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Single-Electron Oxidation of Tungsten Acetylide Complexes $[(\eta^5\text{-}C_5H_5)(CO)(NO)W–C{\equiv}C–R]Li$

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The reaction of a tungsten acetylide complex $[(\eta^5\text{-}C_5H_5)(CO)(NO)W–C{\equiv}C–R]Li$ (**1**) [**1a**, R = C_6H_5; **1b**, R = $C(CH_3)_3$; **1c**, R = $Si(CH_3)_3$] with one equivalent of ferrocenium tetrafluoroborate $[Cp_2Fe][BF_4]$, acting as a one-electron oxidant in THF at –50 °C, leads to the bimetallic tungsten–alkynyl complexes $[(\eta^5\text{-}C_5H_5)(NO)W–C{\equiv}C–R]_2$ (**9**) [**9a**, R = C_6H_5; **9b**, R = $C(CH_3)_3$; **9c**, R = $Si(CH_3)_3$] as pale-orange crystals. The crystal structure of complex **9a** is reported.
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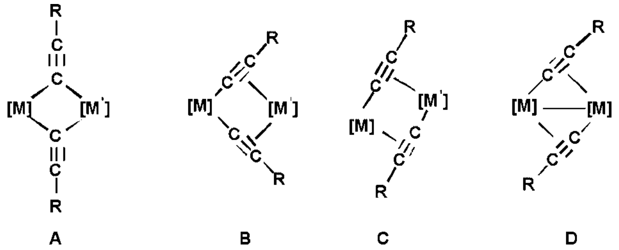
Introduction

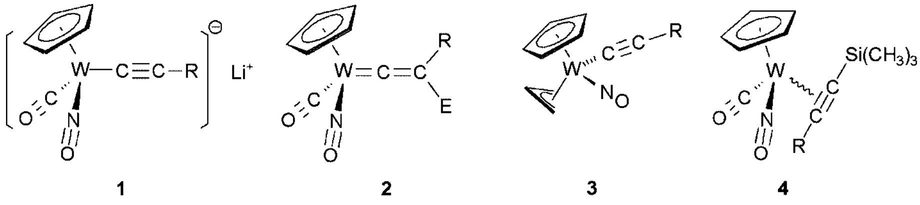
The chemistry of transition-metal acetylides M–C≡C–R and η^2-acetylene complexes has been the subject of much attention in the past years.[1] The nature of the metal–carbon bond in these systems and the possibility of conversion of alkynyl complexes to other organometallic derivatives, such as η^1-vinylidene complexes, are the subject of many investigations.[2] Furthermore, the fascinating properties of some alkynyl complexes in the field of materials science as possible nonlinear optical or luminescent materials as well as polymeric compounds have attracted much interest in recent years.[3]

As a strong σ-donor, the alkynyl group has a strong tendency to bind terminally to a main-group-metal- or transition-metal center. In the presence of a second metal atom, an alkynyl group can act either as a σ-donor to both metals (structure **A**, Scheme 1), or preferably as a σ-donor to one metal and a π-donor to the other metal center (structures **B** or **C**), depending on the nature of the metal and the ligands.[4,5] In this paper we describe the formation of binuclear σ,π-acetylide bridged complexes of type **D**, a structure analogous to **C** and additionally containing a tungsten–tungsten σ-bond.[6]



Scheme 1.

In a series of publications we have described the richly faceted chemistry of the σ-acetylide complexes $[(\eta^5\text{-}C_5H_5)(CO)(NO)W–C{\equiv}C–R]Li$ (**1**).[7] The preferred reactivity mode of these η^1-acetylide complexes is the addition of "hard" electrophiles E^+, such as a proton or alkylating reagents e.g. methyl triflate, to the β-carbon atom, which generates the corresponding η^1-vinylidene complexes **2**.[7g]



E = H or Alkyl

Scheme 2.

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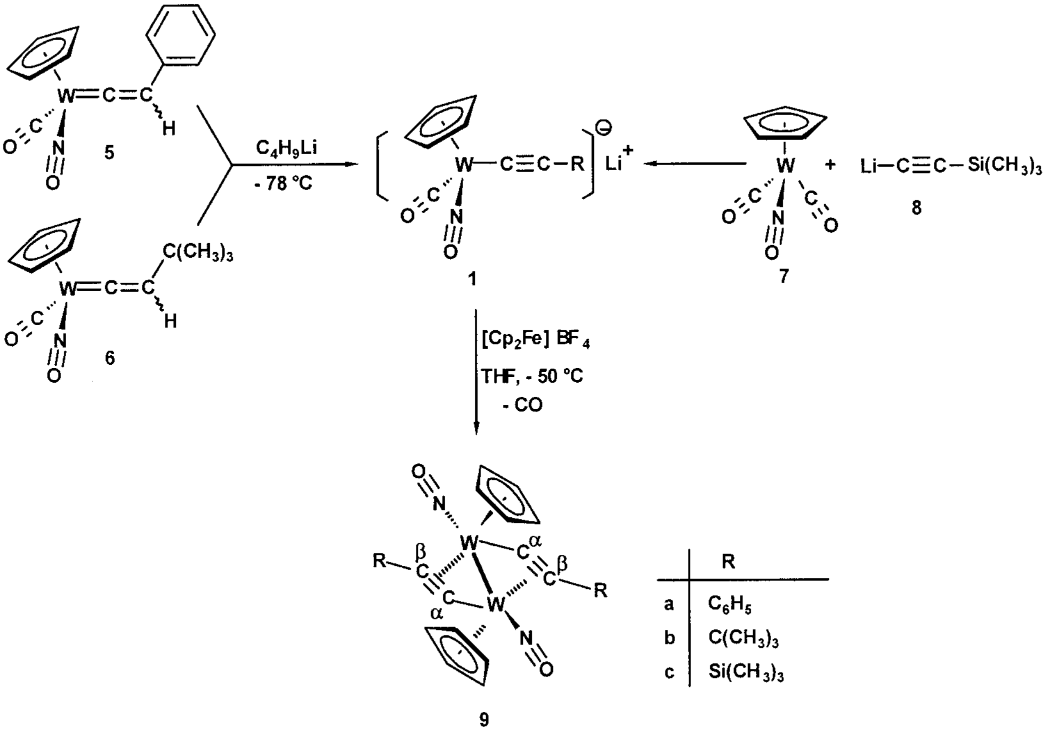
The addition of "soft" electrophiles, such as allyl iodide, furnishes complex **3**[7f] by allylation of the metal center, and η^2-acetylene complexes such as **4** are formed by reaction with trimethylsilylchloride (Scheme 2).[7g] The single-electron oxidation of this tungsten σ-acetylide complex by ferrocenium tetrafluoroborate $[Cp_2Fe][BF_4]$ is the subject of the present study.

Results and Discussion

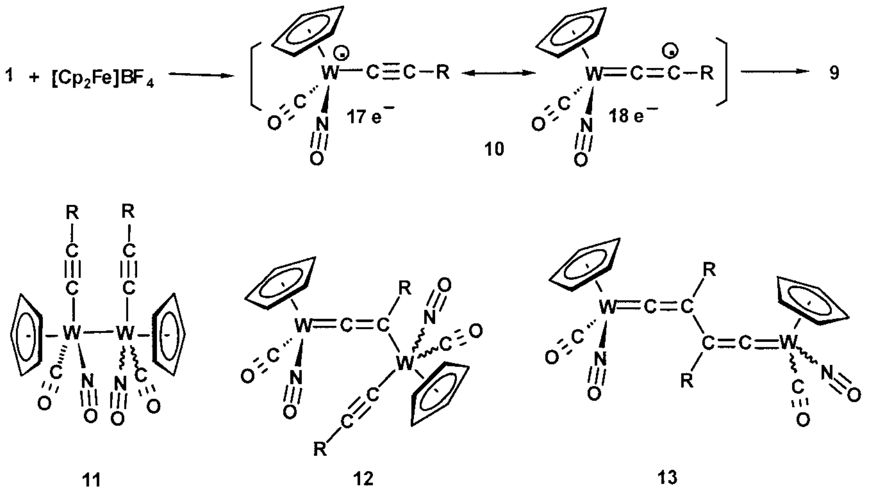
The reactants $[(\eta^5\text{-}C_5H_5)(CO)(NO)W\text{–}C\equiv C\text{–}R]Li$ [**1a**, R = C_6H_5; **1b**, R = $C(CH_3)_3$; **1c**, R = $Si(CH_3)_3$] were prepared as described previously,[7] either by the deprotonation of η^1-vinylidene complexes **5** and **6**, or alternatively by the reaction of lithium η^1-acetylide **8** with the tungsten–carbonyl complex **7**. Reaction of an emerald-green solution of **1** in THF at –50 °C with 1 equiv. of $[Cp_2Fe][BF_4]$, was monitored by IR spectroscopy. After 2 h the typical $\tilde{\nu}$(CO) band for the acetylide **1** (≈1870 cm^{-1}) disappeared while a new band characteristic for the C≡C group, in the range 1820–1852 cm^{-1}, appeared. Workup of the dark-red solution resulted, after purification through chromatography, in the formation of binuclear complexes **9a**–**c** as orange crystals in 25–54% yield (Scheme 3). The complexes **9a**–**c** are sparingly soluble in $CHCl_3$ and CH_2Cl_2 and can be stored under inert gas at –20 °C.

The unequivocal characterization of complexes **9a**–**c** was achieved by means of elemental analysis and by standard spectroscopic techniques. The structure of the products is further confirmed by the result of the single-crystal structure analysis of complex **9a**. In the IR spectrum, the signal for the $\tilde{\nu}$(C≡C) stretch of **9c** at 1820 cm^{-1} and similar IR bands for complexes **9a** (1847 cm^{-1}) and **9b** (1852 cm^{-1}) are in accordance with the related absorptions of the zirconocene complexes $[(RCp)_2Zr]_2(\mu\text{-}C\equiv C\text{–}R)_2$[5a,5c] (1770–1820 cm^{-1}) and the bimetallic tungsten–iron complexes $\{[(\eta^5\text{-}C_5H_5)\text{-}\mu\text{-}(CO)(NO)W][(\eta^5\text{-}C_5H_5)(CO)Fe\text{–}C\equiv C\text{–}R]\}$ (1861–1908 cm^{-1}).[8] The decrease in the $\tilde{\nu}$(C≡C) stretching frequency of **9c** is a result of the strong electron back-donation $Si\leftarrow C_\pi$.[9] Additionally, the IR spectra of complexes **9a**–**c** show for the nitrosyl ligand, as expected, a strong and broad signal in the 1553–1560 cm^{-1} region. At ambient temperature, the ^1H- and ^{13}C NMR spectra of complexes **9b** and **9c** show two singlets for both the Cp ligand and for the methyl groups, in the ratio 6:1 and 5:1 for **9b** and **9c**, respectively, indicating the presence of two isomers. Besides these signals, the most informative absorptions in the ^{13}C NMR spectra are the signals for the α-carbon atoms at δ = 167.7 ppm (**9b**) and 197.9 ppm (**9c**) and for the β-carbon atoms at δ = 124.4 ppm (**9b**) and 108.1 ppm (**9c**), which are characteristic for the π-bridging acetylide ligand.[8] Because of the β-effect of the $(CH_3)_3Si$ group in complex **9c**, the singlet of the α-carbon atom appears at lower-field. We believe that the minor signals of the Cp ligands and methyl groups present in the NMR spectra can be attributed to a stereoisomer of **9b** and **9c**, with (*Z*)-orientation of the cyclopentadienyl rings.[8]

Contrary to complexes **9b** and **9c**, the ^1H NMR spectrum of complex **9a** shows at room temperature, for the cyclopentadienyl ligand, one singlet at δ = 5.71 ppm, and in the ^{13}C NMR spectrum, a broad signal with low intensity at δ = 98.3 ppm. Signals for the acetylide carbon atoms were not detectable. Low-temperature ^{13}C NMR spectroscopy of this



Scheme 3.



Scheme 4.

complex in CD_2Cl_2 at –40 °C revealed sharp singlets for the Cp-carbon atoms (δ = 98.0 ppm), the α-carbon atom (δ = 177.3 ppm), and the β-carbon atom (δ = 112.2 ppm). Additionally, a small signal appeared at δ = 97.5 ppm, and was attributed to the Cp ligand of a second minor stereoisomer. Increasing the temperature to 90 °C ([D_2]-1,1,2,2-tetrachloroethane) also resulted in the sharpening and increased relative intensity of the Cp signal, as well as in the emergence of a signal for the β-carbon atom.[10] The observed dynamic features of complex **9a** are not yet fully understood. One possible explanation would be an (*E*/*Z*) isomerization at the metal center by the reversible opening of the tungsten–tungsten bond.

Mechanistic Considerations

As expected, the single-electron oxidation of the 18-electron tungsten–alkynyl complex **1** generates the reactive species **10**, which can be represented by resonance structures of a 17-electron metal-centered radical and an 18-electron carbon-centered radical (Scheme 4). As a result of metal-centered reactivity, the 17-electron radical dimerizes to form **11**, which has a metal–metal bond. Subsequent elimination of carbon monoxide leads to the binuclear 18-electron complexes **9a**–**c** with bridged σ,π-acetylide ligands. Products such as **12** and **13**, which could be formed by an alternative path through dimerization of radical **10**, could not be detected.[11,12]

Molecular Structure of 9a

The structure of **9a** is further supported by single-crystal X-ray diffraction analysis. Single crystals were obtained by slow diffusion of *n*-pentane into a dichloromethane solution of **9a** at –20 °C. The crystal parameters, data collection parameters, and conditions for structure refinement are summarized in Table 1. Selected bond lengths and angles are given in Table 2. The ORTEP drawing with atomic numbering scheme is provided in Figure 1. Complex **9a** crystallizes in a C_{2h}-symmetric molecular structure with a planar arrangement of the atoms W(1)–C(6)–W($1^{\#}$)–C($6^{\#}$), which have a dihedral angle of 0° and an angle of 163.4° for W(1)–

Table 1. Crystal data and conditions for crystallographic data collection and structure refinement of **9a**.

Empirical formula	$C_{26}H_{20}N_2O_2W_2$
Formula mass	760.14
Color	orange, transparent
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Cell parameters	a = 9.7353(9) Å
	b = 13.0525(13) Å; β = 118.073(9)°
	c = 9.8758(9) Å
V [Å^3]	1107.27(18)
Z	4
$d_{calcd.}$ [g cm^{-3}]	2.280
μ [cm^{-1}]	104.07
Diffractometer	Image Plate Diffractometer System (STOE)
Radiation	Mo-K_α
Monochromator	graphite
2θ [°]	$5.76 \le 2\theta \le 56.16$
h, k, l range	$-12 \le h \le 12$, $-17 \le k \le 17$, $-13 \le l \le 12$
Reflections measured	9994
Independent reflections	2647
R_{int}	0.0413
Reflections with $F_o > 4\sigma(F_o)$	2232
Temperature [K]	293
Applied corrections	Lorentz and polarization coefficients
Structure determination and refinement	W positional parameters from direct methods (SHELXS-97)[a]
Refined parameters	146
$wR2$	0.0567
$R1$	0.0287
$R1$ [$F_o > 4\sigma(F_o)$]	0.0212
max, min in $\Delta\sigma$ [e·Å^{-3}]	1.24, –0.80

[a] Ref.[18a] Further atoms were found from ΔF synthesis.[18b] Refinement by anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; hydrogen position refinement by riding model.

C(6)–C(7$^{\#}$). The W(1)–C(6) bond length (2.025 Å) is shorter than those reported for the σ-acetylide complexes [(η^5-C_5H_5)(η^3-crotyl)(NO)W–C≡C–Ph] (2.104 Å)[7f] and [(η^5-C_5H_5)WRe(μ-I)(C≡C–Ph)(CO)$_5$] (2.09 Å).[13] The C_α–C_β bond length (1.250 Å) is comparable to those reported for {[(η^5-C_5H_5)μ-(CO)(NO)W][(η^5-C_5H_5)(CO)Fe–C≡C–Ph]} (1.25 Å),[8] [{(H_3CCp)$_2$Zr}$_2$(μ-C≡C–Ph)$_2$] (1.261 Å),[5a] and [Cp$_2$Zr(μ-C≡C–SiMe$_3$)(μ-C≡C–Ph)ZrCp$_2$] (1.267 Å),[5b] but elongated compared to non-coordinated C≡C bonds (H–C≡C–H: 1.21 Å; H–C≡C–CH$_3$: 1.207 Å)[14] and σ-acetylide complexes (1.206–1.21 Å).[7f,5a] The tungsten–tungsten distance, with 3.0389 Å, is slightly shorter than the tungsten–tungsten single bond in [{(OC)$_5$W}$_2$C=C=CPh$_2$] (3.15 Å).[15]

Table 2. Selected bond lengths [Å] and angles [°] for **9a**.

Distances		Angles	
W(1)–W(1$^{\#}$)	3.0389(4)	W(1)–C(6)–C(7$^{\#}$)	163.4(4)
W(1)–C(6)	2.025(4)	C(6$^{\#}$)–C(7)–C(8)	151.1(4)
W(1)–C(6$^{\#}$)	2.242(4)	C(6)–W(1)–W(1$^{\#}$)	47.54(11)
W(1)–C(7)	2.298(4)	C(6)–W(1)–C(6$^{\#}$)	89.32(15)
C(6)–C(7$^{\#}$)	1.250(6)	N(1)–W(1)–C(6)	96.23(18)
C(7)–C(8)	1.449(6)	N(1)–W(1)–W(1$^{\#}$)	105.22(13)

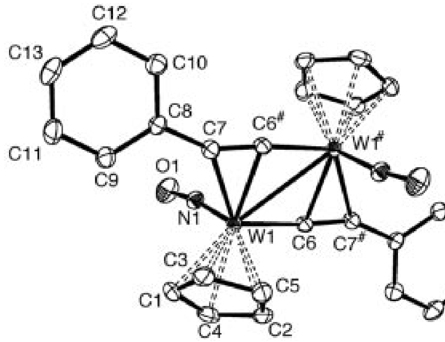


Figure 1. Molecular structure and atom numbering scheme for **9a**. Thermal ellipsoids are shown at the 30% probability level (ORTEP drawing).

Experimental Section

General Procedures: All operations were carried out under argon. All solvents were purified by standard techniques. Literature methods were used to prepare **5**, **6**,[7g] **7**,[16] and [Cp$_2$Fe][BF$_4$].[17] NMR spectra were recorded with a Bruker AM 400 spectrometer. ^{1}H NMR spectra were measured at 400 MHz, ^{13}C NMR spectra were measured at 100 MHz. Proton and carbon-13 chemical shifts are relative to TMS. IR spectra were recorded with a Bruker FT-IR IFS 85. Microanalyses were done with a Carlo–Erba 1104 elemental analyzer.

Preparation of [(η^5-C_5H_5)(NO)W–C≡C–C_6H_5]$_2$ (9a): *n*BuLi (1 mmol) in hexane was added to a solution of [(η^5-C_5H_5)(CO)(NO)W=C=CH(C_6H_5)] (**5**) (409 mg, 1 mmol) in THF (30 mL) at –78 °C. The resulting emerald-green solution was stirred for 15 min and then warmed up to –50 °C. [Cp$_2$Fe][BF$_4$] (273 mg, 1 mmol) was added in small portions to the solution over 30 min and stirred for 2 h. The color of the solution changed from green to dark red. After removing the solvent under reduced pressure at low temperature (–10 °C), the crude product was extracted several times with pentane to remove ferrocene. Chromatography of the residue on silica gel with pentane/diethyl ether (1:1), followed by crystallization from CH_2Cl_2 layered with pentane, gave 130 mg (39%) of complex **9a** as orange crystals [m.p. 252 °C (dec.)]. $C_{26}H_{20}N_2O_2W_2$ (760.16): calcd. C 41.08, H 2.65, N 3.68; found C 41.09, H 2.23, N 3.84. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ = 7.90–7.83 (m, 4 H, Ph), 7.53–7.38 (m, 6 H, Ph), 5.71 (s, 10 H, Cp) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ = 131.9, 131.4, 128.98, 128.5 (4s, Ph), 111.7 (s, C_β), 98.3 (br. s, Cp) ppm. IR (KBr): $\tilde{\nu}$ = 1847 (C≡C), 1553 (NO) cm^{-1}. MS (70 eV): *m*/*z* = 760 [M$^+$, ^{184}W]. HRMS: calcd. for $C_{26}H_{20}N_2O_2{}^{182}W_2$ [M$^+$] 756.0489; found 756.0474.

Preparation of [(η^5-C_5H_5)(NO)W–C≡C–C(CH$_3$)$_3$]$_2$ (9b): The reaction was carried out as described for **9a** by using [(η^5-C_5H_5)(CO)(NO)W=C=CH{C(CH$_3$)$_3$}] (**6**) (389 mg, 1 mmol) instead of **5**. Chromatography followed by crystallization yielded 90 mg (25%) of the product as orange crystals [m.p. 245 °C (dec.)]. $C_{22}H_{28}N_2O_2W_2$ (720.18): calcd. C 36.69, H 3.91, N 3.88; found C 36.45, H 3.59, N 3.30. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ = 5.69, 5.65 (2 s, 6:1, 10 H, Cp), 1.58 and 1.54 (2 s, 6:1, 18 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ = 167.7 (s, C_α), 124.5 [t, ^2J(^{183}W–^{13}C) = 29.6 Hz] and 123.9 (s) (2 C_β), 97.0 and 96.1 (2 s, 2 Cp), 37.9 and 37.5 [2 s, *C*(CH$_3$)$_3$], 33.2 and 32.7 (2 s, CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1852 (C≡C), 1560 (NO) cm^{-1}. MS (70 eV): *m*/*z* = 720 [M$^+$, ^{184}W]. HRMS: calcd. for $C_{22}H_{28}N_2O_2{}^{182}W_2$ [M$^+$] 716.1115; found 716.1107.

Preparation of [(η^5-C_5H_5)(NO)W–C≡C–Si(CH$_3$)$_3$]$_2$ (9c): *n*BuLi (1.2 mmol) in hexane was added to a solution of ethinyltrimethylsilane (0.167 mL, 1.2 mmol) in THF (15 mL) at –78 °C. The resulting green solution of the tungsten acetylide [(η^5-C_5H_5)(NO)(CO)W–C≡C–Si(CH$_3$)$_3$]Li (**1c**) was transferred dropwise to a precooled (–30 °C) solution of [(η^5-C_5H_5)(CO)$_2$(NO)W] (**7**) (335 mg, 1 mmol) in THF (15 mL) and stirred for 3 h. The green solution was treated, as above, with [Cp$_2$Fe][BF$_4$] (273 mg, 1 mmol). Removal of the solvent followed by recrystallization yielded 208 mg (54%) of complex **9c** as orange crystals [m.p. 243 °C (dec.)]. $C_{20}H_{28}N_2O_2Si_2W_2$ (752.33): calcd. C 31.93, H 3.75, N 3.72; found C 31.64, H 3.40, N 3.85. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ = 5.69 and 5.64 (2 s, 5:1, 10 H, Cp), 0.46 and 0.44 (2 s, 5:1, 18 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ = 197.9 (s, C_α), 108.1 (s, C_β), 97.2 and 96.2 (2 s, Cp), 1.6 and 1.2 (2 s, CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1820 (C≡C), 1560 (NO) cm^{-1}. MS (70 eV): *m*/*z* = 752 [M$^+$, ^{184}W]. HRMS: calcd. for $C_{20}H_{28}N_2O_2Si_2{}^{182}W_2$ [M$^+$] 748.0653; found 748.0643.

CCDC-602108 contains the supplementary crystallographic data for compound **9a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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