH_2Cl_2, 2h.

Addition of MeI to **1a** in acetone results in the formation of (*mer*-BQA)$PtMe_2I$, **2**, as a purple solid in very good yield (Figure 1). This reaction proceeds sluggishly at 25 °C in comparison to most oxidative additions reported for organoplatinum(II) complexes with nitrogen-donor ligands and must be heated at 70° C for 18 h to reach completion. Complex **2** has λ_{max}= 534 nm (ε 15 500 $M^{-1}cm^{-1}$) which is slightly shifted to lower energy from **1a**, which has λ_{max}= 527 nm (ε 12 000 $M^{-1}cm^{-1}$).[b] There are three resonances in the ^1H NMR which exhibit strong ^{195}Pt-H coupling: the 2-position proton of the quinoline ring, 8.71 ppm ($^3J_{PtH}$ =41 Hz); the equatorial methyl group, 1.67 ($^2J_{PtH}$ = 60 Hz); and the axial methyl group, 1.43 ($^2J_{PtH}$ = 70 Hz). These initial assignments were made based on literature values for the $^2J_{PtH}$ coupling constants[9] and were confirmed by a 1D-NOE ^1H NMR experiment. The NOE experiment was performed by saturation

(0.5 s mixing time) of the 2-position proton (8.71 ppm) of the quinoline ring. Coupling was observed to the equatorial methyl protons (1.67 ppm) and no coupling to the axial methyl protons (1.43 ppm) was observed. The solid-state structure of **2** was determined by X-ray diffraction (Figure 2), confirming the *cis* relationship between the methyl groups.

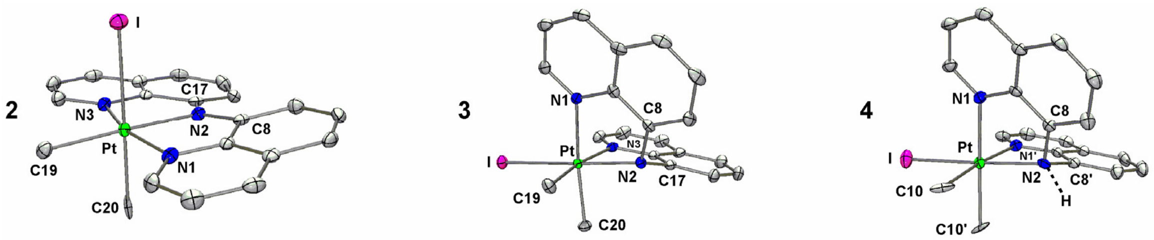

Figure 2: Solid-state molecular structures (50% ellipsoids) for **2**, **3**, and **4** (H atoms and BF$_4$ anion omitted).

Table 1: Bond Lengths and Angles for (*mer*-BQA)PtMe$_2$I (**2**), (*fac*-BQA)PtMe$_2$I (**3**), [H(*fac*-BQA)PtMe$_2$I][BF$_4$] (**4**)

	2	3	4
Pt-N1	2.008(4) Å	2.137(3) Å	2.152(4) Å
Pt-N2	2.033(3) Å	2.036(3) Å	2.135(6) Å
Pt-N3	2.017(4) Å	2.146(3) Å	– [b]
Pt-I	2.783(1) Å	2.630(2) Å	2.598(1) Å
Pt-C19{10} [a]	2.088(5) Å	2.052(3) Å	2.152(4) Å
Pt-C20	2.102(5) Å	2.045(3) Å	– [b]
N2-Pt-I	90.16(9)°	177.73(7)°	177.95(15)°
N2-Pt-N1	81.47(16)°	81.06(10)°	80.62(11)°
N2-Pt-N3	81.82(16)°	80.53(10)°	– [b]
N1-Pt-N3	163.22(17)°	97.50(10)°	94.67(12)°
C19{10}-Pt-C20{10} [a]	87.15(17)°	90.55(12)°	87.08(16)°
C8-N2-C17{8'} [c]	131.93(42)°	114.82(25)°	114.02(17)°

a: C17, C19 and C20 corresponds to **2** and **3**, C8' and C10 corresponds to **4**. *b*: values are omitted because they are generated by the symmetry transformation {x,-y+1/2,z}; *c*: C8' generated by a symmetry transformation {x,-y+1/2,z}

The oxidative addition was also performed using d_3-MeI under the same conditions, and a 1:1 mixture of axial and equatorial CD_3 products was observed, as confirmed by both ^{1}H and ^{2}H NMR experiments. This result is indicative of iodide dissociation in solution which facilitates mixing of the labeled methyl group between the axial and equatorial positions (iii and iv, Figure 1). The 1:1 ratio is expected in this case because both alkyl groups (CH_3, CD_3) are of comparable size and there is no steric preference. These findings are consistent with reports by Puddephatt and co-workers, where analogous results were observed for {*cis*-1-(N=CHC_6H_4)-2-(N=CHC_6H_5)C_6H_{10}}PtMe_2I.

During our study of **2**, we encountered a new product which seemed to grow in over time. It was found that photolysis of **2** in acetone resulted quantitatively in the ligand isomerization product *fac*-BQAPt$(Me)_2$I, **3** (Figure 1).[10] We initially hypothesized that the new isomer was an octahedral Pt^{IV} complex where the methyl groups had migrated from a *cis* to a *trans* conformation and that the iodo group migrates *trans* to the amide of the *mer*-BQA ligand. The ^{1}H NMR spectrum displays a single methyl resonance at 1.25 ppm ($^2J_{PtH}$ = 71 Hz) which integrates to 6H and exhibits no NOE to the 2-position protons of the quinoline rings.

The solid-state molecular structure of **3** (Figure 2) was determined by X-ray diffraction and revealed that the initial model was inaccurate. The structure of **3** is in fact an octahedral Pt^{IV} complex where the BQA ligand is coordinated facially[11] and the two methyl groups are each *trans* to the neutral quinoline nitrogen ligands and *cis* to each other (90.55(12)°). The iodo ligand is *trans* to the amido-nitrogen and the Pt-I bond has shortened by 0.15 Å which is reflective of an increased bonding interaction (Table 1). This is likely a consequence of decreased electron density at Pt resulting from diminished lone-pair donation from the pyramidalized amide-N. The most interesting structural aspect is that the amide is now pyramidalized with *sp*^{3}-hydridization, characterized by the contraction of C8-N2-C17 angle from 131.93(42)° in **2** to 114.82(25)° in **3**. This geometry for nitrogen has not been reported previously for transition metal diaryl amide complexes.[12] Complex **3** is red in color, rather than purple as observed for **2** (Figure 3). It is probable that this results from disruption of the amide-nitrogen lone pair donation to the metal center caused when the ligand assumes a folded geometry.

To the best of our knowledge an anionic tridentate ligand that is able to isomerize from *mer* to *fac* in an octahedral complex has not been reported. Tridentate, monoanionic ligands have been reported that bind to Pt to form either square planar Pt^{II} complexes or octahedral Pt^{IV} complexes with facial geometries.[13,14] The (BQA)Pt^{IV} system is particularly intriguing because the reaction is photolytically driven. Shaw and coworkers have reported the octahedral complex L'Ru(CO)Cl$_2$ {L' = ((Ph$_2$P)CH$_2$(^{t}Bu)C=N-)$_2$}which undergoes a related *mer* to *fac* photoisomerization. However, (BQA)PtMe$_2$I and L'Ru(CO)Cl$_2$ are largely dissimilar because the latter involves isomerization resulting from the photolytic dissociation of CO.[15] Shaw's system also does not present the highly pyramidalized geometry about the central nitrogen.

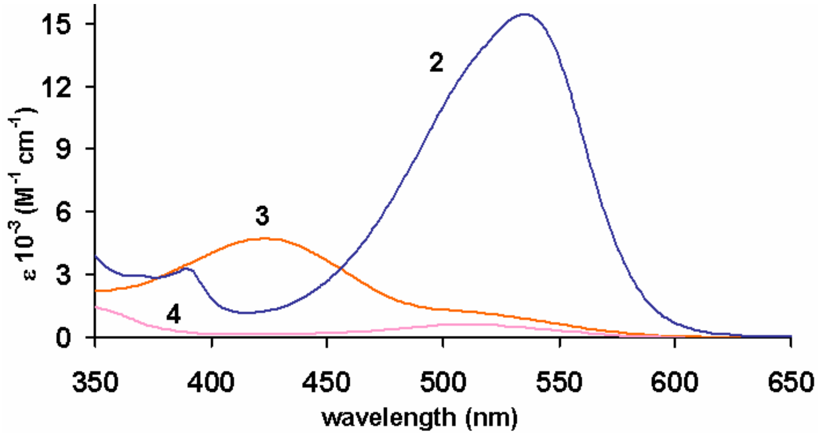

Figure 3: Absorption spectra of **2**, **3** and **4** in CH$_2$Cl$_2$

The tetrahedral geometry at the amide nitrogen suggests that the lone pair on nitrogen donates to Pt to a much lesser extent in **3** than **2** which is also indicated by the drastic change in the Pt-amide MLCT band from λ_{max}= 534 nm in **2** to λ_{max}= 422 nm in **3**. This charge transfer assignment is supported by empirical observation that addition of HBF_4 etherate to **3** in CH_2Cl_2 results in the immediate bleach of the absorption band at 422 nm while preserving the lower energy band at 510 nm (Figure 3).

The protonated complex **4** (Figure 1) was isolated in near quantitative yield (97%) as a rose colored solid. By ^{1}H NMR spectroscopy a distinct downfield resonance assigned to N-H is now present (10.33 ppm) and integrates to one proton and exhibits easily discernable ^{195}Pt satellites ($^2J_{PtH}$ = 21 Hz). The observation of a single methyl resonance (1.54 ppm) with integration of 6H and unchanged ^{195}Pt coupling ($^2J_{PtH}$ = 70 Hz) also indicates that this protonation has not significantly effected the geometry of the complex. A 1D-NOE (1.0 s mixing time) experiment with saturation of the N-H proton resonance (10.33 ppm) indicated coupling to both the 8-position proton of the aryl ring (8.78 ppm) as well as to the methyl resonance (1.54 ppm). A new, broad absorption in the IR spectrum at ν = 3127 cm^{-1} attributed to an N-H vibration is consistent with the assignment of **4**.

The absolute structure of **4** was determined by X-ray diffraction (Figure 3). Notably, the Pt-amide and Pt- methyl bond lengths each elongate by 0.1 Å. Additionally, H11, the proton on N2, is hydrogen bonded to the BF_4^- counter ion (N2−F1: 2.821(7) Å). This is also manifested in the broadened N-H stretch in the solid and solution IR spectrum of **4**. Neutral diaryl amine adducts of transition metals are exceedingly rare and have only been reported as a part of chelating ligands. The Pt-N2 bond of **4** is the shortest of this type to be reported. For comparison unchelated diphenylamine adducts of $AlCl_3$[16] and

$GaMe_2Cl$[17] have been reported which exhibit C_{aryl}-N-C_{aryl} bond angles of 110.5(4)° and 105.2(2)°, respectively. These angles are somewhat more contracted than the comparable C8-N2-C8' angle of **3** (114.82(25)°) and **4** (114.02(17)°).

A possible mechanism for this reaction proceeds through an intermediate whereby the iodide ligand must first dissociate. A photon absorbed by this five-coordinate intermediate then destabilizes the metal-amide bond allowing for relaxation of the structure to accommodate a more sp^3-hybridized geometry about the amide nitrogen. This folded geometry is then trapped by recoordination of the iodide. This postulated mechanism is supported by the observation that the iodide ligand readily dissociates in solution, allowing for the scrambling of the methyl groups. The isomerization is also severely attenuated when photolyzed in a saturated NaI solution in acetone, which would be expected to inhibit iodide dissociation. Shortening of the Pt-I bond distance in **3** compared to **2**, with no appreciable change in the Pt-N2 bond distance, supports the idea of a trapped structure resulting from a stronger Pt-I interaction.

In conclusion, we have presented the first example of an octahedral Pt^{IV} complex containing a diaryl amide moiety. The observation that the (BQA)Pt^{IV} system undergoes an isomerization which results in a facially capped metal complex could lead to the design of novel C-H bond functionalization pathways via proton shuttling followed by reductive elimination in a catalytic cycle. Research in our laboratory into the unique chemical bonding of chelating diaryl amide ligands to metals is ongoing.

Experimental Section

General: All manipulations were carried out using standard Schlenk or glove box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried thoroughly by sparging with N_2 gas followed by passage through an activated alumina column. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective oxygen and moisture removal. The preparation of (BQA)PtMe was previously reported.[1b] Other reagents were purchased from commercial vendors and used without further purification. Elemental analyses were performed by Desert Analytics, Tucson, Az. A Varian Mercury-300 NMR spectrometer or a Varian Inova-500 NMR spectrometer was used to record ^{1}H, ^{2}H, ^{13}C, and ^{19}F NMR spectra. 1D-NOE experiments were conducted using the Varian *GLIDE* software package. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{19}F NMR chemical shifts were referenced to an external C_6F_6 sample with a chemical shift of –165 ppm. Deuterated solvents were purchased from Cambridge Isotope Labs and were degassed and dried over activated 3 Å molecular sieves prior to use. UV-vis spectra were collected on a Cary 50 spectrophotometer in CH_2Cl_2 with 1 cm quartz cuvettes. IR measurements were obtained with a KBr solution cell using a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Bio-Rad Merlin Software (v. 2.97) set at 4 cm^{-1} resolution. X-ray diffraction studies were carried out at the Beckman Institute Crystallographic Facility on a Brüker Smart 1000 CCD diffractometer and solved using SHELX v. 6.14.

Synthesis of (*mer*-BQA)Pt(CH_3)$_2$I / (*mer*-BQA)Pt(CH_3)(CD_3)I, 2: A solution of (BQA)PtMe (400 mg, 0.833 mmol), CH_3I (103 μL, 1.67 mmol), and acetone (50 mL) were combined in a glass reaction bomb, sealed with its Teflon stopcock, and heated to

70 °C for 18 h in the absence of light. The purple solution was evaporated to dryness under reduced pressure, and washed with petroleum ether (2 x 40 mL). Drying *in vacuo* of the powdery-purple solid (470 mg, 92%) yield a spectroscopically pure product. X-ray quality crystals were obtained by vapor diffusion of petroleum ether into acetone. Reactions with CD_3I proceeded under identical conditions. Characterization data for the all protio form: ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 8.71 (m, $^2J_{PtH}$ = 41 Hz, 2H), 8.30 (d, 2H), 7.77 (d, 2H), 7.66 (t, 2H), 7.48 (m, 2H), 7.16 (d, 2H), 1.67 (s, $^2J_{PtH}$ = 60 Hz, 3H), 1.43 (s, $^2J_{PtH}$ = 70 Hz, 3H). ^{13}C NMR (CD_2Cl_2, 126 MHz, 25 °C): δ 155.1, 146.7, 140.3, 139.4, 133.4, 130.9, 122.3, 115.7, 115.6, 15.2 ($^1J_{PtC}$ = 550 Hz), 1.89 ($^1J_{PtC}$ = 582 Hz). UV-vis (nm (ε M^{-1} cm^{-1}), CH_2Cl_2): 292 (30000), 300 (27100), sh 396 (2900), 388 (3400), 534 (15500). IR (cm^{-1}, KBr): 3053 (vw), 2902 (w), 1582 (m), 1564 (s), 1496 (s), 1463 (s), 1400 (s), 1225 (w), 1180 (m), 1134 (m), 813 (m), 770 (m), 736 (m). Anal. Calcd. for $C_{20}H_{18}IN_3Pt$: C, 38.60; H, 2.92; N, 6.75. Found: C, 38.76; H, 3.15, N, 6.51.

Synthesis of (*fac*-BQA)Pt(CH_3)$_2$I / (*fac*-BQA)Pt(CH_3)(CD_3)I, 3: A solution of **2** (196 mg, 0.315 mmol) in acetone (20 mL) was added to a 200 mL reaction bomb, sealed with its Teflon stopcock, and placed 2 in. underneath a 100 watt incandescent light bulb for 48 h, with periodic agitation. During this period, the solution went from purple to red in color. The solvent was removed under reduced pressure affording a red solid which was washed with petroleum ether and dried *in vacuo* (196 mg, >99%). Quantitative conversion was observed by NMR spectroscopy. Reactions with (*mer*-BQA)Pt(CH_3)(CD_3)I proceeded under identical conditions. Characterization data for the all protio form: ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 9.80 (m, $^3J_{PtH}$ = 17 Hz, 2H), 8.25 (m, 2H), 7.96 (d, 2H), 7.58-7.47 (m, 4H), 7.40 (d, 2H), 1.25 (s {Pt-CH_3}, $^2J_{PtH}$ = 71 Hz, 6H). ^{13}C NMR (CD_2Cl_2, 126 MHz, 25 °C): δ 159.7, 150.2, 147.1, 138.3, 131.1, 129.1, 123.4, 122.7, 121.2, -8.0 (${}^{1}J_{PtC}$ = 602 Hz). UV-vis (nm (ε M^{-1} cm^{-1}), CH_2Cl_2): 284 (15900), sh 298 (10600), sh 325 (4000), 422 (4700), sh 502 (1300). IR (cm^{-1}, KBr): 3051 (w), 2962 (w), 2897 (m), 1575 (m), 1565 (m), 1497 (s), 1458 (s), 1374 (s), 1308 (m), 1256 (m), 1224 (m), 1113 (m), 1056 (w), 1031 (w), 841 (w), 810 (m), 772 (m). Anal. Calcd. for $C_{20}H_{18}IN_3Pt$: C, 38.60; H, 2.92; N, 6.75. Found: C, 38.81; H, 3.18, N, 6.50.

Synthesis of [H(*fac*-BQA)Pt(CH_3)$_2$I][BF_4], 4. A 54 wt% solution of HBF_4 in ether (19 μL, 0.137 mmol) was added to a solution of **4** (81 mg, 0.130 mmol) in CH_2Cl_2 (7 mL) in a glass scintillation vial. The reaction was stirred for 2 h at 25 °C and the product was precipitated by addition of petroleum ether (13 mL). The rose colored solid (90 mg, 97%) was collected on a fritted glass funnel and dried *in vacuo*. The product was found to be pure by ${}^{1}H$ NMR spectroscopy and micro analysis. Crystals for X-ray diffraction were obtained by diffusion of petroleum ether in to a concentrated solution of **4** in THF. ${}^{1}H$ NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 10.33 (s {N-H}, ${}^{2}J_{PtH}$ = 21 Hz, 1H), 9.90 (m, ${}^{3}J_{PtH}$ =17 Hz, 2H), 8.78 (d, 2H), 8.50 (m, 2H), 7.96 (m, 2H), 7.83 (t, 2H), 7.74 (m, 2H) 1.54 (s {Pt-CH_3}, ${}^{2}J_{PtH}$ = 70 Hz, 6H). ${}^{13}C$ NMR (CD_2Cl_2, 126 MHz, 25 °C): δ 152.0, 144.8, 143.7, 139.9, 131.5, 130.5, 130.1, 129.9, 125.0, -12.41 (${}^{1}J_{PtC}$ = 514 Hz). ${}^{19}F$ NMR (CD_2Cl_2, 282 MHz, 25°C): δ -147.4 (d, ${}^{1}J_{BF}$ = 15 Hz). UV-vis (nm (ε M^{-1} cm^{-1}), CH_2Cl_2): 302 (12900), 317 (10000), sh 240 (1700), 510 (630). IR (cm^{-1}, KBr): 3077 (br, N-H), 2978 (w), 2903 (w), 1510 (s), 1467 (m), 1398 (m), 1358 (m), 1221 (w), 1081 (s br, B-F), 835 (m), 798 (m), 769 (m) 734 (w). IR (cm^{-1}, CH_2Cl_2 sol. in KBr): 3127 (br, N-H), 2910 (w), 1591 (w), 1567 (w), 1513 1467 (w), 1359 (m), 1080 (s br), 1000 (m), 835 (m). Anal. Calcd. for $C_{20}H_{19}BF_4IN_3Pt$: C, 33.82; H, 2.70; N, 5.92. Found: C, 33.84; H, 2.46, N, 5.73.

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[10] Thermolysis of **2** in acetone (70 ºC) in the absence of light afforded no trace of **3** after 24 h.

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[11] The angle of intersection of the planes defined by the two quinoline arms is 97.5°.

[12] All angles around nitrogen <117º. Cambridge Structural Database; Cambridge University: Cambridge, England (accessed April 2005).

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