Table III. HF and MP2 Mulliken Atomic Orbital Populations *n* and Gross Atomic Charges *q* for Au and P

		Au				P			
molecule	method	*n*(s)	*n*(p)	*n*(d)	*q*	*n*(s)	*n*(p)	*n*(d)	*q*
PH_3	NRHF					1.79	3.28	0.15	−0.21
	NRMP2					1.80	3.31	0.16	−0.26
Au_2	NRHF	0.94	0.06	10.0	0				
	NRMP2	0.94	0.07	9.99	0				
	RHF	1.04	0.02	9.94	0				
	RMP2	1.11	0.01	9.88	0				
$AuPH_3$	NRHF	1.01	0.03	10.01	−0.05	1.77	3.27	0.15	−0.19
	NRMP2	1.01	0.14	9.98	−0.13	1.75	3.32	0.16	−0.23
	RHF	1.01	0.04	10.02	−0.08	1.77	3.24	0.15	−0.16
	RMP2	1.17	0.20	9.81	−0.18	1.72	3.33	0.19	−0.25
$Au_2(PH_3)_2$	NRHF	0.84	0.33	9.92	−0.09	1.76	3.31	0.15	−0.22
	NRMP2	0.76	0.49	9.82	−0.07	1.78	3.37	0.16	−0.31
	RHF	1.22	0.17	9.73	−0.12	1.71	3.33	0.16	−0.22
	RMP2	1.41	0.17	9.59	−0.17	1.69	3.36	0.19	−0.24

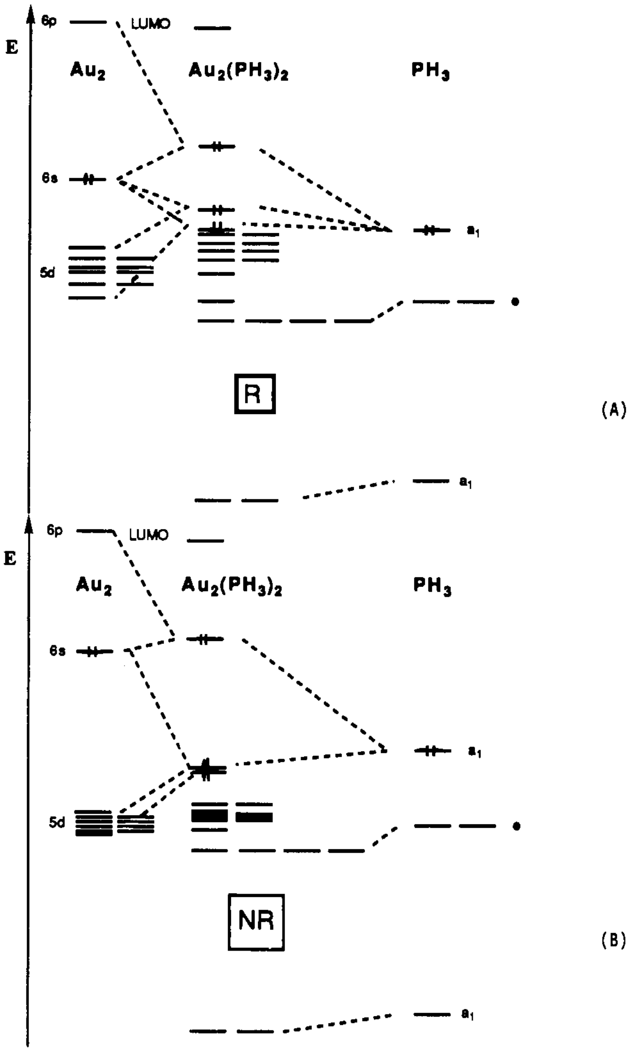

Figure 2. Qualitative MO scheme for the bonding in $Au_2(PH_3)_2$ for the relativistic (A) and nonrelativistic (B) cases.

achieved by improving the basis sets, as this is the case for diatomic Au_2.[34] Table II shows that Au-Au stretching force constants also increase as a consequence of both relativistic effects and the influence of the phosphine ligands. To summarize, (i) relativistic effects stablize the Au-Au bond in $Au_2(PPh_3)_2$ as is the case for diatomic Au_2,[19] and (ii) phosphine ligands play a very important role in stabilizing gold cluster compounds, as suggested by Mingos for the species $Au_6(PR_3)_6^{2+}$ and $Au_9(PR_3)_8^{3+}$.[7]

To analyze the role of the phosphine ligands in gold-gold bonding in more detail, we performed HF and MP2 Mulliken population analyses for the different gold compounds (Table III). As pointed out before,[19] Au(5d) and Au(6p) participation is very small in Au_2 and can be neglected (Table III). However, for the $Au_2(PH_3)_2$ compound, Au(5d) and Au(6p) participations are substantial. Obviously, phosphine ligands activate Au(5d) and Au(6p) orbitals and stabilize the Au-Au bond.[35] The population analysis for the mononuclear compound $AuPH_3$ shows that the PH_3 ligand donates electron density toward the gold radical (negative charge *q* at the gold atom, Table III), which results in an increased stability in the Au-Au bond when undergoing dimerization.

The MO scheme for the bonding in $Au_2(PH_3)_2$ is shown in Figure 2. Note the relativistic increase in the Au(5d)/Au(6s) gap in both compounds, Au_2 and $Au_2(PH_3)_2$. It is sufficient to discuss only the first three HOMOs (in the sequence of orbital energies $2a_1'$, a_2'', and $1a_1'$), which are shown schematically in Chart I and in Figure 2. Figure 2 and an analysis of the orbital coefficients show that the $2a_1'$ orbital consists of large Au(6p) admixture and the two lower lying a_2'' and $1a_1'$ orbitals have large Au(5d) contributions. These contributions are significantly increased by relativistic effects.

We expect similar results for gold cluster compounds of higher nuclearity. Finally, we point out that the $AuPH_3$ radical is not very stable at the MP2 level with respect to dissociation into Au and PH_3, despite the fact that this moiety is often used for isolobal analogies to the hydrogen atom.[3,23,36] In contrast, the positively charged species $AuPH_3^+$ is stable.[23]

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(35) This was suggested before by Mingos using a semiempirical Extended Hückel approach.[7a]

(36) Isolobality is defined as a topological concept[37] using frontier orbitals and their energies. Strictly, however, topology of orbitals cannot be viewed as to be independent of energetic aspects like the stability of the molecule itself.

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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Difluorodinitrosomethane, $ONCF_2NO$, and Hexafluorodinitrosopropane, $ONCF_2CF_2CF_2NO$

Earnest O. John, Robert L. Kirchmeier,
and Jean'ne M. Shreeve*

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Since trifluoronitrosomethane, CF_3NO, was first reported by Ruff and Giese in 1936, this stable blue compound and its derivatives have been studied extensively.[1] Its synthesis from the

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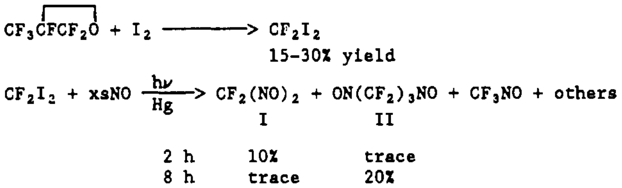
photolysis of a mixture of CF_3I and nitric oxide in the presence of mercury[2-4] or from the pyrolysis of $CF_3C(O)ONO$[5] occurs in a straightforward manner. With the exception of two patents which cover reactions of NO with olefins, dinitroso compounds are conspicuous by their absence from the literature.[6]

We now report the synthesis of a fluorinated C_1 dinitroso compound, difluorodinitrosomethane via the photolysis of a mixture of CF_2I_2 and NO. The products obtained are markedly dependent on the radiation time



$$CF_3CFCF_2O + I_2 \longrightarrow \underset{15\text{-}30\%\ \text{yield}}{CF_2I_2}$$

$$CF_2I_2 + xsNO \xrightarrow[Hg]{h\nu} \underset{I}{CF_2(NO)_2} + \underset{II}{ON(CF_2)_3NO} + CF_3NO + \text{others}$$

2 h 10% trace
8 h trace 20%

While this is the method of choice, several other routes were attempted based largely on those that were successful for the synthesis of CF_3NO. For example, (a) the photolytic or thermal decomposition of $CF_2[C(O)ONO]_2$, prepared by the reaction of $CF_2[C(O)OAg]_2$ with NOCl, results in a complex mixture which was not examined further. (b) Photolysis of a mixture of CF_2N_2 and an excess of NO through Pyrex glass gave a small amount of $CF_2(NO_2)_2$,[7] a variety of nitrogen oxides, and a polymeric solid. When mercury was added to the system (to inhibit NO_2 formation), photolysis did give rise to a mixture of difficult to separate nitrogen oxides, CF_3NO, and others, in which a small amount of $CF_2(NO)_2$ (<5%) could be identified. Photolysis at 3000 Å through quartz improved the yield somewhat. This may well be the most useful route to $CF_2(NO)_2$ based upon CF_2N_2 as an excellent difluorocarbene source.[7] However, CF_2N_2 is not readily synthesized and is not available commercially so we did not optimize the conditions for better yields. (c) Additionally, both nitrosonium tetrachloroborate and nitrosonium tetrafluoroborate failed to yield $CF_2(NO)_2$ when reacted with CF_2I_2 or CF_2Br_2.

Unfortunately, $CF_2(NO)_2$ lacks thermal stability and is sensitive to light. Whether placed in glass, Kel-F, or a passivated metal vessel, the compound proved to be unstable for periods more than 17 h (the maximum time for complete decomposition to occur). Exposure to diffuse light, even through glass, resulted in complete decomposition in 3 h. No conditions were found where the compound could be stored at ambient temperature without decomposition occurring in a short time. The presence of nitric oxide tends to decrease the rate of decomposition of I. However, $CF_2(NO)_2$ can be stored as a liquid in Pyrex glass for extended periods at −78 °C.

The decomposition of this compound is sufficiently slow to allow spectral measurements. Purification by repetitive fractional condensation allows separation from CF_3NO and NO_x, since $CF_2(NO)_2$ passes a trap cooled at −120 °C (CF_3NO retained) and is retained at −135 to −140 °C. In the infrared spectrum, bands at 1613 m and 1343 s cm^{-1} are assigned to NO vibrations. Other bands include 1030 vs (CF), 975 m, 766 s, 676 m, 627 s, and 555 s cm^{-1}. The ^{19}F NMR spectrum shows a single resonance at ϕ −72.5 (J_{N-F} = 15 Hz), which has a poorly resolved five-line structure due to coupling with the nitrogen atoms of the two nitroso groups. A molecular ion M^+ is observed at *m/e* 110 in both CI (4.4%) and EI (26.4%) mass spectra. Due to the low stability of $CF_2(NO)_2$ it was not possible to obtain elemental analysis. However, we were able to derivatize the material by causing it to react with *p*-nitroaniline, thus providing conclusive proof of the existence of I.

$$2p\text{-}O_2NC_6H_4NH_2 + ONCF_2NO \xrightarrow{EtOH} \underset{III}{O_2NC_6H_4N{=}NCF_2N{=}NC_6H_4NO_2}$$

Compound III is a bright yellow solid which is insoluble in ethanol. In the chemical ionization mass spectrum, extremely weak peaks assignable to M^+ and $M^+ + 1$ ions at *m/e* 350 and *m/e* 351 are observed. Additionally, three strongly supporting peaks occur at *m/e* 260 ($M^+ - 2NO_2 + 2$), 3%; *m/e* 259 ($M^+ - 2NO_2 + 1$), 28%; and *m/e* 229 ($M^+ - C_6H_4NO_2 + 1$), 11%. The proton NMR shifts are as would be expected, and the ^{19}F NMR spectrum has a single resonance band at ϕ −107.3.

When the mixture of CF_2I_2 + NO is photolyzed for more than 2 h, the concentration of the blue $ONCF_2CF_2CF_2NO$ (II) begins to build to the point where after ~8 h its yield is around 20%. Only two patents concerning dinitrosoperfluoro- and dinitrosopolyfluoroalkanes synthesized via the photolysis reactions between olefins and nitric oxide have appeared.[6] The hexafluorodinitrosopropane II described here is a new compound prepared by in situ generation of the catenated CF_2 moiety which reacts with NO in the presence of mercury. The absence of $ONCF_2CF_2NO$ may be due to the fact that when $:CF_2$ is generated slowly, $(CF_2)_3$ is formed much more extensively than $(CF_2)_2$ or $(CF_2)_x$ (8:1:1).[4] II is stable in Pyrex glass in the absence of light or in metal at 25 °C for an extended period and is stable in the presence of mercury. Its normal boiling point is below 25 °C. While being purified by using trap-to-trap fractionation, it passes through a trap cooled to −60 °C but is stopped in a trap at −78 °C. In the ^{19}F NMR spectrum a pentet is observed at ϕ 104.9 and a triplet at ϕ 57.8 (area ratio 1:2, *J* = 5.74 Hz). In the infrared spectrum, ν_{NO} is seen at 1620 cm^{-1}. Fluorinated dinitroso compounds have been suggested as precursors to polymeric materials that could have appreciable commercial value.[2,6] Our study of the syntheses and reactions of these compounds is continuing.

Experimental Section

General Methods. All materials were handled in a Pyrex vacuum system equipped with both glass and glass–Teflon valves. Quantities of volatile compounds were determined by *PVT* measurements assuming ideal gas behavior. Pressures were measured with a Heise Bourdon tube gauge. Infrared, NMR, and mass spectra were recorded on Perkin-Elmer 1710 Fourier transform, IBM 200 Fourier transform nuclear magnetic resonance, and VG 7070HS mass spectrometers.

Materials. Perfluoropropylene oxide (PCR), perfluoromalonic acid (gift from 3M Co.), difluorodiazirine (gift from 3M Co.), *p*-nitroaniline (Aldrich), and nitric oxide (Matheson) were used as received.

Synthesis of CF_2I_2. This compound has been synthesized previously by reacting iodine with difluorocarbene generated from either CF_2N_2[7] or $(CF_3)_3PF_2$.[4] In this work, iodine (3 g) and hexafluoropropylene oxide (15 mmol) were heated at 190 °C in a 75-mL stainless-steel vessel for 6 h to form CF_2I_2 (15–20% yield). Iodine with $(CF_3)_2Hg$ in CCl_3F also gives trace amounts of CF_2I_2. The ^{19}F NMR signal is found at ϕ 18.9. The infrared spectrum has strong bands at 1120, 1070, and 745 cm^{-1}.[4]

Synthesis of $CF_2[C(O)ONO]_2$. Perfluoromalonic acid (1.5 mmol) was reacted with Ag_2CO_3 (1.5 mmol) to form $CF_2[C(O)OAg]_2$ in ~100% yield. This salt (1.5 mmol) was contacted with excess NOCl in CH_3CN to form $CF_2[C(O)ONO]_2$ in 80% yield. It was purified by fractional distillation. It is very hygroscopic. This product was photolyzed both at −78 °C and at +25 °C (broad wave length lamp) but no useful nitroso-containing material was identified. Spectral data for $CF_2[C(O)ONO]_2$ are as follows. IR (Capillary): 1769 vs (ν_{CO}), 1672 (vs (ν_{ONO}), 1375 m, 1292 m, 1163 vs, 1078 m, 1039 m, 921 w, 821 w, 758 w cm^{-1}. ^{19}F NMR: ϕ −135; Mass (CI) *m/e* (species), intensity: 181 ($M^+ - F + 2$), 1.17%; 155 ($M^+ - CO_2 + 1$), 2.73%; 111 ($M^+ - 2CO_2 + 1$), 0.8%.

Synthesis of I. (a) Photolysis of CF_2N_2 + NO. Difluorodiazine (3 mmol), mercury (5 mL), and a slight excess of NO (7 mmol) in a quartz vessel were photolyzed at 3000 Å. The mixture of products contained NO_x, CF_3NO, unidentified materials, and less than 5% I. Due to an inadequate supply of CF_2N_2, the reaction was not studied further.

(b) Photolysis of CF_2I_2 + NO. Into a 250-mL Pyrex round-bottomed flask equipped with a Teflon-glass stopcock and a side arm were condensed CF_2I_2 (3 mmol) and NO (7 mmol). The side arm held approximately 5 mL of mercury. The mixture was photolyzed at 25 °C for 2 h. After separation by repetitive trap-to-trap distillation to remove

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CF_3NO, $ON(CF_2)_3NO$, NO_x, and unreacted CF_2I_2 and NO, $CF_2(NO)_2$ (~10% yield) was found in a trap at −135 to −140 °C having passed through a trap at −120 °C. It can be handled in a glass vacuum line in diffuse light for brief periods.

Synthesis of II. When the mixture of CF_2I_2, NO, and Hg described for I was photolyzed for longer time periods, e.g., 8 h, the yield of I was reduced to a trace, and $ONCF_2CF_2CF_2NO$ was formed in ~20% yield. This was separated by trap-to-trap distillation (passes a trap at −60 °C and is stopped at −78 °C) and found to be stable at 25 °C for extended periods (dark).

Synthesis of III. In an effort to conclusively confirm the existence of I, *p*-$O_2NC_6H_4NH_2$ (1.5 mmol) was dissolved in 4 mL of ethanol and I (0.5 mmol) was condensed into the solution. A bright yellow solid (III) began to precipitate immediately. After being stirred for 2 h, the mixture was filtered, and III was washed with ethanol and dried. Mass, ^{19}F and ^1H NMR, and IR spectra confirm the structure. The IR spectrum (KBr disk) has bands at 1710 vw, 1697 vw, 1671 vw, 1650 m, 1591 m, 1516 m, 1480 w, 1449 w, 1407 vw, 1399 s, 1320 s, 1295 s, 1245 vs, 1170 s, 1134 m, 1108 s, 1034 w, 1006 vw, 847 m, 754 m, 692 m, 631 m, 613 m, 561 m, and 486 vw cm^{-1}.

Acknowledgment is made to the Battelle Pacific Northwest Laboratories for financial support.

Registry No. III, 137568-62-8; $CF_2(NO)_2$, 137541-03-8; $ON(CF_2)_3NO$, 137541-04-9; CF_2I_2, 1184-76-5; $(CF_3)_2Hg$, 371-76-6; $CF_2[C(O)ONO]_2$, 137541-05-0; $CF_2[C(O)OAg]_2$, 2624-69-3; CF_2N_2, 814-73-3; CF_3NO, 334-99-6; *p*-$O_2NC_6H_4NH_2$, 100-01-6; hexafluoropropylene oxide, 428-59-1; perfluoromalonic acid, 1514-85-8.

Contribution from the Istituto di Chimica Strutturistica
Inorganica dell'Università, CNR Centro di Studio
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dei Metalli di Transizione nei Bassi Stati
di Ossidazione, and Dipartimento di Chimica
Inorganica e Metallorganica dell'Università,
Via G. Venezian 21, 20133 Milano, Italy

Synthesis and Structural Characterization of the Nitrido-Carbonyl Cluster Anion $[Co_7N(CO)_{15}]^{2-}$, Possessing a Carbonyl Stereochemistry Different from That of Its Rhodium Analogue

G. Ciani,*[,1a] N. Masciocchi,[1a] A. Sironi,[1a] A. Fumagalli,[1b]
and S. Martinengo*[,1c]

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Introduction

Nitrido-carbonyl clusters, a class of compounds including today less than 20 species, exhibit interesting structural features both in the metal atom arrays and in the geometries of the cavities containing the interstitial nitrogen atoms. The first examples reported were the trigonal-prismatic species $[M_6N(CO)_{15}]^-$ (M = Co, Rh),[2,3] from which other higher nuclearity species {up to 14 metal atoms, as $[Co_{14}N_3(CO)_{23}]^{3-}$[4] and $[Rh_{14}N_2(CO)_{25}]^{2-}$[5]} were derived. In particular, condensation of the simple anionic carbonylates $[M(CO)_4]^-$ (M = Co, Rh, Ir) on $[Rh_6N(CO)_{15}]^-$ afforded the $[Rh_6MN(CO)_{15}]^{2-}$ species,[6] containing a trigonal-prismatic cluster capped on a square face. In this case the Rh_7 dianion and the two related Rh_6Co and Rh_6Ir mixed-metal species were found to have the same overall ligand geometry.

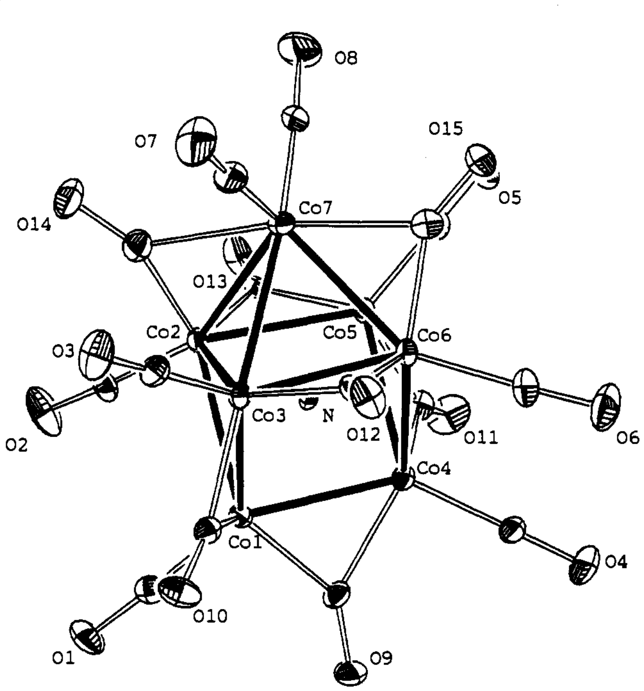

Figure 1. ORTEP drawing of the anion $[Co_7N(CO)_{15}]^{2-}$. For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms. Thermal ellipsoids are drawn at the 30% probability level.

We have now studied the analogous condensations starting from $[Co_6N(CO)_{15}]^-$, and we report here on the synthesis and X-ray characterization of the $[Co_7N(CO)_{15}]^{2-}$ anion, which exhibits a carbonyl disposition different from that observed in the rhodium analogue.

Results and Discussion

The anion $[Co_7N(CO)_{15}]^{2-}$ is synthesized by heating at reflux under nitrogen a THF solution containing equimolar amounts of the $[PPh_4]^+$ salts of $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$. Close IR monitoring shows that the reaction occurs in two stages. At first there is a decarbonylation of the starting nitride to give the octahedral $[Co_6N(CO)_{13}]^-$[7] (eq 1), followed by a slow condensation

$$[Co_6N(CO)_{15}]^- \rightarrow [Co_6N(CO)_{13}]^- + 2CO \qquad (1)$$

$$[Co_6N(CO)_{13}]^- + [Co(CO)_4]^- \rightarrow [Co_7N(CO)_{15}]^{2-} + 2CO \qquad (2)$$

of this anion with $[Co(CO)_4]^-$ to give the heptanuclear species (eq 2). Thus the real condensation occurs on $[Co_6N(CO)_{13}]^-$, which is generated "in situ" by reaction 1. It is essential, for the reaction to proceed, to remove the evolved CO. Beside the condensation some decomposition also occurs, and at the end some insoluble black material and a trace of unreacted $[Co(CO)_4]^-$ are present. Separation is achieved by filtration and fractional crystallization.

The IR spectrum of $[PPh_4]_2[Co_7N(CO)_{15}]$ in THF solution shows bands at 2029 w, 1977 vs, 1963 m, 1930 w, 1815 m, 1805 (sh), and 1775 (sh) cm^{-1}. The $[Co_7N(CO)_{15}]^{2-}$ anion reacts immediately with CO giving directly $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$ according to the reverse of the synthesis reaction. Partial addition of CO does not give $[Co_6N(CO)_{13}]^-$, as expected from the reverse of reaction 2, but gives again $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$, leaving some unreacted $[Co_7N(CO)_{15}]^{2-}$.

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