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Water-Soluble Ir^{III} N-Heterocyclic Carbene Based Catalysts for the Reduction of CO_2 to Formate by Transfer Hydrogenation and the Deuteration of Aryl Amines in Water

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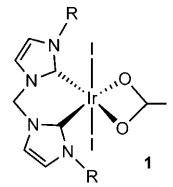
Abstract: Two new water-soluble [IrI_2(AcO)(bis-NHC)] complexes (NHC = N-heterocyclic carbene) incorporating a sulfonate functionality have been synthesized. The two complexes have been tested in the reduction of CO_2 with H_2 and *i*PrOH, and their activity has been compared with similar species without the sulfonate moiety. In both reactions, the complex with the two abnormally bound NHCs shows the best catalytic efficiencies, due to the higher σ-electron-donor character of the ligand. Remarkably, the activities obtained for the reduction of CO_2 under the transfer hydrogenation conditions are the best reported to date in terms of TON value (max. TON = 2700). The two new complexes have also shown very good activity in the selective deuteration of arylamines, a process that is known to proceed through a chelate assisted N-directed process.

Keywords: deuteration · iridium · N-heterocyclic carbenes · reduction · water chemistry

Introduction

During the last two decades, there has been an increasing interest in the use of water as the solvent for many homogeneously catalyzed reactions.[1] Cost, environmental benefits, and safety, are among the advantages of water over organic solvents. However, organic solvents have a series of attractive features, such as their abilities to dissolve organic substrates, their (often) volatile character that makes them easy to remove, and their wide range of properties (polarity, coordination capabilities, etc.). Although many organic substrates require organic solvents for their transformations through homogeneously catalyzed processes, some other reactions are more easily performed in water, for which water-soluble catalysts are then required. Among this latter type of reaction, those involving CO_2 reduction may represent an important class,[2–4] because the solubility of CO_2 in water represents one of the key points to consider in the design of the reaction protocols. For these reactions, one of the limitations is that a water-soluble catalyst that is also able to stand the harsh reaction conditions must be used,[3–5] otherwise mixtures of organic solvents and water have to be utilized to facilitate the solubility of the catalyst.

We have recently described a series of N-heterocyclic carbene (NHC) based iridium and ruthenium catalysts for the reduction of CO_2 to formate.[6,7] In the design of these new catalysts, our initial hypothesis was that the high electron-donor character of NHCs, together with their ability to form stable metal complexes, would constitute a very useful type of ligand for the preparation of catalysts for CO_2 activation, as previously proposed by other authors.[8] In our studies, we proposed for the first time that *i*PrOH could be used as the hydrogen source for the reduction of CO_2 by a transfer-hydrogenation process,[6,7] a reaction that may constitute a valid alternative over the use of hydrogen gas. Following the same idea, we now decided to modify well-known transfer-hydrogenation catalysts to make them soluble in water, so that they can be applied to the effective reduction of CO_2 to formate in the presence of *i*PrOH/H_2O. Among all the iridium-based transfer hydrogenation catalysts reported to date, those described by Crabtree and co-workers of the type [Ir(bis-NHC)(AcO)I_2] (**1**, Scheme 1) are particularly interesting because they gather an extraordinary high stability toward air and moisture, and a very high catalytic activity (TOF > 50000 h^{-1}).[9] Taking this into account, we now describe the preparation of a series of [Ir(bis-NHC)(AcO)I_2] complexes in which the NHC ligand contains a sulfonate functionality to make the complex soluble in water. We have used the complexes obtained in the reduction of carbon dioxide to formate with H_2 and with *i*PrOH. In a parallel study, we have also used these complexes in the selective deuteration of aryl amines with D_2O.



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Scheme 1. R = Me, *n*Bu, *i*Pr, neopentyl, benzyl (Bn), or *t*Bu.

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Results and Discussion

Synthesis and characterization of new compounds: To obtain water-soluble Ir^{III}(bis-NHC) complexes, we used the two sulfonate-functionalized bis-imidazolium salts, which were prepared according to the general strategy used by us[10] and others,[11] consisting of the reaction of the corresponding neutral bisimidazoles with propanesultone. The Ir^{III} complexes **2** and **3** were obtained by reaction of the corresponding sulfonate-functionalized bisimidazolim salts with $[IrCl(cod)]_2$ (COD = 1,5-cyclooctadiene) in the presence of KI and NaOAc in refluxing MeOH. For the preparation of the bis(*a*NHC) (*a*NHC = abnormal NHC) complex **3**, we followed the general strategy of blocking the C2-position of the azolium salt with a methyl group, to force the coordination of the NHC by the C4/C5 carbons.[12–14] We thought that the preparation of the bis-abnormally bound bis-NHC complex may introduce some improvements in the catalytic performance of **3** compared with **2**, due to the higher electron-donor character of the bis-*a*NHC ligand,[13] which may favor the interaction of the metal with the electrophilic CO_2 molecule.

Compounds **2** and **3** were obtained in high yield (69 and 75%, respectively; Scheme 2) as the corresponding potassium salts, and were characterized by NMR spectroscopy and elemental analysis. Both complexes were very soluble in water and DMSO, sparingly soluble in MeOH, and insoluble in most organic solvents such as THF, CH_2Cl_2, Et_2O, and so forth. The NMR spectra of both **2** and **3**, confirms the two-fold symmetries of the molecules. The ^{13}C NMR spectrum of **2** in $[D_6]$DMSO, shows the signal due to the carbene carbon at $\delta = 123.7$ ppm, in the same region as for other similar previously reported Ir^{III} analogues.[9] The ^1H NMR spectrum of **3** shows a singlet due to the equivalent protons of the C2 Me groups at $\delta = 2.8$ ppm. The ^{13}C NMR spectrum shows the signal due to the carbene carbons at $\delta = 146.4$ ppm, in the same region where other abnormally bound bis-(*a*NHC)Ir^{III} appear.[14]

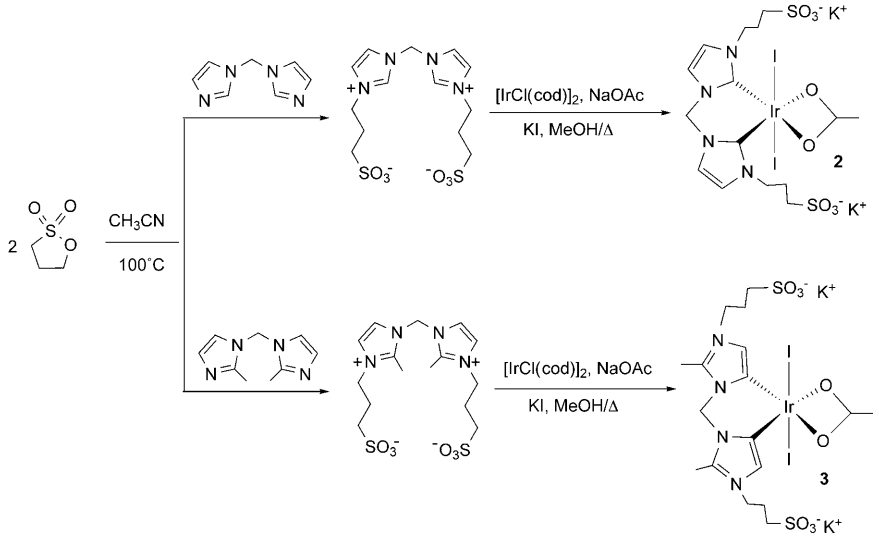
Catalytic reduction of CO_2 to formate: Both **2** and **3** were tested in the catalytic reduction of CO_2 with H_2. The reactions were carried out in a 1 M solution of KOH in water at 80 and 200 °C, using 60 atm of a CO_2/H_2 mixture (1:1). For comparative purposes, catalyst **1** (with R = *n*Bu) was also tested in this reaction. The catalytic results are listed in Table 1.

Table 1. Reduction of CO_2 with H_2.[a]

$$CO_2 + H_2 \xrightarrow[1\,M\ KOH/H_2O,\ 80^\circ C]{cat.} HCOOK + H_2O$$

Entry	Catalyst	t [h]	T [°C]	[Cat.] [mM]	n_{HCOOK} [mmol]	TON[b]
1	none	20	200	–	0.7	–
2	none	20	80	–	0	–
3	none	75	200	–	1.08	–
4	**1**	20	80	2×10^{-2}	0.1	243
5	**2**	20	80	2×10^{-2}	0.25	1247
6	**2**	75	80	2×10^{-2}	0.43	2153
7	**2**	20	80	2×10^{-3}	0.17	8480
8	**2**	20	200	2×10^{-2}	1.90	9500
9	**2**	20	200	2×10^{-3}	1.30	65000
10	**2**	75	200	2×10^{-3}	1.65	82300
11	**3**	20	80	2×10^{-2}	0.33	1663
12	**3**	75	80	2×10^{-2}	0.59	2930
13	**3**	20	80	2×10^{-3}	0.19	9340
14	**3**	20	200	2×10^{-2}	3.05	15240
15	**3**	20	200	2×10^{-3}	3.03	151300
16	**3**	75	200	2×10^{-3}	3.8	190000

[a] Reactions carried out at 60 atm ($30CO_2$:$30H_2$) in 1 M KOH (10 mL) in H_2O. n_{HCOOK} (number of mmols of HCOOK) and TONs corrected according to data obtained without catalysts, entries 1–3. [b] TONs based on the formation of formate, calculated by ^1H NMR spectroscopy.



Scheme 2.

The introduction of the sulfonate functionality results in a very important improvement of the catalytic performance, as can be confirmed by comparing the catalytic performances shown by **1** (Table 1, entry 4, TON = 243) and **2** under the same reaction conditions (Table 1, entry 5, TON = 1247). This, in fact, validates our first hypothesis that the solubility of the catalyst is crucial in the efficiency of this reaction. If we compare the data for the reactions carried out under the same conditions using **2** and **3**, we can see that catalyst **3** always provides the best performances, which actually validates our hypothesis that a

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stronger electron-donor ligand should provide a better catalytic outcome in this reaction.

For the reactions carried out at 200 °C, potassium formate is formed even in the absence of catalyst,[6,15] and thus background corrections to the catalyst TONs based on the data without catalyst were made (Table 1, entries 1 and 3). Under these reaction conditions, catalyst **2** provided a high TON value of 82300 (Table 1, entry 10), whereas **3** afforded an extraordinary high activity with a TON value of 190000. These data are far better than those previously reported by us,[6,7] and lie among the highest outcomes reported to date, together with the Ir pincer complex reported by Nozaki,[15] and the Ir(bpy) (bpy = bipyridine) catalyst reported by Himeda.[4]

Because the activity of **1** was reported to be extraordinarily high in transfer hydrogenation processes,[9] we thought that complexes **1**–**3** may be good catalysts for the reduction of CO_2 to formate using *i*PrOH as the hydrogen source. The reactions were carried out in a mixture of H_2O/*i*PrOH (9:1, 20 mL) so again, for this process, the solubility of the catalyst in water should play an important role. As can be seen from the data shown in Table 2, complexes **2** and **3** are more

Table 2. Transfer hydrogenation of CO_2 with *i*PrOH.[a]

$$CO_2 + \text{/PrOH} \xrightarrow[0.5\text{M KOH/H}_2\text{O, 110°C}]{\text{cat.}} \text{HCOOK} + (CH_3)_2CO$$

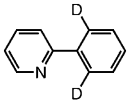
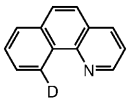
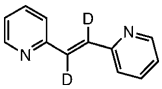
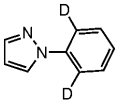
Entry	Catalyst	t [h]	T [°C]	[Cat.] [mM]	n_{HCOOK} [10^{-6} mol]	TON[b]
1	none	16	200	–	90	–
2	none	16	110	–	0	–
3	**1**	16	110	0.018	21.6	60
4	**2**	16	110	0.018	39.2	109
5	**2**	16	200	0.018	64.1	178
6	**2**	16	200	0.0018	32.7	910
7	**2**	75	200	0.0018	62.3	1730
8	**3**	16	110	0.018	48.6	135
9	**3**	16	200	0.018	90	250
10	**3**	16	200	0.0018	47.5	1320
11	**3**	75	200	0.0018	97.2	2700

[â] Reactions carried out at 110 °C, 50 atm CO_2, in the presence of 0.5 M KOH in H_2O/*i*PrOH (9:1, 20 mL). n_{HCOOK} (number of mols of HCOOK generated) and TONs corrected according to data obtained without catalysts, entries 1 and 2. [b] TONs based on the formation of formate, calculated by ^{1}H NMR spectroscopy.

active than **1** (compare entries 3, 4, and 8), so again, the presence of the sulfonate functionalities improves the catalytic activities of **2** and **3** due to the increase of their solubility in water. As seen for the reactions with H_2, the activity of **3** is higher than that shown by **2**. For the reactions carried out at 200 °C, again we had to make background corrections comparing with the data obtained for the reactions without catalyst. Compound **2** provided a highest TON value of 1730 for the reaction carried out at 200 °C with a catalyst loading of 1.8×10^{-3} mol % after 75 h. Under the same conditions, compound **3** provided a maximum TON value of 2700, which is the highest reported so far for this type of process. Notably, the maximum TON value obtained for the reduction of CO_2 to formate using *i*PrOH was 874 for a [Ru(η^6-arene)(bis-NHC)] complex reported by us,[6] under similar reactions conditions.

Regioselective deuteration of arylated heterocycles: Hydrogen/deuterium exchange processes are powerful methods to evaluate the potential of a catalyst for the cleavage and formation of C–H bonds.[16] In general, D_2O is preferred as a deuterating agent over other sources, due to its low cost and low toxicity. We recently reported the N-directed regioselective deuteration of C–H bonds of several arylated N-heterocycles with a [Ru(η^6-arene)(NHC)Cl_2] complex.[17] In that case our results showed the extraordinarily high activity of our catalyst in this unprecedented selective deuteration, although we were unable to make the catalyst effective in D_2O ([D_4]MeOH was the deuterium source). Also, it was recently described that a dirhodium(II) complex was able to selectively deuterate benzo[*h*]quinoline at the C10-position, although in this case the reaction needed a stoichiometric amount of the dimetallic species (the reaction is not catalytic) and base.[18] Aiming to study the same process with our new water-soluble catalysts **2** and **3**, and having proved its activity in C–H activation processes such as those shown in Table 2 for the reduction of CO_2 with *i*PrOH, we thought that these two catalysts should have a high chance of activity in this reaction. The results that we obtained are listed in Table 3.

Table 3. Deuteration of pyridines in D_2O using **2** and **3**.[a]

Entry	Substrate	Product	Cat.	Conv. [%][b]
1	2-phenylpyridine		**2**	45
2			**3**	100
3	benzo[*h*]quinoline		**2**	74
4			**3**	96
5	1,2-bis(2-pyridyl)ethylene		**2**	70
6			**3**	95
7	*N*-phenylpyrazole		**2**	100
8			**3**	100

[a] Reactions were carried out at 120 °C with catalyst (0.0125 mmol), substrate (0.25 mmol), and D_2O (2 mL) for 12 h. [b] Conversions determined by ^{1}H NMR spectroscopy.

The reactions were carried out in D_2O at 120 °C with a catalyst loading of 5 mol % over 12 h. As can be seen from the data shown in Table 3, both catalysts showed a good activity in the deuteration of a variety of aryl amines, although the activity of **3** was higher than that shown by **2**. Remarkably, the reactions proceeded in the absence of a base or any other additive. In general, the search of catalysts capable to selectively deuterate organic molecules is a matter of continuous interest because deuterium-labeled compounds can be

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used in a wide range of applications such as the study of biologically active systems, solvents for NMR spectroscopy, and the study of reaction mechanisms.[19] In particular, our results offer the possibility of selectively deuterating a series of aryl amines through a N-directed process, using the most convenient deuterating agent, D_2O.

Conclusion

Herein, we have prepared two new $[IrI_2(AcO)(bis\text{-}NHC)]$ complexes in which the NHC ligands incorporate a sulfonate substituent. The presence of the sulfonate makes the two Ir^{III} complexes water soluble, so the two species are very good candidates for the study of their catalytic activity in aqueous solvents.

Both complexes have been tested in the reduction of CO_2 to formate using H_2 and *i*PrOH. For comparative purposes a similar complex without the sulfonate functionality was also tested, and for all the reactions studied, both catalysts with the sulfonate group showed better catalytic performances. In both processes the complex with the bis-abnormal coordination of the NHC ligand (**3**), shows the best catalytic outcomes. In the reduction with H_2, compound **3** has an activity that is comparable to the best catalyst reported for this reaction.[4,15] In the reduction with *i*PrOH through a transfer hydrogenation process, compound **3** provides the best catalytic results reported to date.

Both **2** and **3** have also shown to be very active catalysts in the selective deuteration of aryl amines through an N-directed process. The high activity of the complexes is comparable to data previously reported by us,[17] but has the advantage that the reaction can be carried out using D_2O as deuterating agent. This new process suggests that both catalysts and, in particular the one with the bis-abnormal coordination (**3**), may be a promising catalyst for the study of further C–H activation processes in water. Further investigations in this direction are underway.

Experimental Section

General procedures: NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers, using CD_3OD, DMSO and D_2O as solvents. Elemental analyses were carried out in an EA 1108 CHNS-O Carlo Erba analyzer. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, and nitrogen was employed as drying and nebulizing gas. Solvents and reagents were used as received from the commercial suppliers. Complex **1** was prepared according to literature methods.[9]

Synthesis of 1,1′-methylenebis[(2,2′-methyl)(3,3′-propanosulfonate)]imidazolium: A mixture of 1,1′-methylenebis[(2,2′-methyl)]imidazole (828 mg, 4.7 mmol) and 1,3-propanosultone (2.8 g, 23.5 mmol) was stirred in CH_3CN at reflux for 14 h. The suspension was filtered and the solid was washed with CH_2Cl_2, affording a white pure product (1.5 g, 78%). H^1 NMR (D_2O, 300 MHz): $\delta = 7.73$ (s, 4H; H_{imid}), 6.65 (s, 2H; NCH_2N), 4.45(t, $^3J(H-H) = 7.26$ Hz, 4H; $CH_2CH_2SO_3$), 3.22 (t, $^3J(H-H) = 7.26$ Hz, 4H; NCH_2), 2.86 (s, 6H; CH_3), 2.40 ppm (m, 4H; $CH_2CH_2SO_3$); $^{13}C\{^1H\}$ NMR (D_2O, 500 MHz): $\delta = 146.2$ (2C; CCH_3imid), 122.4 (2C; *C*imid), 121.3 (2C; Cimid), 57.3 (1C; NCH_2N), 47.4 (2C; CH_2SO_3), 46.9 (2C; NCH_2), 24.5 (2C; $CH_2CH_2SO_3$), 9.7 ppm (CH_3imid).

Synthesis of 2: A mixture of methylenebis[*N*,*N*′-(propanesulfonate)imidazolium] (78 mg, 0.2 mmol), $[Ir(cod)Cl]_2$ (67 mg, 0.1 mmol), KI (100 mg, 0.6 mmol), and NaOAc (65 mg, 0.8 mmol) was stirred in MeOH at reflux temperature for 16 h. The suspension was filtered through Celite, and after drying under vacuum, the solid was washed with CH_2Cl_2 (40 mL) and acetone (40 mL). The solid was purified by chromatography. Elution with MeOH/acetone (1:1, 40 mL) afforded the separation of a yellow band that contained the compound. The complex was obtained as a yellow solid by precipitation from MeOH/*i*PrOH (134.37 mg, 69%). ^1H NMR (CD_3OD, 300 MHz): $\delta = 7.41$ (s, 2H; H_{imid}), 7.31 (s, 2H; H_{imid}), 6.26 (s, 2H; NCH_2N), 4.56 (t, $^3J(H-H) = 7.27$ Hz, 4H; $CH_2CH_2SO_3$), 2.96 (t, $^3J(H-H) = 7.27$ Hz, 4H; NCH_2), 2.42–2.24 (m, 4H; $CH_2CH_2SO_3$), 1.93 ppm (s, 3H; CH_3COO); $^{13}C\{^1H\}$ NMR (DMSO, 500 MHz): $\delta = 176.4$ (1C; CH_3COO), 123.7 (2C; Ir*C*), 122.1 (1C; *C*imid), 120.5 (1C; *C*imid), 48.3 (2C; CH_2SO_3), 47.8 (2C; NCH_2), 26.9 (2C; $CH_2CH_2SO_3$), 24.5 (1C; CH_3COO); electrospray MS (15 V): m/z: 448 $[M]^{2-}$; elemental analysis calcd (%) for $C_{15}H_{21}N_4O_8S_2I_2IrK_2$ (973.70): C 18.50, H 2.17, N 5.75; found: C 18.37, H 2.50, N 5.61.

Synthesis of 3: A mixture of 1,1′-methylenebis[(2,2′-methyl)(3,3′-propanesulfonate)imidazolium (84 mg, 0.2 mmol), $[Ir(cod)Cl]_2$ (67 mg, 0.1 mmol), KI (100 mg, 0.6 mmol), and NaOAc (65 mg, 0.8 mmol) was stirred in MeOH at reflux for 16 h. The suspension was filtered through Celite, and after drying under vacuum, the solid was washed with CH_2Cl_2 (40 mL) and acetone (40 mL). The complex was obtained as a brown solid by precipitation from MeOH/*i*PrOH (150.26 mg, 75%). ^1H NMR (D_2O, 300 MHz): $\delta = 7.72$ (br s, 2H; H_{imid}), 6.63 (s, 2H; NCH_2N), 4.42 (t, $^3J(H-H) = 7.26$ Hz, 4H; $CH_2CH_2SO_3$), 3.21 (t, $^3J(H-H) = 7.26$ Hz, 4H; NCH_2), 2.8 (s, 6H; CH_3), 2.40–2.28 (m, 4H; $CH_2CH_2SO_3$), 1.94 ppm (s, 3H; CH_3COO); $^{13}C\{^1H\}$ NMR (D_2O, 300 MHz): $\delta = 181.7$ (1C; CH_3COO), 146.4 (2C; Ir*C*), 122.9 (2C; CCH_3imid), 121.5 (2C; *C*imid), 47.5 (2C; CH_2SO_3), 47.3 (2C; NCH_2), 24.5 (2C; $CH_2CH_2SO_3$), 23.6 (1C; CH_3COO), 10.0 ppm (CH_3imid); elemental analysis calcd (%) for $C_{17}H_{25}N_4O_8S_2I_2IrK_2$ (1001.75): C 20.38, H 2.52, N 5.59; found: C 20.51, H 2.38, N 5.23.

Catalytic hydrogenation of CO_2 with H_2: Catalytic reactions were carried out in a Hastelloy Autoclave Mini-Reactor system equipped with a 50 mL cylinder. The catalyst was dissolved in a degassed aqueous KOH solution (10 mL). The reactor was pressurized with 60 bar of CO_2/H_2 (1:1) and heated at 80–200 °C for the appropriate time. After reducing the pressure to 1 bar and cooling to room temperature, the solvent was removed by evaporation, and the residue was dissolved in D_2O. The yield of HCOOK was determined by ^1H NMR in D_2O, using isonicotinic acid as internal standard.

Catalytic hydrogen transfer of CO_2 with 2-propanol: The reactions were carried out in a Hastelloy Autoclave Minireactor system equipped with a 100 mL cylinder. The catalyst and KOH were dissolved in 20 mL of a mixture of H_2O/alcohol (9:1 v/v). The reactor was pressurized with 50 bar of CO_2 and heated at 110–200 °C under 1100 r.p.m. stirring for the experiment time. After equilibration to atmospheric pressure and cooling to room temperature, the solvent was removed by evaporation, and the residue was dissolved in D_2O. The yield of HCOOK was determined by ^1H NMR spectroscopy in D_2O, using isonicotinic acid as internal standard.

Deuteration of N-heterocycles in D_2O: A mixture of the substrate (0.25 mmol) and catalyst **1** and **2** (0.0125 mmol) in D_2O (2 mL) was heated at 120 °C in a thick-walled glass tube fitted with Teflon cap. At the desired reaction times, aliquots were extracted from the reaction vessel with $CDCl_3$ and added to an NMR tube.

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