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# Reactions of metallocene niobium(III) isocyanide complexes with oxidizing reagents

**Manuel Gómez, Jesús M. Martinez de Ilarduya and Pascual Royo** *

*Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, 28871 Alcalá de Henares (Spain)*

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## Abstract

New dicyclopentadienylniobium(III) complexes have been made by reducing $NbCp_2Cl_2$ ($Cp = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4SiMe_3$ and $\eta^5\text{-}C_5H_3(SiMe_3)_2$) with Na/Hg in the presence of isocyanides CNR ($R = Bu^n$, $Bu^t$, Ph and $2,6\text{-}Me_2C_6H_3$). These compounds are readily oxidized by $AgBF_4$, to give the corresponding niobium(IV) cations $[NbCp_2ClL]^+$, by $O_2$ to give peroxoniobium(V) derivatives $NbCp_2Cl(\eta^2\text{-}O_2)$, and by t-butyl hydroperoxide to give the known oxo derivatives $NbCp_2Cl(O)$, which can also be made by oxygen transfer from the peroxo compound to triphenylphosphine.

## Introduction

Dicyclopentadienylniobium(III) complexes are convenient starting materials for preparing certain organoniobium(IV) and -(V) compounds. They are oxidized to cationic niobium(IV) derivatives by silver salts containing non-coordinating anions [1] and to neutral niobium(V) derivatives by halogens [2]. Oxidation by oxygen can give oxo or peroxo compounds depending on the electron donating or accepting ability of the substituents [3].

We describe here the isolation of some new isocyanide niobocene complexes and their oxidation to cationic niobium(IV) species and to oxo- and peroxo-niobium(V) compounds, which have been examined as oxygen-transfer agents.

## Results and discussion

### *Synthesis of niobocene isocyanide complexes*

The reduction of $NbCp_2Cl_2$ ($Cp = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$) with one equivalent of Na/Hg (1%) in the presence of isocyanide gives the corresponding niobium(III) complexes, according to eq. 1 in Scheme 1.

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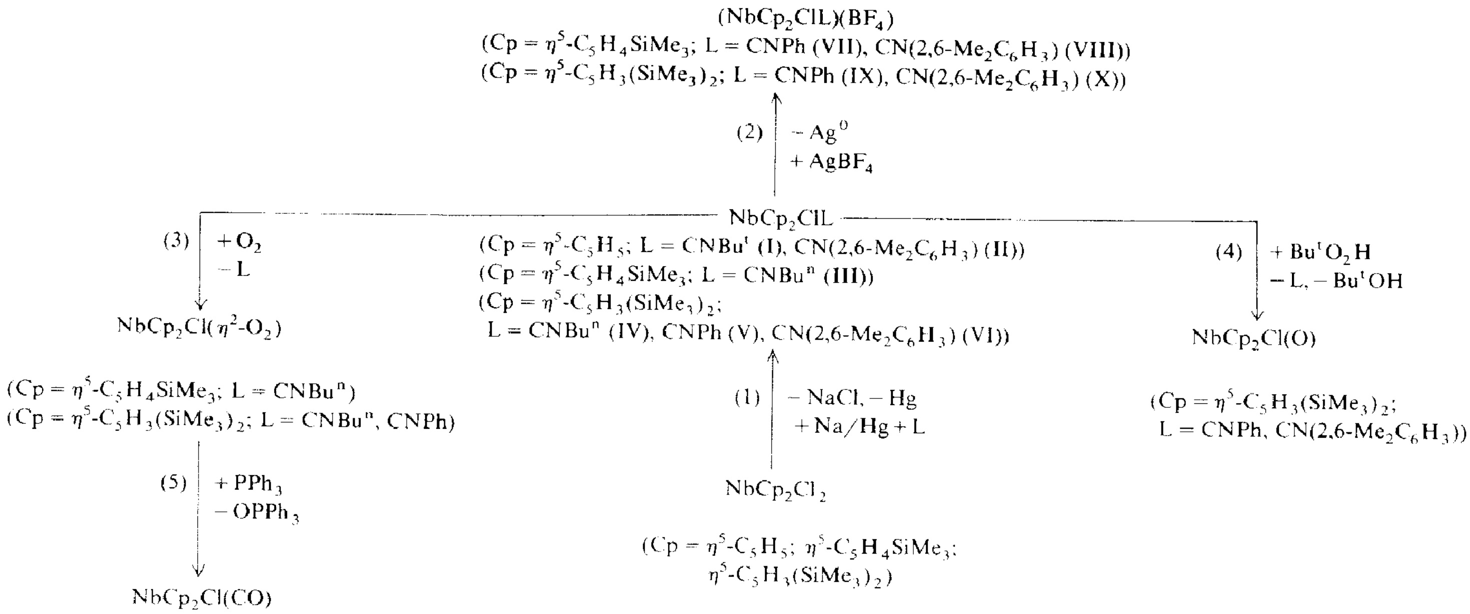
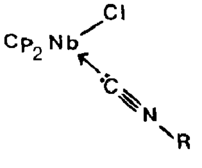
Scheme 1

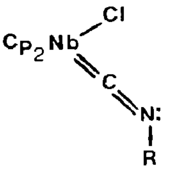

$(NbCp_2ClL)(BF_4)$
$(Cp = \eta^5\text{-}C_5H_4SiMe_3;\ L = CNPh\ (VII),\ CN(2,6\text{-}Me_2C_6H_3)\ (VIII))$
$(Cp = \eta^5\text{-}C_5H_3(SiMe_3)_2;\ L = CNPh\ (IX),\ CN(2,6\text{-}Me_2C_6H_3)\ (X))$
(2)
$-Ag^0$
$+AgBF_4$
$NbCp_2ClL$
(3)
$+O_2$
$-L$
(4)
$+Bu^tO_2H$
$-L,\ -Bu^tOH$
$NbCp_2Cl(\eta^2\text{-}O_2)$
$(Cp = \eta^5\text{-}C_5H_5;\ L = CNBu^t\ (I),\ CN(2,6\text{-}Me_2C_6H_3)\ (II))$
$(Cp = \eta^5\text{-}C_5H_4SiMe_3;\ L = CNBu^n\ (III))$
$(Cp = \eta^5\text{-}C_5H_3(SiMe_3)_2;$
$L = CNBu^n\ (IV),\ CNPh\ (V),\ CN(2,6\text{-}Me_2C_6H_3)\ (VI))$
$NbCp_2Cl(O)$
$(Cp = \eta^5\text{-}C_5H_4SiMe_3;\ L = CNBu^n)$
$(Cp = \eta^5\text{-}C_5H_3(SiMe_3)_2;\ L = CNBu^n,\ CNPh)$
(1)
$-NaCl,\ -Hg$
$+Na/Hg+L$
$(Cp = \eta^5\text{-}C_5H_3(SiMe_3)_2;$
$L = CNPh,\ CN(2,6\text{-}Me_2C_6H_3))$
(5)
$+PPh_3$
$-OPPh_3$
$NbCp_2Cl_2$
$(Cp = \eta^5\text{-}C_5H_5;\ \eta^5\text{-}C_5H_4SiMe_3;$
$\eta^5\text{-}C_5H_3(SiMe_3)_2)$
$NbCp_2Cl(CO)$

Complexes I–VI, isolated as air sensitive solids, were analytically (see Table 1) and spectroscopically characterized. They are soluble in most organic solvents, but with decomposition in chloroform and dichloromethane. The solubility increases with increasing ring substitution.

The IR spectra of complexes I–VI show the characteristic absorptions expected for the ring and its $SiMe_3$ substituents [4,5], along with the $\nu$(Nb–Cl) stretching vibration around 250 $cm^{-1}$ (see Table 1). The $\nu(C\equiv N)$ absorption of the coordinated isocyanide appears at frequencies lower than those for the free ligands (CNR; R = Bu$^t$, 2135; Bu$^n$, 2180; Ph, 2110; 2,6-$Me_2$Ph, 2118 $cm^{-1}$) as a consequence of the $\pi$-electron acceptor nature of the antibonding ligand orbitals, which lower the C–N bond order. This lowering is particularly large (ca. 250 $cm^{-1}$) in complexes containing the more strongly donating substituted $C_5H_5$ ring and for the more electronegative phenyl-substituted isocyanides, whereas complexes containing $SiMe_3$-substituted rings show lower displacements (< 100 $cm^{-1}$) as a result of the $-M$ mesomeric effect of the silyl group. This behaviour reflects the relative contributions of the two canonical structures, increasing donation from the $a'(a_1)$ orbital of the $Cp_2NbCl$ fragment enhancing the contribution of the bent structure **B**.



(A)



(B)

Complexes I–II show the expected singlet for the $\eta^5$-$C_5H_5$ protons (see Table 2). Complex III shows one singlet, and complexes IV–VI two singlets attributable to one or two $SiMe_3$ groups, respectively, along with several multiplets from the remaining ring protons. All the complexes show the expected signals for the organic substituent of the isocyanide ligand.

Table 1

Analyses and selected IR data for niobium(III) isocyanide complexes

| Complex | Found (calcd.) (%) | | | IR | | Colour |
|---|---|---|---|---|---|---|
| | C | H | N | $\nu(C\equiv N)$ | $\nu$(Nb–Cl) | |
| I | 52.60 | 5.54 | 4.05 | 1890m | 250w | Red |
| | (52.73) | (5.60) | (4.10) | | | |
| II | 58.35 | 4.90 | 3.54 | 1860br | 250w | Red |
| | (58.54) | (4.92) | (3.59) | | | |
| III | 52.00 | 7.12 | 2.95 | 2135s | 250w | Red |
| | (51.90) | (7.26) | (2.88) | | | |
| IV | 52.20 | 7.93 | 2.63 | 2110s | 250w | Red |
| | (51.44) | (8.15) | (2.22) | | | |
| V | 54.30 | 7.60 | 2.35 | 2025m | 250w | Green |
| | (53.55) | (7.28) | (2.15) | 1790br | | |
| VI | 54.58 | 7.76 | 2.08 | 1965m | 270–250w | Green |
| | (54.88) | (7.58) | (2.06) | 1882s | | |
| | | | | 1837m | | |

Table 2

$^1$H NMR $^a$ spectra for niobium(II) isocyanide complexes

| Complex | $\eta^5$-$C_5H_5$ | $\eta^5$-$C_5H_4SiMe_3$ | | $\eta^5$-$C_5H_3(SiMe_3)_2$ | | CNR |
|---|---|---|---|---|---|---|
| | | $\eta^5$-$C_5\mathit{H}_4SiMe_3$ | $\eta^5$-$C_5H_4Si\mathit{Me}_3$ | $\eta^5$-$C_5\mathit{H}_3(SiMe_3)_2$ | $\eta^5$-$C_5H_3(Si\mathit{Me}_3)_2$ | |
| I | 4.90(s,10) | | | | | 1.15(s,9), R = $Bu^t$ |
| II | 4.99(s,10) | | | | | 7.05(s,3);2.19(s,6),<br>R = 2,6-$Me_2C_6H_3$ |
| III | | 5.50(m,2),5.43(m,2) | | | | |
| | | | 0.17(s,18) | | | 1.16(s,9), R = $Bu^n$ |
| | | 4.90(m,2),4.75(m,2) | | | | |
| IV | | | | 5.62(m,2) | 0.37(s,18) | 3.12(s,2);1.21(s,4) |
| | | | | 4.83(m,4) | 0.20(s,18) | 0.87(s,3), R = $Bu^n$ |
| V | | | | 5.19(m,2) | 0.37(s,18) | 7.38–6.87(m,5), R = Ph |
| | | | | 5.18(m,2) | 0.23(s,18) | |
| | | | | 5.07(m,2) | | |
| VI | | | | 5.79(m,2) | 0.35(s,18) | 6.79(s,3);2.51(s,6) |
| | | | | 5.18(m,2) | 0.17(s,18) | R = 2,6-$Me_2C_6H_3$ |
| | | | | 4.90(m,2) | | |

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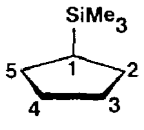
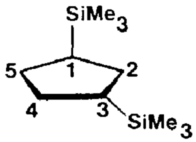
[a] In benzene-$d_6$. Chemical shifts with respect to TMS; positive signals downfield. In parentheses are shown the multiplicity and relative intensity.

Table 3

$^{13}C\{^1H\}$ NMR[a] spectra for niobium(III) isocyanide complexes ($\delta$ ppm)

| Complex | $\eta^5$-$C_5H_5$ | $C^1$ | $C^2$ | $C^3$ | $C^4$ | $C^5$ | $SiMe_3$ | $C^1$,$C^3$ | $C^2$ | $C^4$ | $C^5$ | CNR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | |  | | | |  | | | | |
| I | 98 | | | | | | | | | | | R = Bu$^t$, 61.0($C^1$); 31.4(Me) |
| II | 102.5 | | | | | | | | | | | R = 2,6-$Me_2C_6H_3$, 135.8–125.0 several Ph; 20.7(Me) |
| III | | 91.7 | 108.9 | 102.9 | 100.3 | 95.1 | 0.5 | | | | | R = Bu$^n$, 46.9($C^1$); 32.8($C^2$)<br>20.5($C^3$); 13.8($C^4$) |
| IV | | | | | | | 0.4 | 98.2;117.2 | 124.2 | 93.2 | 91.6 | R = Bu$^n$, 46.7($C^1$); 32.6($C^2$)<br>20.5($C^3$); 13.8($C^4$)<br>CN 193.5 |
| V | | | | | | | 0.4 | 101.8;121 | 124.3 | 97.0 | 97.0 | R = Ph, 138.3($C^1$); 126.3($C^2$,$C^6$)<br>130.2($C^3$,$C^5$); 127.9($C^4$)<br>CN 214.3 |
| VI | | | | | | | 0.5 | | | | | |
| | | | | | | | | 98.3;123.6 | 120.9 | 97.0 | 96.2 | R = 2,6-$Me_2C_6H_3$, 133.3($C^1$);<br>135.4($C^2$,$C^6$)<br>129.0($C^3$,$C^5$)<br>128.2($C^4$)<br>20.7(Me)<br>CN 197.4 |
| | | | | | | | 0.2 | | | | | |

[a] In THF.

The presence of five resonances due to the ring carbon atoms in complexes III–VI (see Table 3) indicates that they are non-equivalent as was observed for similar complexes containing different substituents in the reflection plane of the rings [6,7]. They also show a singlet for the methyl carbon atoms of the $SiMe_3$ fragment. Complexes I–II show the expected singlet for the ring carbon atoms.

It has not been possible to observe the CN singlet in complexes I–III, apparently owing to the long relaxation time [8], but weak singlets at ca. $\delta$ 201.4 ppm are observed for complexes III–VI, indicating the carbenoid character of the isocyanide carbon atoms.

*Oxidation with silver(I) salts*

When $AgBF_4$ is added to a THF solution of any of the niobium(III) complexes in a molar ratio 1/1, oxidation takes place inmediately at room temperature, with deposition of metallic silver, according to eq. 2 in Scheme 1. Silver(I) can oxidize these niobium(III) complexes in spite of their lower reducing ability, due to the stabilizing effect [3] of less electron-donating $SiMe_3$-substituted cyclopentadienyl rings.

Complexes VII–X are brown crystalline solids, which were characterized by analysis (see Table 4) and by the data presented below.

All these cationic compounds are paramagnetic at room temperature, with expected $\mu_{eff}$ values for $d^1$ species (see Table 4). Molar conductivities are in the range corresponding to 1/1 electrolytes [9]. The IR spectra show absorptions due to the cyclopentadienyl ring and its $SiMe_3$ fragment [4,5] along with the $\nu$(Nb–Cl) vibration between 295 and 307 $cm^{-1}$ and the strong absorption at ca. 1080 $cm^{-1}$ due to the $BF_4^-$ anion. The stretching $\nu$(C≡N) appears at ca. 2175 $cm^{-1}$, which is about 60 $cm^{-1}$ higher than that for the free ligand (2110 $cm^{-1}$ for CNPh; 2118 $cm^{-1}$ for CN-2,6-$Me_2$Ph) [10], indicating a $\sigma$-donating character of the isocyanide ligand, which favours a linear structure for the ligand.

*Oxidation with oxygen*

The isocyanide niobium(III) complexes are oxidized by bubbling $O_2$ through their THF solutions, in accord with eq. 3 in Scheme 1, to give the previously prepared [3]

Table 4

Anaylses, selected IR, magnetic and conductivity data for cationic niobium(IV) complexes

| Complex | Found(calcd.) (%) | | | IR [a] | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | $\nu$(CN) | $\nu(BF_4^-)$ | $\nu$(Nb–Cl) | $\mu_{eff}$ [b] | $\Lambda_m$ [c] |
| VII | 46.90 | 5.14 | 2.30 | 2185s | 1075s,br | 300w | 1.70 | 125.6 |
| | (46.60) | (5.27) | (2.36) | | | | | |
| VIII | 46.73 | 5.63 | 2.15 | 2168s | 1085s,br | 295w | 1.79 | 127.5 |
| | (48.36) | (5.68) | (2.26) | | | | | |
| IX | 48.48 | 6.98 | 1.98 | 2180s | 1070s,br | 305w | 1.67 | 127.7 |
| | (47.25) | (6.43) | (1.90) | | | | | |
| X | 49.46 | 7.60 | 1.92 | 2160s | 1080s,br | 307w | 2.19 | 135.2 |
| | (48.66) | (6.72) | (1.83) | | | | | |

[a] In Nujol-polyethylene mulls. [b] In BM, at 298 K, under nitrogen. [c] Values in $ohm^{-1}$ $cm^2$ $mol^{-1}$ from $10^{-4}$ $M$ aquo-solutions.

peroxo complexes $NbCp_2Cl(\eta^2\text{-}O_2)$ ($Cp = \eta^5\text{-}C_5H_4SiMe_3$; $\eta^5\text{-}C_5H_3(SiMe_3)_2$), as has been observed for other isocyanide niobocene derivatives.

### *Oxidation with t-butyl hydroperoxide*

The intermediate formation of hydroperoxides in catalytic oxidation of alkanes prompted us to investigate the reaction of the mentioned isocyanide niobocene complexes with $Bu^tO_2H$. The oxidation takes place with transfer of oxygen to give the previously described [3] oxo compound, $NbCp_2Cl(O)$, ($Cp = \eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$), as shown in eq. 4 in Scheme 1, with elimination of t-butyl alcohol, which was identified and determined by liquid chromatography in the resulting solution.

Like $NbCp_2Cl(\eta^2\text{-}O_2)$ ($Cp = \eta^5\text{-}C_5H_5$) [11], our peroxo complexes with $Cp = \eta^5\text{-}C_5H_4SiMe_3$ or $\eta^5\text{-}C_5H_3(SiMe_3)_2$ react with triphenylphosphine to give triphenylphosphine oxide and the corresponding oxo complexes $NbCp_2Cl(O)$ [3], according to eq. 5 in Scheme 1. The products were analytically and spectroscopically identified (IR and NMR).

## Experimental

All operations were carried out under vacuum or under nitrogen or argon by use of Schlenk-type glassware. Solvents were dried, distilled under nitrogen, and degassed before use.

$NbCp_2Cl_2$ ($Cp = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$) were made by published methods [12–14], as were the isocyanides [15].

IR spectra in the range 4000–200 $cm^{-1}$ were recorded on a Perkin–Elmer 599 spectrophotometer as Nujol mulls between polyethylene films. C, H and N analyses were performed with a Perkin–Elmer 240B microanalyzer.

The $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian FT 80A instrument with $SiMe_4$ as internal reference, and with samples prepared under an inert atmosphere. Magnetic susceptibilities were measured by the Faraday method at room temperature under an inert atmosphere with a Bruker B-E15 magnetic system. Conductivity molar measurements were made with a WTW Messgerät LF-42 conductimeter and LTA 100 cell, using $10^{-4}$ M aqueous solutions of the cationic complexes.

### *Synthesis of $NbCp_2Cl(CN\text{-}R)$ complexes*

An excess of the ligand CNR (2.250 mmol) in THF (50 $cm^3$) was added to a mixture of $NbCp_2Cl_2$ (2 mmol) and sodium amalgam (0.046 g, 2 mmol). The mixture was stirred for 8 h, the coloured suspension was then filtered and the solvent evaporated under reduced pressure. The residue was extracted with toluene ($Cp = \eta^5\text{-}C_5H_5$) or n-hexane ($Cp = \eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$) and the extract filtered. The solution obtained was concentrated and cooled to −40 °C to give red (I–IV) or green (V,VI) crystals. Yields ca. 80% (I 75%; II 70%; III and V 85%; IV 90%; VI 80%).

### *Synthesis of $[NbCp_2Cl(CN\text{-}R)]\ BF_4$ complexes*

Solid $AgBF_4$ (0.226 g, 1.160 mmol) was added to a solution of $NbCp_2Cl(CNR)$ (1.160 mmol) in THF (50 $cm^3$). The mixture was stirred for 12 h, affording a fine black precipitate of Ag. The solution was filtered, the solvent was removed in vacuo, and the oily residue was washed with cold diethyl ether (2 × 15 $cm^3$). The brown crystalline solids obtained were characterized as VII–X. Yields ca. 75% (VII and IX 70%; VIII and X 80%).

*Reaction of* $NbCp_2Cl(CN\text{-}R)$ *(*$Cp = \eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$*) with oxygen*

$O_2$ was bubbled through THF solutions of complexes III–V (2.500 mmol). The clear yellow solution obtained was filtered and evaporated to dryness. The yellow residue was extracted with cold n-hexane and the extract cooled to −40 °C to give $NbCp_2Cl(\eta^2\text{-}O_2)$ as yellow crystals. Yield ca. 80%.

*Reaction of* $Nb\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2Cl(CNR)$*, (*$CNR = CNPh$, $CN(2,6\text{-}Me_2C_6H_3)$*) with* $Bu^tO_2H$

Solid $Nb\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2Cl(CNR)$ (0.590 mmol) was added to a 3 *M* toluene solution of $Bu^tO_2H$ (0.590 mmol, 0.20 $cm^3$). After 4 h the solid had dissolved to give a clear yellow solution. The solution was filtered and evaporated to dryness, and the oily residue extracted with n-hexane (2 × 15 $cm^3$). The resulting solution was kept overnight to −40 °C to give $Nb\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2Cl(O)$ as yellow crystals. Yield 75% (0.256 g).

*Reaction of* $NbCp_2Cl(\eta^2\text{-}O_2)$*, (*$Cp = \eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5H_3(SiMe_3)_2$*) with* $PPh_3$

Solid $NbCp_2Cl(\eta^2\text{-}O_2)$ (0.953 mmol) was added to a stirred solution of $PPh_3$ (0.250 g, 0.953 mmol) in 25 $cm^3$ of THF. After 24 h the clear yellow solution obtained was concentrated to ca. 10 $cm^3$ and kept overnight at −40 °C to give white crystals, which were filtered off and shown to be $OPPh_3$ (75% yield). n-Hexane (10 $cm^3$) was added to the filtrate, and the solution was kept at −40 °C. The yellow crystals formed were filtered off, washed with diethyl ether, and dried in vacuo, to give a 60% yield of $NbCp_2Cl(O)$.

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