Iron Catalysis

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Low-Pressure Hydrogenation of Carbon Dioxide Catalyzed by an Iron Pincer Complex Exhibiting Noble Metal Activity**

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Owing to its high abundance, low price and relatively low toxicity, the use of carbon dioxide as a C_1 source in chemical reactions and processes is an attractive alternative to common C_1 starting compounds, such as carbon monoxide and phosgene. For example, the direct, low-pressure hydrogenation of carbon dioxide to formic acid and its derivates is a desirable transformation, considering that formic acid is widely used in the chemical industry as acid, reductant, and importantly as carbon source.[1–3]

In most transition-metal-catalyzed hydrogenations of carbon dioxide, high pressures ($p(H_2+CO_2) \geq 40$ bar) have to be applied.[4,5] Highly active catalysts with rhodium,[6] ruthenium,[7] iridium,[8–10] and palladium[11] have been reported in the last 20 years. For example, in pioneering work Leitner and co-workers reported various rhodium phosphine complexes that catalyze the hydrogenation of carbon dioxide under a total pressure of 40 bar with turnover numbers up to 3439.[6h] At the same time ruthenium phosphine complexes were applied in the hydrogenation of supercritical carbon dioxide by Noyori and co-workers.[7d,e] Half-sandwich iridium(III) complexes with 4,4′-dihydroxy-2,2′-bipyridine or 4,7-dihydroxy-1,10-phenanthroline ligands were successfully applied in the hydrogenation of carbon dioxide by Himeda et al. with turnover numbers up to 222 000. Interestingly, these complexes showed catalytic activity even under ambient pressure.[8] The most active system for the hydrogenation of carbon dioxide was recently reported by Nozaki and co-workers, using an iridium(III) trihydride pincer complex and 60 bar of a 1:1 mixture of carbon dioxide and hydrogen (TON = 3 500 000, TOF = 150 000 h^{-1}).[9] In a recent important finding, an in situ formed iron complex has been applied in the hydrogenation of bicarbonates and carbon dioxide by Beller and Laurenczy.[12] With this system turnover numbers up to 610 were achieved in the hydrogenation of sodium bicarbonate to sodium formate, using 60 bar of hydrogen pressure (TOF = 30.5 h^{-1}). Formamides are obtained with this catalytic system when carbon dioxide is hydrogenated in the presence of a secondary amine under total pressure of 90 bar of a 1:2 mixture of carbon dioxide and hydrogen (TON = 727, TOF = 36.4 h^{-1}).

Encouraged by the recent development of iron pincer complexes for the hydrogenation of ketones[13] and the hydrogenation of carbon dioxide with iridium pincer complexes, we investigated the application of iron pincer complexes in this catalytic transformation. Calculations for Ru^{II} complexes predict that strong donor ligands facilitate the insertion of carbon dioxide into the ruthenium–hydride bond.[14] In addition, the *trans*-influence of the ligand opposite the hydride was shown to have a major effect on the favorability of CO_2 insertion into Ir–H bonds.[10] Owing to the strongly σ-donating properties of carbon monoxide and hydride ligands, the *trans*-dihydride carbonyl complexes of the type [(PNP)Fe$(H)_2$(CO)] seemed to be promising candidates for this goal (PNP = 2,6-bis(dialkylphosphinomethyl)-pyridine). However, our previously reported complex [(*i*Pr-PNP)Fe$(H)_2$(CO)] with isopropyl groups bound to the phosphorus atoms was too unstable to allow for its isolation.[13]

Herein we report the synthesis and characterization of the iron(II) pincer complex *trans*-[(*t*Bu-PNP)Fe$(H)_2$(CO)] (**4**). The dihydride complex **4** is the most active iron catalyst reported to date for the hydrogenation of carbon dioxide and sodium bicarbonate to formate salts and displays similar activity to known noble metal catalysts. Carbon dioxide and sodium bicarbonate are efficiently hydrogenated in aqueous media at 80 °C under remarkably low pressures (6–10 bar), with turnover numbers up to 788 and turnover frequencies up to 156 h^{-1}. The hydrido formate complex [(*t*Bu-PNP)-Fe(H)(CO)(η^1-OOCH)] (**5**) was characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. Based on these observations a possible reaction mechanism is discussed.

Reaction of the *t*Bu-PNP ligand with $FeBr_2$ in a 1:1 acetonitrile/ethanol mixture and one or more equivalents of sodium borohydride cleanly results within minutes in formation of the hydride complex **1** (Scheme 1). Complex **1** exhibits a triplet resonance at $\delta = -13.65$ ppm in the ^{1}H NMR spectrum and a singlet resonance at $\delta = 102.7$ ppm in the $^{31}P\{^1H\}$ NMR spectrum, indicating equivalence of the two phosphorus atoms. Complex **1** is isolated by exchanging the counter ion with tetraphenylboron. The crystal structure of **1** shows that a cationic hydride complex is formed under these

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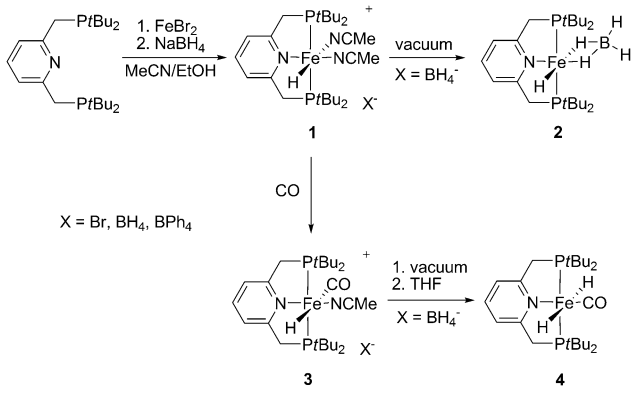
Supporting information for this article (detailed description of the synthesis and the spectroscopic data for complexes **1**–**6**, as well as crystallographic data for **1**–**5**) is available on the WWW under http://dx.doi.org/10.1002/anie.201104542.



Scheme 1. Reaction pathways in the synthesis of **4**.

conditions, in which the iron(II) center exhibits a distorted octahedral environment formed by the pincer ligand, the hydride and two acetonitrile ligands. One of the two acetonitrile ligands is located in the apical position *trans* to the hydride ligand, while the second one coordinates to the iron center *trans* to the pyridine nitrogen.[15]

Performing the above mentioned reaction with an excess of $NaBH_4$ (> 2 equiv) followed by evaporation of the volatiles leads to the loss of the coordinated acetonitrile ligands and formation of the hydrido borohydride complex **2**.[15]

Treatment of a solution of **1** with carbon monoxide in a 1:1 mixture of acetonitrile and ethanol results in a color change from deep red to orange within two hours. The $^{31}P\{^1H\}$ NMR spectrum of the product exhibits a singlet resonance $\delta =$ 107.22 ppm (slightly shifted compared to **1**) and a triplet at $\delta = -5.98$ ppm for the hydride ligand in the ^1H NMR spectrum, indicating that a stronger σ-donor ligand is now bound *trans* to the hydride. The appearance of a strong band at 1951 cm^{-1} in the IR spectrum supports the formation of an iron carbonyl complex. The molecular structure of **3** shows the iron(II) center of the cationic complex in an octahedral environment with the carbon monoxide ligand *trans* to the hydride and the remaining acetonitrile *trans* to the pyridine nitrogen.[15] Owing to the strong *trans* effect of the hydride ligand the acetonitrile ligand in the apical position in of **1** is exclusively substituted.

The *trans*-dihydride complex **4** is obtained by solvent evaporation after two hours stirring under an atmosphere of carbon monoxide, followed by addition of tetrahydrofuran to the residue and stirring of the suspension for 24 to 48 h. The treatment of complex **3** with THF was necessary for the reaction to proceed. It is likely that the coordinated acetonitrile is slowly released during this period and a borohydride counter ion becomes coordinated. The corresponding hydrido borohydride complex could not be detected, indicating that once the borohydride is coordinated the release of BH_3 occurs rapidly. The solvent THF may have a mediating role in this step.

Complex **4** gives rise to a singlet resonance at $\delta =$ 132.99 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a triplet resonance for the hydride ligands at $\delta = -7.30$ ppm, which integrates to two hydrogens in the ^1H NMR spectrum. The higher symmetry of this complex is reflected in the appearance of only one signal at $\delta = 1.44$ ppm for the *tert*-butyl groups and one signal at $\delta = 3.04$ ppm for the benzylic positions of the coordinated *t*Bu-PNP ligand. The infrared spectrum of **4** exhibits a strong carbonyl band centered at 1865 cm^{-1}, consistent with an electron-rich iron(II) center. In accordance with the NMR spectra, the crystal structure of **4** displays an iron(II) center with a distorted octahedral environment (Figure 1). The CO ligand and the *t*Bu-PNP ligand form a plane, while the two hydride ligands occupy the apical positions.

Initially, the *trans*-dihydride complex **4** was investigated as a catalyst for the hydrogenation of sodium bicarbonate under various conditions. Significant activity was observed only when water was used as solvent, with small amounts of THF as co-solvent (Table 1). Experiments at different temperatures were conducted using 8.3 bar of hydrogen pressure (entries 1–5). The highest activities of complex **4** in the hydrogenation of sodium bicarbonate are observed at 60 °C (entry 3, TON = 200) and 80 °C (entry 4, TON = 320), while at 100 °C turnover numbers of only 70 are achieved (entry 5).

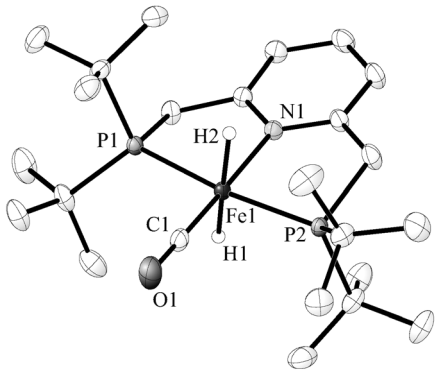


Figure 1. Molecular structure of **4**, selected bond lengths [Å] and angles [°]: Fe1–P1 2.1777(4), Fe1–P2 2.1802(4), Fe1–N1 2.0155(11), Fe1–C1 1.7062(15), Fe1–H1 1.42(2), Fe1–H2 1.57(2), C1–O1 1.1705(18) (thermal ellipsoids set at 50% probability, the hydrogen atoms of the *t*Bu-PNP ligand are omitted for clarity).

Table 1: Iron-catalyzed hydrogenation of bicarbonate.[a]

$$NaHCO_3 + H_2 \xrightarrow[H_2O/THF\ (10:1)]{0.1\ mol\%\ \mathbf{4}} NaOOCH + H_2O$$

Entry	$p(H_2)$[b] [bar]	T [°C]	Yield[c] [%]	TON[d]
1	8.3	23	0.2	2
2	8.3	40	3.2	32
3	8.3	60	20.0	200
4	8.3	80	32.0	320
5	8.3	100	7.0	70
6	6.2	80	26.7	267
7	10	80	13.9	139
8[e]	8.3	80	1.5	15

[a] Reaction conditions: **4** (0.005 mmol), $NaHCO_3$ (5 mmol), H_2O (5 mL), THF (0.5 mL), 16 h. [b] Pressure at room temperature. [c] Based on ^1H NMR analysis using dimethylformamide as internal standard. [d] Mol of sodium formate per mol of catalyst. [e] Na_2CO_3 (5 mmol) was used instead of $NaHCO_3$.

Interestingly, even at ambient temperature the formation of sodium formate is still observed (entry 1, TON = 2) and activity is significantly increased at 40 °C (entry 2, TON = 32).

When Na_2CO_3 is employed under the same conditions instead of $NaHCO_3$ the reaction proceeds very slowly and only very low conversion is obtained (Table 1, entry 8, TON = 15). With turnover numbers of 320 at 8.3 bar hydrogen pressure, complex **4** is a considerably more efficient catalyst for the hydrogenation of bicarbonates than the most active previously reported iron catalyst, which achieved a turnover number of 112 at 30 bar of hydrogen pressure.[12] Catalyst **4** can also compete with known noble metal catalysts, such as $[\{RuCl_2(tppms)_2\}_2]$/tppms (TON = 108, $p(H_2) = 10$ bar)[7i] or $[HRu(ac)(tppms)_3]$/tppms (TON = 284, $p(H_2) = 10$ bar) (tppms = sodium 3-sulfonatophenyldiphenylphosphine).[16]

When a 1:1 mixture of carbon dioxide and hydrogen with aqueous sodium hydroxide is utilized instead of sodium bicarbonate under the same total pressure of 8.3 bar, sodium formate was formed with a similar turnover number of 337 after 14 h (Table 2, entry 1). Changing the ratio of hydrogen to carbon dioxide from 1:1 to 2:1 resulted in significantly increased turnover numbers of 480 and turnover frequencies of 60 h^{-1} (entry 2). In contrast to the case of bicarbonate, in which increased hydrogen pressure (10 bar, Table 1, entry 7) did not result in greater efficacy, the hydrogenation of carbon dioxide at a total pressure of 10 bar gave a turnover number of 458 with a 1:1 ratio of hydrogen and carbon dioxide (entry 3) and 532 with 2:1 ratio (entry 4).

Table 2: Iron-catalyzed hydrogenation of CO_2.[a]

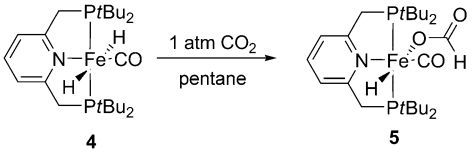
$$CO_2 + H_2 + NaOH \xrightarrow[H_2O/THF\ (10:1)]{0.1\ mol\%\ \mathbf{4}} NaOOCH + H_2O$$

Entry	$p(H_2)$[b] [bar]	$p(CO_2)$[b] [bar]	c_{NaOH} [M]	t [h]	Yield[c] [%]	TON[d]	TOF [h^{-1}]
1	4.15	4.15	1	14	33.7	337	24
2	5.52	2.76	1	8	48.0	480	60
3	5	5	1	10	45.8	458	46
4	6.66	3.33	1	10	53.2	532	53
5	6.66	3.33	0.5	10	34.0	340	34
6	6.66	3.33	1.5	5	37.8	567	113
7	6.66	3.33	2	5	39.4	788	156
8	6.66	3.33	3	5	19.9	597	119

[a] Reaction conditions: **4** (0.005 mmol), NaOH, H_2O (5 mL), THF (0.5 mL). [b] Pressure at room temperature. [c] Based on ^1H NMR analysis using dimethylformamide as internal standard. [d] Mol of sodium formate per mol of catalyst.

Next, we examined the effect of base concentration on the reaction. Typically, base concentrations of 1 mol L^{-1} or less are used in transition-metal-catalyzed hydrogenations of carbon dioxide. When the reaction is carried out in a 0.5 M NaOH solution lower turnover numbers values are obtained (Table 2, entry 5). With increasing sodium hydroxide concentration the activity of catalyst **4** steadily increased and resulted in the highest activity observed so far in 2 M NaOH solutions, with a turnover number of 788 and a turnover frequency of 156 h^{-1} (entries 4–7). In comparison with state-of-the-art noble metal catalysts for the hydrogenation of carbon dioxide, complex **4** displays a surprisingly similar activity. For example, one of the most active catalysts reported to date is the iridium(III) complex [Cp*Ir(dhpt)-Cl]Cl (Cp* = η^5-pentamethylcyclopentadienyl, dhpt = 4,7-dihydroxy-1,10-phenanthroline), which is capable of hydrogenating CO_2 in aqueous KOH with turnover numbers of 8500 under a total pressure of 10 bar.[8] Although the turnover number is approximately one order of magnitude higher than with complex **4**, significantly lower turnover frequencies (93.4 h^{-1}) and lower yields of the formate salt (17%) were achieved under these conditions with the iridium catalyst. Hazari and co-workers achieved turnover numbers of 3932 and turnover frequencies of 164 h^{-1} with the iridium(III) pincer complex $[(PNP)IrH_2(OOCH)]$, employing 13.8 bar of total pressure at 185 °C (yield = 1%; PNP = $HN(CH_2CH_2P\mathit{i}Pr_2)$).[10]

In order to gain mechanistic understanding of the iron-catalyzed hydrogenation of carbon dioxide, complex **4** was investigated in stoichiometric reactions. Exposure of a pentane solution of **4** to carbon dioxide resulted in the immediate formation of an orange precipitate (Scheme 2).



4 **5**

Scheme 2. Reaction of complex **4** with CO_2.

The $^{31}P\{^1H\}$ NMR spectrum of the newly formed compound exhibits a singlet at $\delta = 109.51$ ppm and in the ^1H NMR spectrum a triplet resonance for the hydride ligand is observed at $\delta = -22.64$ ppm that integrates to one. Appearance of two virtual triplets for the *tert*-butyl groups and a ABX spin system for the benzylic protons of the pincer ligand indicate reduced symmetry in comparison to **4**. In addition, a singlet resonance at $\delta = 8.41$ ppm is observed in the ^1H NMR spectrum which correlates to a singlet resonance at $\delta = 172.35$ ppm in the $^{13}C\{^1H\}$ NMR spectrum (by ^1H-^{13}C-HSQC NMR), suggesting that the corresponding hydrido formate complex [(*t*Bu-PNP)Fe(H)(CO)(η^1-OOCH)] (**5**) is formed in the reaction with carbon dioxide. The IR spectrum exhibits a strong absorption centered at 1885 cm^{-1}, confirming that carbon monoxide is bound to the iron(II) center in this complex. The formate ligand gives rise to a strong absorption at 1613 cm^{-1} for asymmetric stretching vibration and at 1319 cm^{-1} for symmetric stretching vibration in IR spectrum. Finally, the molecular structure is confirmed by single-crystal X-ray diffraction (Figure 2). The iron(II) center adopts a distorted octahedral coordination by the pincer ligand, carbon monoxide, a hydride and a formate ligand, with the hydride ligand located *trans* to the formate ligand.

This stoichiometric reaction suggests that reduction of carbon dioxide proceeds through a direct attack on the *trans*-dihydride complex **4** followed by formation of the oxygen-bound hydrido formate complex **5**. When **5** is dissolved in D_2O, or when **4** is reacted with $NaHCO_3$ in D_2O, a new

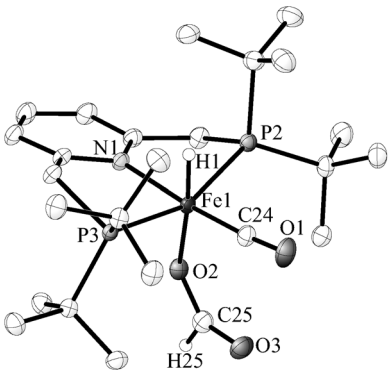
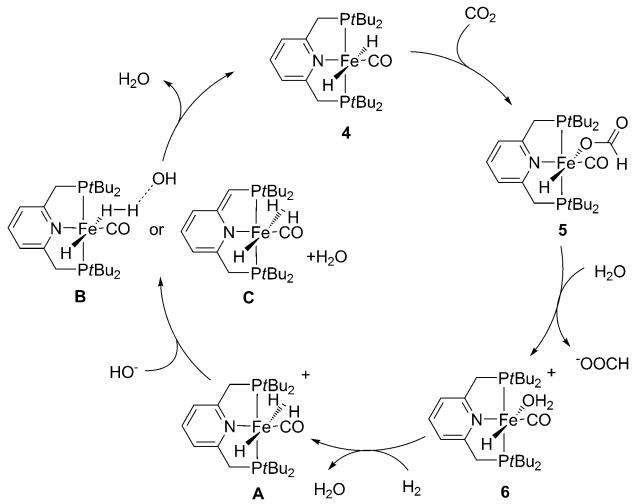


Figure 2. Molecular structure of complex **5**, selected bond lengths [Å] and angles [°]: Fe1–P2 2.2392(4), Fe1–P3 2.2434(4), Fe1–N1 2.0314(10), Fe1–C24 1.7351(13), Fe1–H1 1.41(2), Fe1–O2 2.0709(10), C24–O1 1.1624(16), C25–O3 1.2341(17), C25–O2 1.2596(17), C25–H25 1.015(17); P2-Fe1-P3 158.025(15), O2-Fe1-H1 170.7(8), O3-C25-O2 128.79(14), O3-C25-H25 118.1(9), O2-C25-H25 113.1(9), C25-O2-Fe1 130.91(9) (the thermal ellipsoids are set at 50% probability, the hydrogen atoms of the *t*Bu-PNP ligand are omitted for clarity).

hydridic species is observed, with a triplet resonance centered at $\delta = -24.55$ ppm in the ^{1}H NMR spectrum and a singlet resonance at $\delta = 100.00$ ppm in the ^{31}P{^{1}H} NMR spectrum. The shift of the hydride resonance to a higher field by ca. 2 ppm indicates that the formate ligand *trans* to the hydride ligand in **5** is replaced by a weaker donor ligand in the new complex. It is likely that a cationic water-coordinated complex [(*t*Bu-PNP)Fe(H)(CO)(H_2O)]$^+$ (**6**) is formed under these conditions. Upon addition of an excess of KOH (20 equiv) no change in the NMR spectra was detected.

Based on these observations, a possible reaction mechanism for the hydrogenation of carbon dioxide is outlined in Scheme 3. Following direct attack of CO_2 on the hydride ligand of **4** the oxygen-bound formate complex **5** is formed. The formate ligand in **5** is easily replaced by a water molecule, to give the cationic complex **6**. Under hydrogen pressure the dihydrogen-coordinated species **A** is possibly formed, which



Scheme 3. Plausible mechanism for hydrogenation of CO_2 catalyzed by complex **4**.

regenerates complex **4** by heterolytic cleavage of the coordinated H_2 by $^-$OH (**B**) or by dearomatization and subsequent proton migration (**C**). Recently, similar catalytic cycles have been postulated in computational studies on iridium, cobalt and iron pincer complexes using density functional theory.[10,17]

In conclusion we have developed an efficient iron catalyst, which is capable of hydrogenating carbon dioxide under remarkably low pressures and with high turnover numbers. The reaction likely proceeds through direct attack of the iron hydride to the carbon dioxide, followed by replacement of the resulting formate ligand by water. Dihydrogen coordination, prior to heterolytic cleavage of H_2 by hydroxide or dearomatization and subsequent proton migration are plausible pathways for the regeneration of the *trans*-dihydride complex **4**. The observed activity is comparable to known noble metal catalysts and highlights the enormous potential of iron-based catalysts for possible applications in the future.

The reaction of the *trans*-dihydride complex [(*t*Bu-PNP)-Fe$(H)_2$(CO)] (**4**) with carbon dioxide in aprotic solvents such as pentane resulted in the formation of the isolable hydrido formate complex [(*t*Bu-PNP)Fe(H)(CO)(η^1-OOCH)] (**5**). NMR investigations show that the formate ligand is easily replaced by a water ligand in aqueous solution.

Experimental Section

General procedure for catalytic hydrogenation of $NaHCO_3$: A 90 mL Fischer–Porter tube was charged under nitrogen with the catalyst **1** (0.005 mmol) dissolved in 0.5 mL THF and $NaHCO_3$ (5 mmol) dissolved in 5 mL H_2O. The tube was pressurized at ambient temperature with hydrogen and the solution was stirred at the specified temperature for 16 h (Table 1). After the reaction, the Fischer–Porter tube was cooled to room temperature with water and the pressure was released. Dimethylformamide (1 mmol) was added to the reaction mixture as an internal standard and 0.05 mL of the mixture were dissolved in D_2O for determination of the yield by ^{1}H NMR spectroscopy.

General procedure for catalytic hydrogenation of CO_2: A 90 mL Fischer–Porter tube was charged under nitrogen with the catalyst **1** (0.005 mmol) dissolved in 0.5 mL THF and 5 mL of an aqueous NaOH solution with the specified concentration (Table 2). The tube was pressurized with CO_2 and allowed to equilibrate for 5 min. After this period the specified hydrogen amount was added to the tube and the reaction mixture was heated to 80 °C. After the reaction, the Fischer–Porter tube was cooled with water and the pressure was released. Dimethylformamide (1 mmol) was added to the reaction mixture as an internal standard and 0.05 mL of the mixture were dissolved in D_2O for determination of the yield by ^{1}H NMR spectroscopy.

CCDC 830169 (**1**), 830170 (**2**), 830171 (**3**), 830172 (**4**), and 830173 (**5**) contain the supplementary crystallographic data for this paper. 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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