N_2H_x Coordination at the Tripod-Cobalt Template $CH_3C(CH_2PPh_2)_3Co$: the Transformation of η^2-$HNNMe_2$ into η^1-$NNMe_2$ Ligands

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While η^2-coordination of N_2H_4 and $N_2H_3^-$ to tripod-cobalt entities has been reported, stabilization of N_2H_2 in this system has not yet been achieved. It is observed that [tripodCo(η^2-$HNNMe_2$)]$^+$ (**3**) is transformed into [tripodCo(η^1-$NNMe_2$)]$^+$ (**4**) by reaction with $LiN(TMS)_2$ as a base. The deprotonation of **3** is accompanied by a redox reaction, and the overall reaction corresponds to the transformation of **3** to **4** with the loss of an electron and a proton. The observed coupling of deprotonation and oxidation is just the reverse of the processes assumed to occur during nitrogen fixation. The results are established by the usual analytical and spectroscopic techniques as well as by X-ray analyses.

Even though the structure of the FeMo-cofactor of nitrogenase is now known[1] it is not yet known how dinitrogen is activated and transformed by the biological system. Coordination chemistry on the other hand has developed quite a number of models relevant to one or the other step illustrating potential pathways of transformation that might also be active in the natural system[2].

Even though there are different ideas about how the whole reduction cycle from dinitrogen to ammonia might work, all of the schemes developed agree in the assumption that metal coordination of N_2H_x intermediates plays a key role[2]. The potential intermediacy of side-on coordinated N_2H_x ligands ($x = 2-4$) has been specifically stressed by Schrock and his group[3]. One of the key steps reported in this work is the transformation of η^2-coordinated N_2H_3 ligands into η^1-coordinated NNH_2 ligands[3a]. This transformation has clearly been demonstrated by NMR experiments[3,4]. The structure of the η^1-N_2H_2 compound or of a related η^1-N_2R_2-species could, however, not be obtained in the system developed by Schrock.

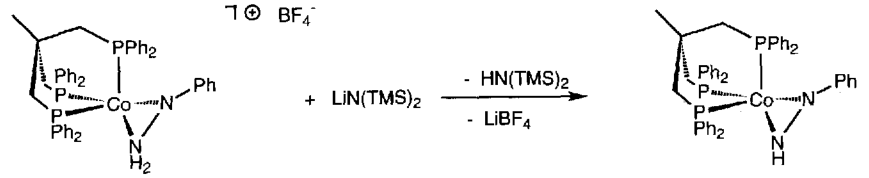
Based on the observation that tripod-cobalt templates $CH_3C(CH_2PPh_2)_3Co$ allow for η^2-N_2H_x coordination of N_2H_4 as well as of N_2H_3 ligands[5] we tried to analyze the transformation of η^2-N_2H_3 into η^1-N_2H_2 in this system. With the N_2H_3 analogue $NHNMe_2$, it was found that [$CH_3C(CH_2PPh_2)_3Co$-(η^2-$NHNMe_2$)]$^+$ (**3**) can be converted to [$CH_3C(CH_2PPh_2)_3Co$-(η^1-$NNMe_2$)]$^+$ (**4**). Both compounds are characterized by X-ray analyses.

Initial attempts to generate N_2H_2 ligands by deprotonation and/or oxidation[6] of N_2H_3 or N_2H_4 ligands in the system tripod-cobalt-N_2H_x did not lead to well-defined products. With the aim to stabilize the reaction products by organic substituents at one of the nitrogen atoms, Ph_2NNH_2 was used as the starting hydrazine. This species did however not react with tripod-cobalt(II) at all. Upon deprotonation with *n*-BuLi, a compound was obtained, which by its correct FAB-MS and an IR band at 1585 cm^{-1} attributable to an ν_{NN} stretch, presumably has the constitution $CH_3C(CH_2PPh_2)_3Co$-(η^1-$NNPh_2$). While this compound could not be isolated in an analytically pure state the presence of a NN band in the infrared was taken as an indication that bulky substituents at one of the nitrogen atoms would promote end-on coordination of NNR_2. On the other hand the reluctance of Ph_2NNH_2 to coordinate to the tripod-cobalt template as such led to the assumption that two phenyl substituents were just too bulky to fit into the reaction hole formed by the tripod-cobalt template. The less bulky analogue $PhNHNH_2$ was found to form [$CH_3C(CH_2PPh_2)_3Co$-(η^2-$NPhNH_2$)]$^+$ (**1**). The constitution of the analytically pure brown BPh_4 salt of **1** was further corroborated by an X-ray analysis. Since the salt crystallizes as a solvate containing one equivalent of THF the crystals gradually decompose by loss of solvate molecules so that by collecting a total of 7000 data from several crystals only the overall geometry could safely be inferred from this analysis. Together with the appearance of two ν_{NH} bands in the infrared the constitution is thus unequivocally clear. Deprotonation of **1** by one equivalent of $LiN(TMS)_2$ leads to the neutral species **2** (Scheme 1).

The analytically pure red compound **2** easily dissolves in toluene and exhibits a characteristic NH absorption at 3315 cm^{-1}. The ESR spectrum of **2** reveals the pattern characteristic for five coordinate tripod-cobalt(II) compounds[7]: at 296 K in solution two resonances are observed that correspond to the two alternative conformations (square pyramidal, trigonal bipyramidal) accessible in such species[7]; at

0009–2940/97/0404–0489 $ 17.50+.50/0

Scheme 1

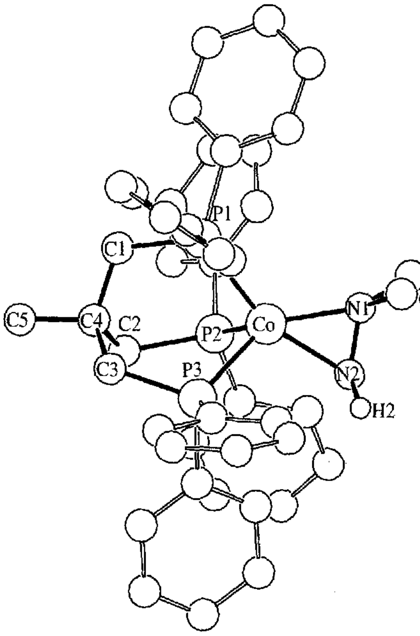


1

2

100 K in THF glass only one conformation is populated[7] leading to a signal from which the g values and also the hyperfine coupling constants are in part apparent (g_1 = 2.12, $A_{^{59}Co}$ = 35 G; g_2 = 2.06, $A_{^{59}Co}$ = 35 G). Isomerization of **2** to a compound containing an end-on NNHPh ligand could, however, not be observed.

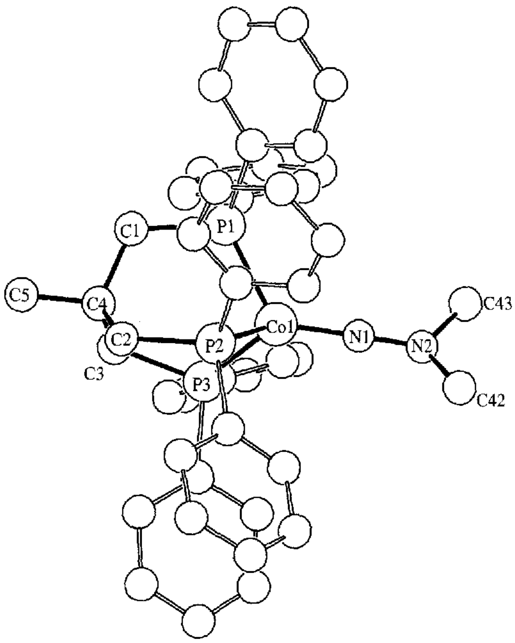
Figure 1. Structure of $[CH_3C(CH_2PPh_2)_3Co(\eta^2\text{-}HNN(CH_3)_2)]^+$ (**3**), selected angles [°] and distances [pm][8]: P1−Co1−P2 91.5(1), P2−Co1−P3 90.0(1), P1−Co1−P3 92.6(1), N1−Co1−N2 41.0(5), Co1−N1−N2 68.2(8), Co1−N2−N1 70.7(8); Co1−N1 193.8(12), Co1−N2 197.1(15), N1−N2 136.9(17), Co1−P1 220.7(3), Co1−P2 222.8(3), Co1−P3 220.5(3)



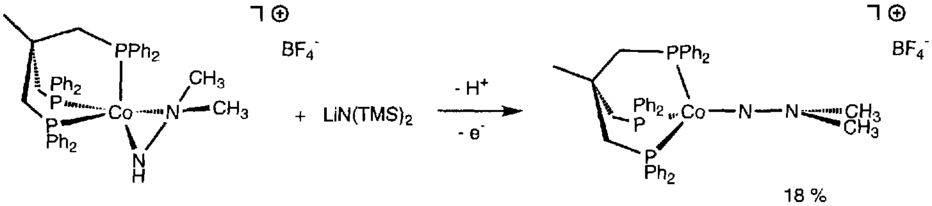
Arguing that *N*,*N*-disubstitution of the hydrazine by bulky phenyl groups was too demanding to allow for coordination while mono-substitution as in **2** with one phenyl group did not impose a steric strain strong enough to make end-on coordination of NNHPh favourable, the reactions were carried out with H_2NNMe_2. It had already been found[5] that η^2-coordination of the corresponding hydrazide leads to the green compound $[CH_3C(CH_2PPh_2)_3Co(\eta^2\text{-}NHNMe_2)]^+$ (**3**) which was isolated and fully characterized. The structure of **3** as determined by X-ray analysis of **3** · BPh_4 · 1.5 · THF[5] is shown in Figure 1.

Green CH_2Cl_2 solutions of **3** react with $LiN(TMS)_2$ to form a red-brown solution (Scheme 2) from which **4** could be isolated by crystallization. The BF_4 salt of **4** shows a new ν_{NN} band at 1580 cm^{-1} and no absorption is observed in the NH region of the IR spectrum. All the signals expected for the organic groups of **4** are observed in the ^{1}H-NMR spectrum (Experimental Section); the signals are broad however and a high-spin low-spin equilibrium, as

Figure 2. Structure of $[CH_3C(CH_2PPh_2)_3Co(\eta^2\text{-}(NNCH_3)_2)]^+$ (**4**), selected angles [°] and distances [pm][8]: Co1−N1−N2 176.3(7), N1−N2−C42 119.1(13), N1−N2−C43 125.2(13); P1−Co1−P2 90.67(12), P2−Co1−P3 91.50(12), P1−Co1−P3 92.92(11), P1−Co1−N1 124.0(3), P2−Co1−N1 127.6(3), P3−Co1−N1 120.5(3); Co1−N1 166.8(9), N1−N2 129.6(11), Co1−P1 218.1(3), Co1−P2 216.8(3), Co1−P3 219.9(3)



Scheme 2



3

4

might be expected for the distorted tetrahedral coordination in **4**, might be a reason for this broadening. The structure of **4** is shown in Figure 2.

The Co–N–N arrangement is linear. The Co–N distance as well as the N–N distance are significantly shorter than single bonds (Figure 2). The Co–N distance, amounting to only 167 pm, suggests some triple bond character for this bond while the N–N distance of 130 pm indicates only partial double bond character for this bond. The coordination around the terminal nitrogen is approximately planar; a rotational disorder of the NMe_2 group around the N–N bond is apparent from the X-ray data. The overall geometry of the $MNNR_2$ fragment of **4** is well in accord with numerous accounts of this type of bonding in the literature[11]. While the transformation from **3** to **4** clearly demonstrates that an η^2-$HNNR_2$ ligand may be transformed to an η^1-NNR_2 ligand, **4** is not just the product of a deprotonation of **3**. An oxidation has taken place at the same time and while the nature of the necessarily accompanying reduction product is not known, the overall reaction amounts to the transformation of **3** to **4** with the loss of an electron and a proton. This flow of electrons and protons is just the reverse of what is believed to occur during N_2 fixation, where a coupled transfer of protons and electrons to the substrate is at work.

Experimental Section

Experimental techniques and equipment were as described in ref.[12].

[{Phenylhydrazido(1–)}{1,1,1-tris(diphenylphosphanylmethyl)ethano}cobalt(II)] Tetraphenylborate (**1** · BPh_4): $CH_3C(CH_2PPh_2)_3$ (624 mg, 1 mmol) is dissolved in 15 ml of THF and mixed with $Co(BF_4)_2 \cdot 6\,H_2O$ (340 mg, 1 mmol) dissolved in 15 ml of ethanol. Phenylhydrazine is added dropwise to the stirred orange-red solution. The reaction mixture turns brown immediately. After addition of $NaBPh_4$ (1 mmol, 342 mg) dissolved in 5 ml of ethanol the mixture is stirred for 2 h and filtered. The solvent is slowly removed from the filtrate until brown crystals begin to form. The solution is allowed to stand at room temperature overnight to produce brown crystals of $[CH_3C(CH_2PPh_2)_3Co\text{-}(\eta^2\text{-}NPhNH_2)]BPh_4 \cdot$ THF. The solvent is decanted, the crystals are washed with pentane and dried to yield brown, crystalline $[CH_3C(CH_2PPh_2)_3Co\text{-}(\eta^2\text{-}NPhNH_2)]BPh_4 \cdot$ THF (398 mg, 0.35 mmol, 35%). MS (FAB, NIBEOL); *m/z* (%): 790 (4) $[M^+]$, 683 (100) $[CH_3C(CH_2PPh_2)_3Co]$. – IR (Nujol) $[cm^{-1}]$: 3265 (s), 3197 (s). – $C_{71}H_{66}BCoN_2P_3 \cdot$ THF: calcd. C 76.14, H 6.39, N 2.37, P 7.85; found C 75.75, H 6.45, N 2.19, P 7.85.

When in the synthesis of **1** · BPh_4 no $NaBPh_4$ is added, **1** · BF_4 is obtained as a brown microcrystalline solid.

[{Phenylhydrazido(2–)}{1,1,1-tris(diphenylphosphanylmethyl)ethano}cobalt(II)] (**2**): $LiN(TMS)_2$ (1 M in THF, 1 ml, 1 mmol) is added to a stirred solution of **1** · BF_4 (877 mg, 1 mmol) in CH_2Cl_2. The reaction mixture turns red immediately, and the solution is stirred for 30 min. $LiBF_4$ precipitates from the solution, and the suspension is filtered through cellite (2 cm) to remove the white solid. The solvent is removed from the red filtrate in vacuo to produce a red solid which is extracted with toluene. The toluene is then removed in vacuo to produce red $CH_3C(CH_2PPh_2)_3Co\text{-}(\eta^2\text{-}NPhNH)$ (310 mg, 0.31 mmol, 31%). – MS (FAB); *m/z* (%): 789 (2) $[M^+]$, 683 (38) $[CH_3C(CH_2PPh_2)_3Co]$. – IR (Nujol) $[cm^{-1}]$: 3350 (w). – ESR (CH_2Cl_2): 298 K: $g_1 = 2.12$, $A_{^{59}Co} = 35$ G; $g_2 = 2.06$, $A_{^{59}Co} = 35$ G; 100 K: $g_x = 2.23$, $A_{^{59}Co} = 60$ G; $g_z = 1.99$, $A_{^{59}Co} = 40$ G. – CV (CH_2Cl_2): ox. –325 mV (rev.), +240 mv (irrev.); red. –875 mV (quasirev.). – $C_{47}H_{45}CoN_2P_3 \cdot$ THF: calcd. C 71.48, H 5.74, N 3.55, P 11.77; found C 71.02, H 6.13, N 3.10, P 11.02.

[{N,N-dimethylhydrazido(1–)}{1,1,1-tris(diphenylphosphanylmethyl)ethano}cobalt(II)] Tetraphenylborate (**3** · BPh_4): The preparation of **3** · BPh_4 is analogous to that of **1** · BPh_4. Addition of *N,N*-dimethylhydrazine (0.07 ml, 1 mmol) to the orange mixture of $CH_3C(CH_2PPh_2)_3$ (624 mg, 1 mmol) and $Co(BF_4)_2 \cdot 6\,H_2O$ (340 mg, 1 mmol) yields $[CH_3C(CH_2PPh_2)_3Co\text{-}(\eta^2\text{-}(CH_3)_2NNH)]BPh_4 \cdot 1.5$ THF as green crystals (643 mg, 0.55 mmol, 55%). Recrystallization from tetrahydrofuran/ether provides crystals suitable for an X-ray diffraction study. – MS (FAB): *m/z* (%): 742 (96) $[M^+]$, 683 (100) $[CH_3C(CH_2PPh_2)_3Co]$. – IR (Nujol) $[cm^{-1}]$: 3210 (w). – $C_{47}H_{45}CoN_2P_3 \cdot 1.5$ THF: calcd. C 74.93, H 6.72, N 2.40, P 7.49; found C 74.83, H 6.65, N 2.76, P 8.21. – When in the synthesis of **3** · BPh_4 no $NaBPh_4$ is added, **3** · BF_4 is obtained as a green microcrystalline solid.

[{N,N-dimethylhydrazido(2–)}{1,1,1-tris(diphenylphosphanylmethyl)ethano}cobalt(III)] Tetrafluoroborate (**4** · BF_4): **3** · BF_4 is dissolved in CH_2Cl_2 and $LiN(TMS)_2$ (1 M in THF, 1 ml, 1 mmol) is added to the stirred solution. The green solution turns red-brown immediately. After 1 h the solution is filtered through cellite (5 cm), and the solvent is removed in vacuo to produce a red-brown solid, which is washed with ether. Recrystallization from CH_2Cl_2: Et_2O mixtures (1:1) provides analytically pure crystals of **4** · BF_4. Crystals suitable for an X-ray diffraction analysis are available as $[CH_3C(CH_2PPh_2)_3Co\text{-}(\eta^1\text{-}(CH_3)_2NN)]BF_4 \cdot 1.65\,CH_2Cl_2$ by gas phase diffusion of diethyl ether into a saturated solution of **4** · BF_4 in CH_2Cl_2. – ^1H NMR (CD_2Cl_2): $\delta = 1.6$ [br, C_qCH_3)], 2.3 [br, CH_2PPh_2], 3.0 [br, NCH_3], 6.9–7.8 (br, ar. H). – ^{31}P NMR (CD_2Cl_2): $\delta = 47.0$ (s). – MS (FAB, NIBEOL); *m/z* (%): 741 (100) $[M^+]$. – IR (Nujol) $[cm^{-1}]$: 1580 (s), 1060 (s). – $C_{43}H_{45}BCoF_4N_2P_3$: calcd. C 62.35, H 5.47, N 3.38; found C 61.23, H 5.68, N 3.28.

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[1] J. Kim, D. C. Rees, *Science* **1992**, *257*, 1677.

[2] [2a] A. E. Shilov, *Pure and Appl. Chem.*, **1992**, *64*, 1409. – [2b] R. R. Eady, G. J. Leigh, *J. Chem. Soc. Dalton Trans.* **1994**, 2739. – [2c] Masanobu Hidai, Yasushi Mizobe, *Chem. Rev.* **1995**, *95*, 1115. – [2d] G. J. Leigh, *Science* **1995**, *268*, 827.

[3] [3a] R. R. Schrock, A. H. Liu, M. B. O'Regan, W. C. Finch, J. F. Payack, *Inorg. Chem.*, **1988**, 3574. – [3b] R. R. Schrock, T. E. Glassmann, M. G. Vale, *J. Am. Chem. Soc.*, **1991**, *113*, 725. – [3c] T. E. Glassmann, M. G. Vale, R. R. Schrock, *Inorg. Chem.*, **1992**, *31*, 1985. – [3d] T. E. Glassmann, M. G. Vale, R. R. Schrock, *J. Am. Chem. Soc.*, **1992**, *114*, 8098. – [3e] R. R. Schrock, T. E. Glassmann, M. G. Vale, M. Kol, *J. Am. Chem. Soc.*, **1993**, *115*, 1760. – [3f] M. G. Vale, R. R. Schrock, *Inorg. Chem.*, **1993**, *32*, 2767.

[4] S. Wagenknecht, J. R. Norton, *J. Am. Chem. Soc.*, **1995**, *117*, 1841.

[5] S. Vogel, A. Barth, G. Huttner, Th. Klein, L. Zsolnai, R. Kremer, *Angew. Chem.* **1991**, *103*, 325; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 303.

[6] [6a] D. Sellmann, W. Soglowek, F. Knoch, M. Moll, *Angew. Chem.*, **1989**, *101*, 1244; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271. – [6b] D. Sellmann, E. Böhlen, M. Waeber, G. Huttner, L. Zsolnai, *Angew. Chem.*, **1985**, *97*, 984; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 981. – [6c] T.-Y. Cheng, A. Ponce, A. L. Rheingold, G. Hillhouse, *Angew. Chem.*, **1994**, *106*, 703; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 657.

[7] [7a] V. Körner, A. Asam, G. Huttner, L. Zsolnai, M. Büchner, *Z. Naturforsch.* **1994**, *49b*, 1183. – [7b] C. Bianchini, D. Masi, C. Mealli, A. Meli, G. Martini, F. Laschi, P. Zanello, *Inorg. Chem.*, **1987**, *26*, 3683.

[8] G. M. Sheldrick, SHELX93, Program for Crystal Structure Refinement, Universität Göttingen, **1993**.

[9] X-ray structural determination of **3**-$(BPh_4) \cdot 1.5$ THF: $C_{67}H_{66}BCoN_2P_3$, $M = 1170.18$, monoclinic, space group $C2/c$, $a = 2386.4(9)$, $b = 1705.8(9)$, $c = 3292(1)$, $\beta = 95.75(3)$, $V = 13334 \cdot 10^6$ pm^3, $Z = 8$, $T = 210$ K, Θ region $2.9° \le 2\,\Theta \le$

47.1°, scan velocity [°min^{-1}] $2.0 \le \dot{\omega} \le 29.3$, independent reflexes 9540, reflexes observed ($I \geq 2\sigma$) 6089, refined parameters 601, residual electron density $2.35 \cdot 10^{-6}$ e/pm^3, R_I = 13.6 %, R_w = 43.9 % (F^2 refinement). X-ray structural determination of **4**-(BF_4) · 1.65 CH_2Cl_2: $C_{43}H_{45}BCoF_4N_2P_3$, M = 828.5, monoclinic, space group $P2_1/c$, a = 1456.2(8), b = 1431.1(8), c = 2460.0(1), β = 94.72(2), V = $5109.2 \cdot 10^6$ pm^3, Z = 4, T = 200 K, Θ region $3.3° \le 2\Theta \le 50.0°$, scan velocity [°min^{-1}] $8.0 \le \dot{\omega} \le 60.0$, independent reflexes 5889, reflexes observed ($I \geq 2\sigma$) 3613, refined parameters 630, residual electron density $0.82 \cdot 10^{-6}$ e/pm^3, R_1 = 8.6 %, R_w = 27.1 % (F^2 refinement). All data sets were collected on a Siemens-Nicolet R3m/V diffractometer. Mo-K_α radiation (λ = 71.07 pm), graphite monochromator, solution and refinement: SHELXL93 [9] and SHELXTL Plus [10]. Atomic coordinates, bond lengths and angles, and thermal parameters of **3** have been deposited at the Cambridge Crystallographic Data Centre; requests for data should be accompanied by declaration of the reference code NABGOM. Full tables of positional and thermal parameters of **4**, including those of counterions and solvate molecules, and of the structure factor amplitudes are available as supplementary material at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by declaration of the CSD-406450 the author names and the quotation.

[10] G. M. Sheldrick, SHELXTL PLUS, Program for Crystal Structure Refinement, Universität Göttingen, **1988**.

[11] [11a] K. Gebreyes, J. Zubieta, T. A. George, L. M. Koczon, R. C. Tisdale, *Inorg. Chem.*, **1986**, *25*, 405. – [11b] J. R. Dilworth, J. A. Zubieta, *J. Chem. Soc. Chem. Comm.*, **1981**, 132. – [11c] J. Chatt, B. A. L. Crichton, J. R. Dilworth, P. Dahlstrom, R. Gutkoska, J. Zubieta, *Inorg. Chem.*, **1982**, *21*, 2383.

[12] V. Körner, S. Vogel, G. Huttner, L. Zsolnai, O. Walter, *Chem. Ber.* **1996**, *129*, 1107.

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