4d vs. 5d – Reactivity and Fate of Terminal Nitrido Complexes of Rhodium and Iridium

Julia Schöffel,^[a] Nevena Šušnjar,^[a] Stefan Nückel,^[a] Daniel Sieh,^[a] and Peter Burger*^[a]

Dedicated to Jürgen Heck on the occasion of his 60th birthday

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The stability of (pyridinediimine)rhodium– and -iridium– azido complexes was studied by a combination of thermoanalytical methods (DTG/MS and DSC) and DFT calculations. On a preparative scale, the isolation and X-ray crystallographic characterization of the thermolysis products confirmed intramolecular C–H activation processes with concomitant reorganisation of C–C, C–N, N–H and Ir–N bonds to yield tuck-in complexes with a different constitution of the ligand framework for the Rh and Ir products. The tentatively formed (Rh) or initially present (Ir) nitrido unit was converted into either an amine (Rh) or amido (Ir) moiety. Furthermore,

Introduction

In the last decade the status of the class of electron-rich late transition complexes ($> d^4$ configuration) with terminal metal-heteroatom multiple bonds, i.e. M=XR and M=X (X = N, O, S), changed from exotic to well-established.^[1,2] Imido complexes, $L_{\mu}M=NR$ (M = Co, Ni, Cu), are among the most prominent representatives and display a high reactivity in a variety of reactions, e.g. the aziridination of olefins.^[3] For complexes with terminal unsubstituted heteroatom ligands, M=X (e.g. metal-nitrido, -oxido, -sulfido units), on the other hand, the situation has only little changed. Apart from X-ray crystallographically characterized metal-oxido complexes of the Pd, Pt and Au transition metals reported by Hill et al.^[4] and the Pd-oxido complex reported by Milstein et al.,^[5] most compounds of this type were proposed based on circumstantial experimental evidence rather than their direct observation.^[6] Recently, we reported the synthesis and preliminary reactivity studies of the first isolated d⁶-configured late transition nitrido example, i.e. the square-planar complex 2-Ir, which displays a terminal Ir≡N unit.^[7] Herein, we report on the thermal stathe dimerization of the nitrido complexes to the corresponding dinitrogen compounds, i.e. $2 L_n M \equiv N \rightarrow L_n M - N_2 - M L_n$, was investigated. Experimental evidence for the relevance of this step was provided by the isolation and X-ray crystallographic characterization of a related dinuclear N₂-bridged (pyridinediimine)dirhodium complex. DFT calculations revealed that the formation of dinitrogen complexes is thermodynamically strongly favourable and evidenced that the previous isolation of a terminal iridium–nitrido complex was possible due to a high barrier for the dimerization process and a sizeable barrier for the intramolecular C–H activation step.

bility and thermochemistry of **2-Ir** and compare it to the corresponding acclaimed 4d congener, the rhodium–nitrido compound **2-Rh**.

Results and Discussion

Our previous thermoanalytical study of the Ir–azido complex **1-Ir** revealed *two* consecutive exothermic steps: Initially, the nitrido complex **2-Ir** is formed by N₂ extrusion, which then undergoes further conversion *without* further mass loss to a previously unidentified product at elevated temperature. From heating of either **1-Ir** and **2-Ir** at 150 °C in the solid state, we were now able to isolate **3-Ir** as the product of the second thermolysis step in quantitative yield (Scheme 1). The NMR spectroscopic and X-ray single-crystal structure analysis of **3-Ir** confirmed our previous suggestion that a tuck-in amido complex is formed in this reaction step by an apparent intramolecular C–H activation step of *one* isopropyl methine C–H bond.

By contrast, the absence of a reaction up to 200 °C in the TG/MS (Figure 1) and differential scanning calorimetry (DSC) measurements of **1-Rh** documented that the corresponding rhodium–azido complex is thermally significantly more robust than its iridium congener **1-Ir**.^[8] In the TG/MS measurements an exothermic reaction sets in at T > 200 °C, which is accompanied by a mass loss of 10% and a concomitant signature of m/z = 28 and 14 (N₂⁺, N₂²⁺) in the mass spectral trace evidencing extrusion of N₂. The observed

 [[]a] Institut für Angewandte und Anorganische Chemie, Department Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany Fax: +49-40-42838-6097

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SHORT COMMUNICATION



Scheme 1. Formation of rhodium and iridium tuck-in complexes **3-Ir** and **3-Rh** and ORTEP plots of **3-Ir** and **3-Rh** at the 50% probability level. Selected bond lengths [Å]: **3-Ir**: Ir1–N1 1.853(6), Ir1–N2 1.952(7), Ir1–N3 2.017(7), Ir1–N4 1.875(7), N4–C40 1.464(1), C1–N2 1.314(11); **3-Rh**: Rh1–N1 1.942(3), Rh1–N2 1.962(3), Rh1–N3 2.014(3), Rh1–N4 2.148(3), N4–C40 1.537(5), C1–N2 1.512(11), C1–C43 1.590(5).^[7]

mass loss is higher than the expected mass loss of 4.5%, caused by the thermal degeneration due to the chosen heating rate.

The DSC measurements of **1-Rh** are in agreement with the TG/MS experiments and display only *one* strongly exothermic step with an enthalpy of $\Delta H = -36$ kcal/mol. This compares to enthalpy values of $\Delta H = -6$ and -21 kcal/mol for the *two* consecutive transformations **1-Ir** \rightarrow **2-Ir** and **2-**Ir \rightarrow **3-Ir** and a total ΔH_{tot} value of -27 kcal/mol leading to the nitrido and tuck-in iridium complexes. The identity of the thermolyis product **3-Rh** could be established unambiguously from an X-ray single-crystal structure analysis for a recrystallized sample obtained from heating **1-Rh** in the solid state at 200 °C (Scheme 1).^[8]

While the formation of an anticipated rhodium tuck-in complex was indeed confirmed, to our surprise, its constitution differed from the one of the aforementioned iridium compound **3-Ir**. In fact, *two* rather than just one isopropyl methine C–H bonds were activated yielding the amine-amido complex **3-Rh**. The 1-D and 2-D correlated NMR spectra of **3-Rh** also document complete loss of symmetry upon thermolysis.

Upon inspection of the rhodium and iridium tuck-in complexes, it might be at first glance anticipated that the structure observed for the single tuck-in iridium derivative **3-Ir** corresponds to an intermediate leading to an analogue



Figure 1. DTGA/MS measurements for the transformations of 1-Ir (top). Black: weight loss; light grey: DTG signal; grey: DTA signal; black dots: ion current. (a) 1-Ir \rightarrow 2-Ir \rightarrow 3-Ir, $\Delta m_{\text{calcd.}} =$ 3.9% (included for comparison),^[7] reproduced with permission from *Angew. Chem.*; (b) 1-Rh \rightarrow 3-Rh, $\Delta m_{\text{calcd.}} =$ 4.5% (bottom).

of the double tuck-in rhodium compound **3-Rh**. However, even upon extended and elevated heating, there is *no* conversion of **3-Ir** to the iridium double tuck-in analogue of **3-Rh**. This circumstantial evidence suggests that the single tuck-in Rh analogue of **3-Ir** is not a transient on the pathway leading to **3-Rh**.

The formation of tuck-in complexes by reactive transition metal complexes is a well-known process. Recently, Power et al. reported for instance on the C–H activation in a phenyl substituent of a putative two-coordinate manganese complex.^[9] Especially, in the chemistry of late transition metal complexes with terminal multiple-bonded π -donor ligands, tuck-in formation is a well-known reaction pathway, which allows to relax π - π metal–ligand repulsive interactions.^[10]

At present, we cannot offer a conclusive answer for the apparent disparity of the rhodium and iridium systems. Even from extensive DFT calculations, in which open-shell systems and different spin states were considered for the C– H activation processes in the Ir and Rh nitrido systems, only the following tentative explanations can be provided (Figure 2): We assume that the tuck-in formation for the rhodium system is initiated by the nitrido species. The extrusion of N₂ for the rhodium complex is calculated to be an uphill process by 15 kcal/mol, consistent with the observed stability of the Rh^I–azido complex. The consecutive



Figure 2. Conceivable mechanisms for the formation of the tuck-in model complexes **3-Rh**_{model} and **3-Ir**_{model} with DFT-calculated (BP86 functional) reaction barriers ΔE_a and total energies ΔE_r (relative to **2-M**_{model}) in kcal/mol.^[8]

formation of the tuck-in complex may be initiated by hydrogen atom abstraction from the isopropyl methine group of the nitrido unit to give the diradical imido (Rh=NH) intermediate b (Figure 2). This view is supported by DFT calculations with the BP86 and B3LYP functionals for the model Rh and Ir complexes, in which one of the iminoaryl substituents was replaced by a hydrogen atom. The calculated energy differences revealed that this process is uphill by 21 (19) kcal/mol for the iridium system and only 15 (10) kcal/ mol for the rhodium compound (B3LYP values are given in parentheses).^[8] It seems therefore likely that radical pathways are more prevalent for the tentative Rh-nitrido complex 2-Rh. A possible scenario for the formation of 3-Rh is depicted in Figure 2.

For the Ir system on the other hand, it is anticipated that the initial C-H activation step proceeds by direct C-H bond addition of the isopropyl methine group to the nitrido unit. This would correspond to our previously proposed pathway for the intermolecular addition of dihydrogen to the nitrido unit yielding the amido complex ([Ir] \equiv N + H₂ \rightarrow [Ir]-NH₂).^[7] Finally, it deserves a special mention that the experimentally determined enthalpies for the formation of the Rh and Ir tuck-in complexes are in good agreement with the energy differences derived by DFT calculations.

Previous reports of Peters and Taube et al. of terminal Fe- and Os-nitrido complexes to undergo dimerization to more stable bridging N₂ complexes according to 2 $L_n M \equiv N$ \rightarrow L_nM–N=N–ML_n prompted us to look into similar pathways for the iridium-nitrido complex 2-Ir.[11] This was further substantiated by the independent synthesis of the stable dinuclear end-on bridging dinitrogen-Rh complex 4-Rh with the sterically less demanding 2,6-dimethylphenyl substituent of the N_{imine} donor and the terminal dinitrogen-Rh complex 5-Rh with the sterically more demanding 2,6diisopropylphenyl substituent (Figure 3). Both complexes 4-Rh and 5-Rh were obtained by reduction of the corresponding Rh^I-chlorido or -methoxido precursors with sodium amalgam under dinitrogen.^[12]

Initially, we studied the dimerization of the model iridium-nitrido complex depicted in Figure 4 under C_2 symmetry constraints, i.e a colinear approach of the two Irnitrido units. Whereas the overall process is thermodynamically very favourable with an energetic drop of -110 kcal/ mol, this process displays a substantial barrier of +35 kcal/ mol (Figure 4).



Figure 3. ORTEP plots of 4-Rh (left) and 5-Rh (right) at the 50% probability level. Selected bond lengths [Å] and angles [°]: 4-Rh: Rh1-N1 1.924(4), Rh1-N2 2.014(3), Rh1-N3 2.025(4), Rh1-N4 1.936(4), N4-N4' 1.130(7); 5-Rh: Rh1-N1 1.914(1), Rh1-N2 2.011(1), Rh1-N3 2.012(1), Rh1-N4 1.950(2), N4-N5 1.087(3), Rh1-N4-N5 178.8(3).



Figure 4. Potential-energy scan for a colinear approach of two iridium-nitrido model complexes (DFT, BP86).[8]

It deserves a special notion with this regard that our previous NBO analysis of the iridium-nitrido complex 2-Ir revealed sp hybridization for the nitrido N donor atom with the lone pair located on the dimerization axis.^[6] Therefore, this type of barrier was clearly expected based on a highly unfavourable 4 electron/2 orbital situation for the direct frontal attack. This parallels the findings for the dimerization of singlet carbenes, which dimerize by a so called "nonleast-motion pathway" that involves the attack of the occupied in-plane σ lone pair of one singlet carbene center on the vacant out-of-plane p_{π} orbital of a second carbene (cf.

SHORT COMMUNICATION

Figure 5).^[13] Finally, a spin-state change to a more stable triplet from an initial S = 0 state during the dimerization process shall be noted in passing (Figure 4).^[8]



Figure 5. Frontier orbitals and nonleast-motion pathway for the dimerization of iridium-nitrido complexes.

Next in our DFT study, we released the colinear constraints for the dimerization of the iridium model complex. Based on the isolobal relation of the nitrido complex and singlet carbenes a similar nonleast-motion pathway for dimerization of the nitrido compounds was probed (Figure 5). This indeed revealed an essentially *barrierless* reaction. We also investigated the dimerization of the corresponding (unknown) iridium–nitrido complex with 2,6-dimethylphenyl ketimine substituents, which also collapses without barrier to the iridium anologue of the dinuclear N_2 -bridged dirhodium compound **4-Rh**.

Conclusions

The observation of sizeable barriers for dimerization and tuck-in formation provides an explanation for our previous isolation of the exclusive nitrido complex **2-Ir**. Nevertheless, the presented system is viewed with mixed feelings. On the one hand we are able to prevent dimerization of the nitrido units through the proper choice of the ligand and can witness the desired, yet intramolecular, aptitude for C–H bond activiation by the terminal nitrido unit. On the other hand, new design rules for nitrido complexes are anticipated to avoid the undesired step leading to tuck-in complexes and are currently under investigation in our laboratory.

Experimental Section

General: Synthetic and selected spectroscopic data for **1-Rh**, **3-Rh**, **3-Ir**, **4-Rh**, and **5-Rh** are included here. The complete spectroscopic and crystallographic data^[14] as well as the used labelling scheme for the assignment of the NMR resonances can be found in the Supporting Information; the data for the starting materials can be found in ref.^[7,15]

1-Rh: To a solution of $[Rh(iPr_4N_3)OMe]$ (428 mg, 695 µmol) in THF (10 mL) was added Me₃SiN₃ (200 µL, 1.68 mmol). After stirring at room temp. for 24 h, the solvent and the volatile side products were removed by vacuum distillation. The remainder was then triturated with alternate pentane and vacuum treatment. The obtained green product can be used without further purification. Correct elemental analysis data could not be obtained in several attempts, even after repeated recrystallizations. ¹H NMR

(400 MHz, [D₈]THF, room temp.): $\delta = 8.47$ [t, ${}^{3}J = 8$ Hz, 1 H, C_{py}(4)*H*], 7.87 [d, 2 H, C_{py}(3,5)*H*], 7.08–7.20 (m, 6 H, C_{arom}*H*), 3.06 [sept, ${}^{3}J = 7$ Hz, 4 H, C*H*(CH₃)₂], 1.65 (s, 6 H, N=CCH₃), 1.14 [d, ${}^{3}J = 7$ Hz, 12 H, CH(CH₃)₂], 1.05 [d, ${}^{3}J = 7$ Hz, 12 H, CH(CH₃)₂] ppm. ${}^{13}C{}^{1}H{}$ NMR (100 MHz, [D₈]THF, room temp.): $\delta = 166.6$ (N=CCH₃), 155.2 [$C_{py}(2,6)$], 145.3 [$C_{arom}(1)$], 139.5 [$C_{arom}(2,6)$], 126.1 [$C_{arom}(3, 5 \text{ or 4})$], 124.5 [$C_{py}(3,5)$], 122.5 [$C_{arom}(3, 5 \text{ or 4})$], 122.2 [$C_{py}(4)$], 27.9 [CH(CH₃)₂], 22.7 [CH-(CH₃)₂], 16.4 (N=CCH₃) ppm.

3-Rh: 55 mg (88 μ mol) [Rh(*i*Pr₄N₃)N₃] (**1-Rh**) were placed as solvent free solid in a teflon tapped Schlenk tube and heated under vacuum at 150 °C for 5.5 d. After this time the solid changed its color from green to violet and the ¹H-NMR spectrum revealed a quantitative conversion. Single crystals suitable for X-ray crystal structure analysis were obtained from a concentrated toluene/diethyl ether (2:1) solution at -35 °C. C₃₃H₄₃N₄Rh (598.64): calcd. C 66.21, H 7.24, N 9.36; found C 66.16, H 7.15, N 8.85, ¹H NMR (400 MHz, [D₈]THF, room temp.): $\delta = 8.06$ [d, ${}^{3}J = 7.2$ Hz, 1 H, C_{py}(3)H], 7.82-7.78 [m, 1 H, C_{py}(4)H], 7.73-7.71 [m, 1 H, C_{py}-(5)H], 7.31–7.17 [m, 3 H, C_{arom}(3,4,5)H_I], 6.71 [d, ³J = 7.0 Hz, 1 H, $C_{arom}(5)H_{K}$], 6.57 [d, ${}^{3}J$ = 7.0 Hz, 1 H, $C_{arom}(3)H_{K}$], 5.95 [t, ${}^{3}J$ = 7.0 Hz, 1 H, $C_{arom}(4)H_{K}$], 4.23 (d, ³J = 11.2 Hz, 1 H, NH₂), 3.93 (d, ${}^{3}J = 11.2$ Hz, 1 H, NH₂), 3.52 [sept, ${}^{3}J = 6.8$ Hz, 1 H, CH- $(CH_3)_2$], 2.79 [sept, ${}^{3}J = 6.8$ Hz, 1 H, $CH(CH_3)_2$], 1.82 [s, 3 H, CC(CH₃)₂], 1.75 (s, 3 H, N=C-CH₃), 1.56 [s, 3 H, NC(CH₃)₂], 1.46 [d, ${}^{3}J$ = 6.8 Hz, 3 H, CH(CH₃)₂], 1.10 [s, 3 H, NC(CH₃)₂], 1.05– 1.04 [m, 6 H, CH(CH₃)₂], 0.95 [d, ${}^{3}J$ = 6.8 Hz, 3 H, CH(CH₃)₂], 0.90 [s, 3 H, CC(CH₃)₂], 0.23 (s, 3 H, N-C-CH₃) ppm.

3-Ir. (a) From Complex $[Ir(iPr_4N_3)N_3]$ (1-Ir): $[Ir(iPr_4N_3)N_3]$ (1-Ir) (100 mg, 145 µmol) was placed as solvent-free solid in a Teflon[®]tapped Schlenk tube and heated under vacuum at 150 °C for 13 h. The solid changed its color from green to violet. The ¹H NMR spectra showed an essentially quantitative conversion. Recrystallization was carried out from a concentrated THF/pentane (2:1) solution at -35 °C. By the same procedure single crystals suitable for X-ray crystal structure analysis were obtained. (b) Alternative Synthesis from [Ir(*i*Pr₄N₃)N] (2-Ir): Analogous to synthesis (a) starting from [Ir(iPr₄N₃)N] (2-Ir). C₃₃H₄₃IrN₄ (687.95): calcd. C 57.61, H 6.30, N 8.15; found C 57.66, H 6.68, N 7.41, ¹H NMR (400 MHz, [D₈]THF, room temp.): δ = 8.53 [d, ³J = 7.8 Hz, 1 H, $C_{py}(3 \text{ o. } 5)H$], 8.43 [d, ${}^{3}J$ = 7.8 Hz, 1 H, $C_{py}(3 \text{ o. } 5)H$], 7.52 [t, ${}^{3}J$ = 7.8 Hz, 1 H, $C_{py}(4)H$], 7.43 [d, ${}^{3}J$ = 7.8 Hz, 1 H, $C_{arom}(3)H_{K}$], 7.33-7.29 [m, 3 H, C_{arom}(3 or 5)H_I, C_{arom}(5)H_K], 7.26-7.21 [m, 2 H, $C_{arom}(4, 3 \text{ or } 5)H_I$ and (NH)], 7.14 [t, ${}^{3}J$ = 7.8 Hz, 1 H, C_{arom} -(4) $H_{\rm K}$], 3.48 [sept, ${}^{3}J$ = 6.8 Hz, 1 H, CH(CH₃)_{2(K)}], 2.88 [sept, ${}^{3}J$ = 6.8 Hz, 1 H, $CH(CH_3)_{2(I)}$], 2.76 [sept, ${}^{3}J$ = 6.8 Hz, 1 H, CH- $(CH_3)_{2I}$, 1.86 [s, 3 H, NC $(CH_3)_2$], 1.48 [d, ${}^{3}J$ = 6.8 Hz, 3 H, CH(CH₃)_{2(K)}], 1.39 (s, 3 H, N=C-CH₃), 1.22-1.20 [m, 6 H, NC(CH₃)₂, N=C-CH₃] 1.17 [d, ${}^{3}J$ = 6.8 Hz, 3 H, CH(CH₃)_{2(I)}], 1.11 [d, ${}^{3}J$ = 6.8 Hz, 3 H, CH(CH₃)_{2(I)}], 1.08 [d, ${}^{3}J$ = 6.8 Hz, 3 H, $CH(CH_3)_{2(I)}$, 0.71 [d, ${}^{3}J$ = 6.8 Hz, 3 H, $CH(CH_3)_{2(I)}$], 0.52 [d, ${}^{3}J$ = 6.8 Hz, 3 H, $CH(CH_3)_{2(K)}$] ppm.

Crystallographic Data for 3-Ir: M = 760.04 g/mol, triclinic, $P\overline{1}$ (no. 2), a = 11.6656(19), b = 12.176(2), c = 13.376(2) Å, $a = 78.743(3)^{\circ}$ $\beta = 103.168(2)^{\circ}$, $\gamma = 76.307(3)^{\circ}$, V = 1670.2(5) Å³, Z = 2, $\rho_{\text{calcd.}} = 1.511 \text{ g/cm}^3$, T = 153(2) K, $\lambda(\text{Mo-}K_a) = 0.71073$ Å. 7269 reflections collected, which were used in all calculations. $R_1 = 0.0601$, $wR_2 = 0.1265$ for observed unique reflections $[F^2 > 2\sigma(F^2)]$. Max./min. residual electron densities $3.548/-3.460 \text{ e/Å}^3$.

4-Rh: A solution of $[Rh(Me_4N_3)OMe]$ (84 mg, 167 µmol) in THF (5 mL) was added quickly to NaHg (Na content 0.77%, 554 mg, 184 µmol), which was covered by THF (2 mL). The mixture was

stirred under N₂ at room temp. for 0.5 h. The color changed from green to brown. The supernatant was decanted, filtered, and the solvent was removed in vacuo. The resulting brown solid was washed with pentane $(2 \times 3 \text{ mL})$ and dried in vacuo. This crude product was extracted with diethyl ether. The diethyl ether solution was concentrated to 20% and cooled to -35 °C yielding a brown microcrystalline solid. Alternatively, the material can be recrystallized from THF/pentane. Yield: 53% (45 mg, 44.7 µmol) Single crystals suitable for X-ray crystal-structure analysis were obtained by recrystallization at -35 °C. $C_{52}H_{59}N_8O_{0.5}Rh_2$ [4-Rh·(THF)_{0.5}] (1009.3): calcd. C 61.84, H 5.89, N 11.10; found C 61.85, H 5.94, N 10.95. ¹H NMR (400 MHz, [D₈]toluene, room temp.): $\delta = 4.94$, 5.09, 16.76 (v. br.), 20.31 ppm; (400 MHz, C_6D_6 , room temp.): $\delta =$ 1.11 (Et₂O), 3.25 (Et₂O), 5.01, 5.26, 17.16 (v. br.), 20.2 ppm. Raman (solid): $\tilde{v} = 2059 (v_{NN}) \text{ cm}^{-1}$. ESR (toluene, room temp.): g =2 (3494 G).

5-Rh: [Rh(*i*Pr₄N₃)Cl] (100 mg, 161 µmol) was dissolved in THF (5 mL) and added to Na/Hg (0.77%, 550 mg, 183 µmol) covered by a layer of THF. The mixture was stirred for 1.5 h, upon which the color of the mixture changed from green to brown. The supernatant brown solution was decanted and concentrated to dryness. The solid residue was washed with pentane (2×5 mL). After removing the pentane in vacuo, the brown product was extracted into toluene and filtered. The filtrate was then concentrated to dryness in vacuo. Crystalline material was obtained from a toluene/pentane solution at -35 °C. Yield: 76% (75 mg, 122 µmol). C₃₃H₄₃N₅Rh (612.64): calcd. C 64.70, H 7.07, N 11.43; found C 65.04, H 7.39, N 9.59. ¹H NMR (400 MHz, C₆D₆): $\delta = 2.28$ (br.), 3.55 (br.), 5.60 (br.) ppm. IR (toluene): $\tilde{v} = 2139$ (v_{NN}) cm⁻¹. ESR (toluene, room temp.): g = 1.99 (3500 G).

Supporting Information (see footnote on the first page of this article): Complete spectroscopic and thermoanalytical data, crystallographic and computational details of the DFTcalculations.

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