Articles

Conversion of Diamino-Substituted Carbene Complexes into the Isocyanide by Acylation

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Treatment of cyclic diaminocarbene complexes $(CO)_5M{=}\overline{CNH(CH_2)_m}NH$ (**1**) (M = Cr, Mo, W; ***m*** = 2, 3) with acylating agents resulted in the formation of the corresponding isocyanide complexes $(CO)_5MCN(CH_2)_mNH_{2-n}(COR)_n$ (M = Cr, Mo, W; ***m*** = 2, 3; ***n*** = 1, 2; R = Ph CH_3) in high yields. It appears that the ***N***-acyl group destabilizes the diaminocarbene complexes and causes the cleavage of the C−N bond to form the isocyanide product. The reaction pathway leading to the isocyanide complexes is discussed. The crystal structure of $(CO)_5WC{\equiv}N(CH_2)_2N(COPh)_2$ has been determined.

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Introduction

Diamino-substituted carbene complexes have received much attention recently due to the discovery that nitrogen atoms direct carbene ligands to be good σ-donors, similar to phosphines.[1−8] Such carbene ligands are able to incorporate with various metal ions to form stable complexes.[1−8] Indeed, the unusually stable palladium complex $[MeN\overline{CH{=}CHN(Me)C}]_2PdI_2$ was found by Herrmann and co-workers to be a useful catalyst for the Heck reaction.[3d] However, the nitrogen-substituted carbenes of these studies are typically tertiary amines, few are secondary amine moiety.[9] As mentioned, the better the donor nitrogen, the stronger the metal−carbon bond in the related metal complexes. Thus, electronic modification of the donor character of the nitrogen substitutents in order to weaken the metal−carbon bonds becomes an interesting prospect. It has been reported by Dötz and co-workers that the ***N***-acylated products of $(CO)_5Cr{=}C(NHR)R'$ have better reactivities toward alkynes in annelation reactions.[10] As part of our studies on the properties of metal carbene complexes, we have prepared the cyclic diamino-substituted carbene complex **1** which holds secondary amine moieties.[11] In view of the modification of the secondary amine functionality, we report that isocyanide complexes are formed instead of ***N***-acylated carbene species when diaminocarbene **1** is reacted with acylating agents.

Results and Discussion

The reaction of **1c** with an excess of benzoyl chloride in the presence of pyridine at 100 °C did not provide the ***N***-acylated carbene product as expected. Instead, the isocyanide tungsten complex **2c** was obtained in 92% yield. The isocyanide complex was characterized by both spectroscopic and elemental analyses. The infrared spectrum of **2c** in dichloromethane clearly shows the carbonyl and isocyanide functionalities of the molecule. Thus absorptions at 2174 (w), at 2068 (w) and 1948 (s), and at 1697 and 1660 (s) cm^{-1} are consistent with the coordinated isocyanide, the pentacabonyltungsten and the amidocarbonyl moieties. Both the ^1H and ^{13}C NMR spectra are also in agreement with the proposed structure. Finally, the composition of **2c** is confirmed by X-ray single-crystal determination (see crystallography).

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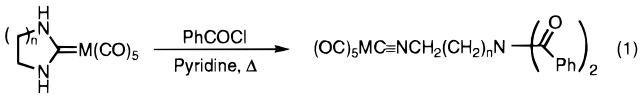
Table 1. Spectral Data of Isocyanide Complexes

compd	isolated yield (%)	IR (cm^{-1}) −C≡N	IR (cm^{-1}) M−C≡O	IR (cm^{-1}) N−C(=O)R	^{13}C NMR δ_{CN}, (ppm)[a]
2a	77	2169	2066, 1944	1700, 1658	166.0
2b	48	2169	2070, 1959	1699, 1658	155.2
2c	92	2174	2068, 1948	1697, 1660	145.6
2d	80	2177	2070, 1945	1684, 1653	146.7
3a	51[b]	2171	2061, 1945	1646,	163.5
3c	33[b]	2177	2066, 1945	1640,	144.8
4a	52	2165	2067, 1942	1720, 1708	145.9
4b	51	2181	2071, 1936	1720, 1678	144.0

[a] Due to the weak intensity and broadening of the peak, the values of J_{W-C} are not available. [b] Accompanied with the formation of **2a** (25%) or **2c** (20%).

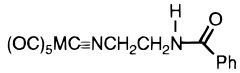
Under the same conditions, both the chromium and molybdenum carbene complexes (**1b** and **1c**) yielded their corresponding isocyanide complexes (eq 1). In



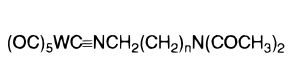
(1)

1a M = Cr n = 1 **2a** M = Cr n = 1
1b Mo 1 **2b** Mo 1
1c W 1 **2c** W 1
1d W 2 **2d** W 2

addition, cyclic diaminocarbene in different ring sizes, such as **1d**, proceeded under the same type of reaction to yield **2d**. We also tried to prepare the monoacylated product, but we found that a mixture of monobenzoylated amidoisocyanide complexes **3** and **2** (ca 2:1 ratio) was obtained from the reaction of an equimolar amount of carbene and acylating agent at the temperature of refluxing a tetrahydrofuran solution. Other acylating agents under various conditions also provide the corresponding ***N***-acylated isocyanide complexes. Treatment of **1c** and **1d** with an excess of acetic anhydride in the presence of sulfuric acid or acetyl chloride in the presence of pyridine produced **4a** and **4b**, respectively.



3a M = Cr
3c W



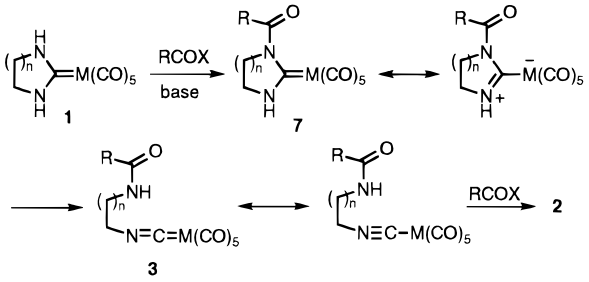
4a n = 1
4b n = 2

Some of the spectral data of these complexes are summarized in Table 1.

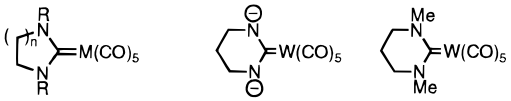
It is reported by Dötz and co-workers that aminocarbene chromium complexes [$(CO)_5Cr{=}C(R)NHR$] readily underwent acylation with acetic anhydride or di-***tert***-butyl dicarbonate in the presence of 4-(***N,N***-dimethylamino)pyridine at 25 °C.[10] Diamino-substituted carbenes, however, do not react with acyl chloride under mild conditions, which is attributed to the high stability of such complexes. But at elevated temperatures, the acylation proceeds, followed by the cleavage of the C−N bond to form the isocyanide complex.

In our previous investigation, we were able to obtain the ***N***-alkylated products **5** by the deprotonation of **1** with NaH followed by treatment with various alkyl iodides.[11] By adopting a similar strategy, the dianion **6** was prepared by the treatment of **1d** with 2 equiv of

Scheme 1. Possible Mechanism for the Formation of Isocyanide Complexes



n-butyllithium in tetrahydrofuran at − 78 °C. Followed by addition of an excess of acetyl chloride to the dianion solution, the reaction mixture was allowed to warm to room temperature slowly. Monitoring the acylation by NMR spectroscopy reveals that the reaction took place at − 20 °C, but the observed outcome is the isocyanide product. None of the ***N***-acylated carbene species **7** was detected by NMR. As a control run, the reaction of **6** with methyl iodide was carried out under similar conditions, which provided the methylated product **8** exclusively. This indicates that the first ***N***-acylation takes



5 R = alkyl, allyl, M = Cr, Mo, W n = 1, 2 **6** **8**

place prior to the cleavage of the C−N bond. Such an acylation also results in the immediate cleavage of the C−N bond to provide the isocyanide product.

A possible mechanism for the formation of isocyanide complexes from the carbenes is illustrated in Scheme 1. The carbenes undergo ***N***-acylation first to yield the intermediate **7**. The amido group decreases the stability of the aminocarbene dramatically, which causes the ring-opening reaction that leads to the isocyanide complex. It is noted by Aumann and co-workers that reaction of aminocarbene $(CO)_5Cr{=}C(NH_2)R$ with R′CHO in the presence of base yields a mixture of a 2-azaallenyl complex and an isocyanide complex $(CO)_5CrCN{-}R$ **10**.[12] The formation of **10** is clearly involved in the migration of the substituent. In our investigation, the isocyanide complexes are simply created via the cleavage of C−N bonds and the driving force is presumably due to the electronic destabilization of the amido group toward the carbene functionality and the relief of the steric interaction between the substituted cyclic carbene constituent and the carbonyl ligands.

Crystallography

The data for the crystal of complex **2c** is summarized in Table 2, and the ORTEP plot of **2c** is depicted in Figure 1. As expected, the tungsten metal ion displays a typical octahedral geometry with the isocyanide donor and five carbonyl ligands. All bond distances and angles lie within normal ranges, as given in Table 3. The distance of the metal to isocyanide ligand (W−C6 2.10-

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Table 2. Crystal Data, Collection, and Refinement Details for Complex 2c

formula	$C_{22}H_{14}N_2O_7W$
cryst size, mm	0.30 × 0.50 × 0.50
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.591(3)
b, Å	25.520(5)
c, Å	7.701(5)
β, deg	96.21(5)
Z	4
V, Å^3	2264.5 (16)
D_{calcd}, gcm^{-3}	1.766
μ, cm^{-1}	52.513
radiation	Mo Kα (0.7107 Å)
temp, K	298
F(000)	1156
diffractometer	Enraf-Nonius CAD 4
scan type	$\theta-2\theta$
scan width, deg	2(0.70 + 0.35 tan θ)
hkl ranges	−13 to 13, 0−30, 0−9
scan speed (deg/min)	2.75−8.24
no. of reflns measd	3871
no. of reflns obsd ($I > 2.0\ \sigma(I)$)	2768
no. of params refined	290
refinement program	NRCVAX
R_f, R_w[a]	0.056; 0.064
GOF	2.15
resid in final *D*-map, e Å^{-3}	−2.620 and 2.110

[a] $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$; $R_w = [\Sigma(w(F_o - F_c))^2/\Sigma(wF_o^2)]^{1/2}$. GOF = $[\Sigma(w(F_o - F_c))^2/(\text{no. of reflns} - \text{no. of params})]^{1/2}$.

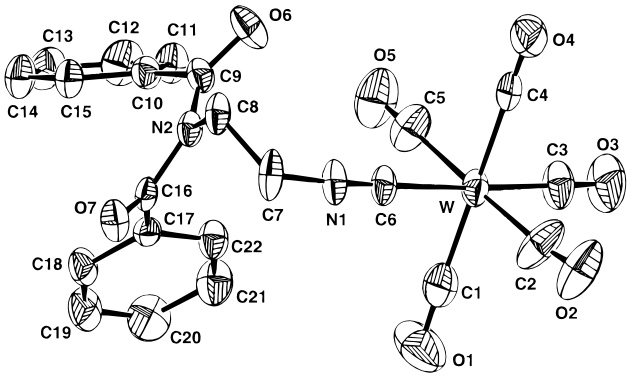

Figure 1. ORTEP plot of **2c**.

(2) Å) is identical to that of the species $CH_3C[CH_2NCW(CO)_5]_3$ (**9**; 2.08(2) Å) reported by Hahn and co-workers.[13] Due to the isoelectronic nature of the isocyanide and carbonyl ligands, the distances between the metal and carbonyl ligands either cis or trans to the isocyanide are essentially indistinguishable, which is similar in the structure of **9.** Apparently, there is not much of a trans influence in this kind of structure. The bond length of C6−N1 (1.17(2) Å) is typical for C≡N in the coordinated isocyanide ligand, which is consistent with the spectral data for this functionality.

Summary

It has been demonstrated in this report that the stable diaminocarbene ligand can be converted into the isocyanide complex via the cleavage of the C−N bond. Along with this, it is also found that the mono-***N***-alkylated diaminocarbene $(CO)_5WCN(Et)CH_2CH_2NH$ does not react with benzoyl chloride in the presence of pyridine in refluxing tetrahydrofuran. This appears that formation of the ***N***-acylated diaminocarbene complexes is a challenge. We are currently working on developing the synethetic approach to the ***N***-acylated diaminocarbene complexes.

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Experimental Section

General Information. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on either a Bruker AC-E 200 or AM-300 spectrometer. Infrared spectra were measured on a Biorad FT-30 instrument in CH_2Cl_2 solution, unless otherwise stated.

All of the reaction, manipulation, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was dried by CaH_2 and then distilled under nitrogen. Pyridine was dried over sodium hydroxide and distilled before use. Other chemicals and solvents were used from commercial sources without further purification. Complexes **1a**−**d** were prepared by the method previously reported.[11]

General Procedure of the Acylation of 1a−**c**. A mixture of **1** (0.1 mmol), benzoyl chloride (0.3 mmol), and pyridine (5 mL) was heated at 100 °C for 8−10 h. After the reaction mixture was cooled to room temperature, it was poured into water (20 mL) and extracted with dichloromethane. The organic portion was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel with ethyl acetate/hexane (1:4) as the eluent. After concentration of the elute, the isocyanide complex was obtained.

$(CO)_5WCN(CH_2)_2N(COPh)_2$ (2c). Into a flask equipped with a refluxing condenser were placed **1c** (1.0 g, 2.54 mmol), benzoyl chloride (0.9 mL, 7.81 mmol), and pyridine (5 mL). The resulting mixture was heated at 100 °C for 8 h. Water (20 mL) followed by dichloromethane (25 mL) were added to the reaction mixture. The organic layer was separated, dried, and concentrated. The residue was chromatographed on silica gel (60 g) with ethyl acetate/hexane (1:4) as the eluent. Complex **2c** was obtained as a white solid (1.16 g, 92%). Recrystallization from a solution of dichloromethane and hexane gave **2c** as a clear, colorless crystalline solid that is suitable for X-ray crystal determination. Complex **2c**: white solid; mp 142−144 °C (dec); IR 2174 ($\upsilon_{C\equiv N}$), 2068, 1948 (υ_{CO}), 1697, 1660 cm^{-1} (υ_{N-CO}); ^{1}H NMR (200 MHz) δ 7.4−7.0 (m, 10 H, Ar−***H***), 4.44 (t, ***J*** = 6 Hz, 2 H), 4.16 (t, ***J*** = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 195.8, 194.0 (J_{W-C} = 60 Hz), 173.7, 145.6 (−***C***≡N−), 135.8, 132.3, 128.9, 128.3, 45.0, 43.2. Anal. Calcd for $C_{22}H_{14}N_2O_7W$: C, 43.88; H, 2.34; N, 4.65. Found: C, 44.14; H, 2.33; N, 4.60.

$(CO)_5CrCN(CH_2)_2N(COPh)_2$ (2a): white solid (77%), mp 150−151 °C (dec); IR 2169 ($\upsilon_{C\equiv N}$), 2066, 1944 (υ_{CO}), 1700, 1658 cm^{-1} (υ_{N-CO}); ^{1}H NMR (200 MHz) δ 7.40−7.11 (m, 10 H, Ar−***H***), 4.40 (t, ***J*** = 6.0 Hz, 2 H), 4.07 (t, ***J*** = 6.0 Hz, 2 H); ^{13}C NMR δ 216.6, 214.5 (Cr-***C***O), 173.7, 166.0 (−***C***≡N−), 135.8, 132.2, 128.8, 128.3, 45.0, 43.4. Anal. Calcd for $C_{22}H_{14}N_2O_7Cr$: C, 56.18; H, 3.00; N, 5.96. Found: C, 55.92; H, 2.94; N, 5.88.

$(CO)_5MoCN(CH_2)_2N(COPh)_2$ (2b): white solid (48%), mp 133−134 °C (dec); IR 2169 ($\upsilon_{C\equiv N}$), 2070, 1959 (υ_{CO}), 1699, 1658 cm^1 (υ_{N-CO}); ^{1}H NMR (200 MHz) δ 7.41−7.09 (m, 10 H, Ar−***H***), 4.41 (t, ***J*** = 6.0 Hz, 2 H), 4.09 (t, ***J*** = 6.0 Hz, 2 H); ^{13}C NMR δ 206.4, 203.5 (Mo−***C***O), 173.7, 155.2 (−***C***≡N−), 135.8, 132.2, 128.8, 128.2, 45.0, 43.0. Anal. Calcd for $C_{22}H_{14}N_2O_7Mo$: C, 51.38; H, 2.74; N, 5.45. Found: C, 50.86; H, 2.75; N, 5.31.

$(CO)_5WCN(CH_2)_3N(COPh)_2$ (2d): white solid (80%), IR 2177 ($\upsilon_{C\equiv N}$), 2070, 1945 (υ_{CO}), 1684, 1653 cm^{-1} (υ_{N-CO}); ^{1}H NMR (300 MHz) δ 7.41−7.11 (m, 10 H, Ar−***H***), 4.18 (t, ***J*** = 6.6 Hz, 2 H), 3.84 (t, ***J*** = 6.6 Hz, 2 H), 2.26 (pent, ***J*** = 6.6 Hz, 2 H); ^{13}C NMR δ 196.2, 194.3 (J_{W-C} = 62 Hz), 174.0, 146.7

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Table 3. Selected Bond Distances (Å) and Angles (deg)

W−C1	1.93(2)	C1−O1	1.22(3)	W−C5	2.08(2)	C5−O5	1.08(3)
W−C2	2.06(2)	C2−O2	1.12(3)	W−C6	2.10(2)	C6−N1	1.17(2)
W−C3	1.97(2)	C3−O3	1.16(2)	N1−C7	1.42(2)		
W−C4	1.97(2)	C4−O4	1.18(2)				
C6−W−C1	88.5(7)	C6−W−C3	177.1(8)	C6−W−C5	89.0(6)	C6−N1−C7	176(2)
C6−W−C2	91.6(6)	C6−W−C4	89.1(6)	W−C6−N1	178(2)		

(−***C***≡N−), 136.0, 132.1, 128.8, 128.3, 43.8, 42.2, 28.9. Anal. Calcd for $C_{23}H_{16}N_2O_7W$: C, 44.83; H, 2.62; N, 4.55. Found: C, 44.44; H, 2.72; N, 4.42.

$(CO)_5CrCN(CH_2)_2NH(COPh)$ (3a). To a flask was added **1a** (0.2 g, 0.76 mmol), C_6H_5COCl (0.22 mL, 1.9 mmol), and pyridine (0.15 mL, 2.48 mmol) in tetrahydrofuran (5 mL). The mixture was heated to reflux for 30 h. After the reaction mixture was cooled to room temperature, it was washed with water and the organic layer was separated. The organic extract was dried and concentrated. The residue was chromatographed on silica gel with ethyl acetate/hexane (1:4) as the eluent. Two fractions were collected and concentrated, which were identified as **2a** (25%) and **3a** (51%). Complex **3a** was obtained as a white solid: mp 112−113 °C (dec); IR 3358 (υ_{N-H}) 2171 ($\upsilon_{C\equiv N}$); 2061, 1945 (υ_{CO}) 1646 cm^1 (υ_{N-CO}); ^{1}H NMR (200 MHz) δ 7.79−7.76 (m, 2 H, Ar−***H***), 7.57−7.40 (m, 3 H, Ar−***H***), 6.5 (br, 1H, N-***H***), 3.89 (t, ***J*** = 6 Hz, 2 H), 3.76 (t, ***J*** = 6.0 Hz, 2 H); ^{13}C NMR δ 216.6, 214.7 (Cr-***C***O), 168.2, 163.5 (−***C***≡N−), 133.3, 132.0, 128.7, 126.9, 44.1, 39.3. Anal. Calcd for $C_{15}H_{10}N_2O_6Cr$: C, 49.19; H, 2.75; N, 7.65. Found: C, 49.21; H, 2.92; N. 7.59.

$(CO)_5WCN(CH_2)_2NH(COPh)$ (3c). The preparation of **3c** was similar to the procedure described for **3a**. Complex **3c** is a light-yellow solid (33%); mp: 131−132 °C (dec); IR 3363 (υ_{N-H}), 2177 ($\upsilon_{C\equiv N}$), 2066, 1945 (υ_{CO}), 1640 cm^1 (υ_{N-CO});^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76 (m, 2 H), 7.54−7.40 (m, 3 H), 6.74 (br, 1 H), 3.93 (m, 2 H), 3.74 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 195.8, 194.2 (J_{W-C} = 62 Hz), 168.1, 144.8 (−***C***≡N−), 133.2, 132.2, 128.8, 129.9, 44.0, 39.3. Anal. Calcd for $C_{15}H_{10}N_2O_6W$: C, 36.17; H, 2.62; N, 5.62. Found: C, 35.92 H, 2.14; N, 5.53.

$(CO)_5WCN(CH_2)_2N(COCH_3)_2$ (4a). To a mixture of complex **1c** (2.0 g, 5.07 mmol) and acetic anhydride (10 g, 98 mmol) was added a few drops of concentrated sulfuric acid. The resulting mixture was heated at reflux for 12 h. After concentration under vacuum, the residue was chromatographed on silica gel (ethyl acetate/hexane, 1:4). Upon concentration, complex **4a** was obtained as a light yellow solid (1.26 g, 52%): mp 60−62 °C (dec); IR 2165 ($\upsilon_{C\equiv N}$), 2067, 1943 (υ_{CO}), 1720, 1708 cm^{-1} (υ_{N-CO}); ^{1}H NMR (200 MHz) δ 4.04−3.98 (m, 4 H), 2.47 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 195.4, 193.8 (J_{W-C} = 63 Hz), 172.5 (Me-***C***O−), 145.9 (−***C***≡N), 43.4, 42.9, 26.4. Anal. Calcd for $C_{12}H_{10}N_2O_7W$: C, 36.17; H, 2.62; N, 5.62. Found: C, 35.92 H; 2.14; N, 5.53.

$(CO)_5WCN(CH_2)_3N(COCH_3)_2$ (4b). This compound was prepared similarly to **4a** and isolated as a white solid (51%): IR 2181 ($\upsilon_{C\equiv N}$), 2071, 1936 (υ_{CO}), 1720, 1678 cm^{-1} (υ_{N-CO}); ^{1}H NMR (300 MHz) δ 3.81 (t, ***J*** = 7 Hz, 2 H), 3.74 (t, ***J*** = 7 Hz, 2 H), 2.42 (s, 6 H), 2.03 (m, 2 H); ^{13}C NMR δ 195.8, 194.1 (J_{W-C} = 63 Hz), 172.8, 144.0 (−***C***≡N−), 42.1, 42.0, 28.8, 26.3. Anal. Calcd for $C_{13}H_{12}N_2O_7W$: C, 31.73; H, 2.46; N, 5.69. Found: C, 32.44; H, 2.42; N, 5.44.

Crystallography. Cell parameters were determined on a CAD-4 diffractometer at 298 K by a least-squares treatment. Atomic scattering factors were taken from ref 14. Calculations were performed using the NRCC SDP VAX package.[15] The crystal data is listed in Table 2, and selected bond distances and angles are summarized in Table 3. The atomic coordinates as well as other crystal data are collected as Supporting Information.

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Supporting Information Available: Tables listing atomic coordinates, anisotropic thermal parameters, and complete bond distances and bond angles for **2c** (3 pages). Ordering information is given on any current masthead page.

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