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A Closed-Shell Monomeric Rhenium(1-) Anion Provided by *m*-Terphenyl Isocyanide Ligation

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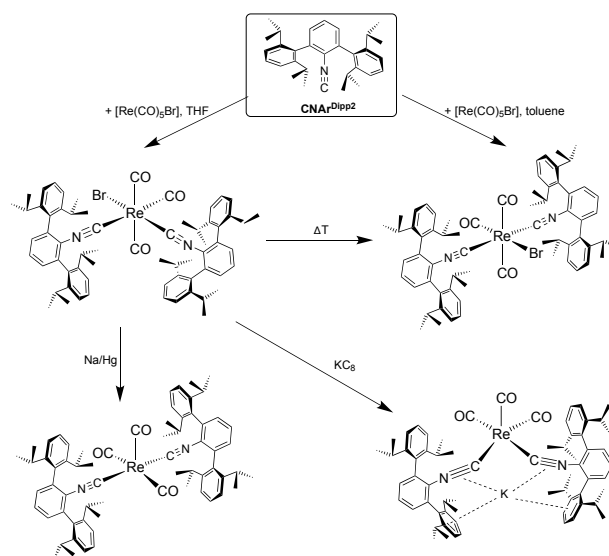
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The mixed isocyanide/carbonyl complexes *cis*- and *trans*-[Re(CO)₃Br(CNAr^{Dipp2})₂] (Ar^{Dipp2} = 2,6-(2,6-(*i*-Pr)₂C₆H₃)₂C₆H₃) can be synthesized from reactions of [Re(CO)₅Br] and CNAr^{Dipp2} depending on the conditions applied. Reduction of the neutral Re(I) species gives the monoanionic complex [Re(CO)₃(CNAr^{Dipp2})₂]⁻ or the neutral [Re(CO)₃(CNAr^{Dipp2})₂], which contain rhenium in the formal oxidation states “-1” and “0”, respectively.

Apart from the well-known carbonylmetallate [Re(CO)₅]⁻,¹ highly reduced rhenium species containing the transition metal in the formal oxidation state “-1” are practically unknown. This is in contrast to the related manganese chemistry, where some of such compounds could be isolated and structurally characterized.²⁻⁵ The interest in corresponding rhenium species arises from the observation that [Re(CO)₅]⁻ can act as a transition metal-centered nucleophile, and readily undergoes reactions with a number of electrophiles.⁶⁻⁹ Electrophilic addition to a basic metal center is arguably one of the easiest ways to form transition metal-carbon or metal-metal σ-bonds. For more than five decades, metal carbonyl anions have been used for that purpose due to their nucleophilic reactivity, ready availability and relatively high stability. Nevertheless, very little is known about other metallate anions of rhenium. An exception is given with the [Re(CO)₃(bpy)]⁻ anion, which is reported to be involved in the electrocatalytic reduction of CO₂ using members of the [Re(CO)₃Cl(bpy)] family of compounds (bpy = 2,2'-bipyridines).^{10,11} While the [Re(CO)₅]⁻ anion can be regarded as a ‘real’ Re⁻¹ compound, because of the absence of redox-active ligands able to store additional charge, the bpy ligands have been shown to possess a non-innocent character in the two-electron reduction of [Re(CO)₃Cl(bpy)]. According to XAS analysis and theoretical calculations, the [Re(CO)₃(bpy)]⁻ species is better described as {Re⁰(bpy⁻)}, rather than {Re⁺(bpy²⁻)} or {Re⁻¹(bpy)}.¹²

This demonstrates that the nature of such metallate anions may be strongly defined by the electronic properties of the ligand systems.

Due to their isolobal relation to CO, isocyanide ligands are also able to form stable reduced metallate species, allowing at the same time for electronic and steric modulation of the ligand system, by changes in substituent in a manner, which is inaccessible for CO.¹³⁻¹⁶ Recent work has demonstrated that isocyanides bearing sterically encumbering *meta*-terphenyl groups are very versatile ligands, able to foster unusual coordination modes and to stabilize highly reduced metal complexes, through steric protection and electronic delocalization.¹⁷⁻²² Following this approach, we synthesized mixed Re(I) carbonyl/isocyanide complexes bearing the highly encumbering ligand CNAr^{Dipp2} (Dipp2 = 2,6-diisopropylphenyl) and studied their isomerization and reactions with different reducing agents (Scheme



1).

Scheme 1. Synthesis of tricarbonylrhenium complexes with CNAr^{Dipp2}.

Very recently, we reported the formation of *trans,mer*-[Tc(CO)₃Cl(CNAr^{Dipp2})₂] from the reaction of *fac*-[Tc₂(CO)₆Cl₃](NBu₄) and CNAr^{Dipp2}.²³ The highly encumbering substituents of the isocyanide

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ligands create a considerable steric pressure, which is responsible for the unprecedented *fac/mer* isomerization of three carbonyl ligands in a Tc(I) complex. In contrast, the related reaction between $[\text{Re}(\text{CO})_5\text{Br}]$ and $\text{CNAr}^{\text{Dipp}2}$ in boiling THF led to the formation of *cis*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$. The IR spectrum of the compound shows three absorptions in the range 2025–1933 cm^{-1} , which can be assigned to $\nu(\text{C}=\text{O})$ of a *facial* tricarbonyl set, and an absorption at 2120 cm^{-1} for $\nu(\text{C}\equiv\text{N})$ of the isocyanide ligands. The ^1H NMR spectrum clearly shows signals for two non-equivalent isocyanides, which also indicates *cis* geometry. In fact, four doublets are found (with an overlap of two of them) around 1 ppm for the methyl groups of the isopropyl side chains, instead of two, as would be expected for four equivalent 2,6-diisopropylphenyl substituents with hindered rotation of the flanking aromatic rings. Almost no frequency shift is observed for the $\text{C}\equiv\text{N}$ stretch upon coordination (uncoordinated $\text{CNAr}^{\text{Dipp}2}$ 2124 cm^{-1}), which indicates a prevalent sigma donor character of the isocyanide. An X-ray crystal structure determination confirms the *cis*-coordination of the two isocyanides under retention of the facial bonding mode of the CO ligands (see

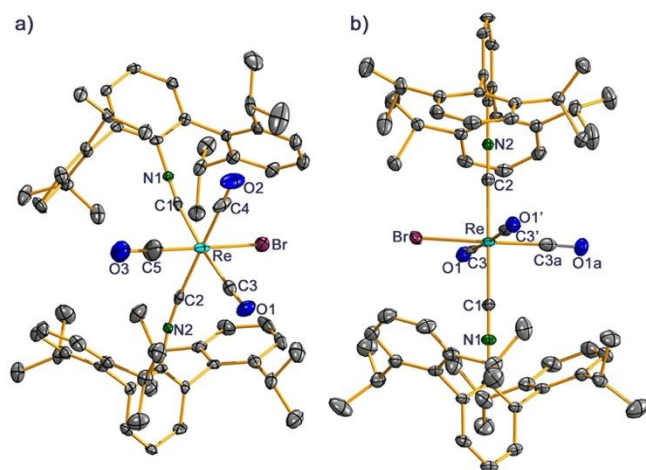


Fig. 1a).

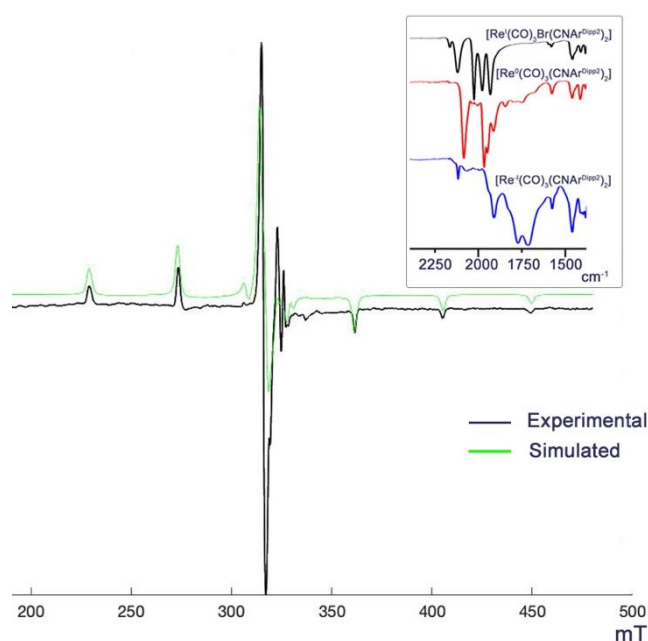
Figure 1. a) Molecular structure of *cis,fac*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$. Selected bond lengths (Å) and angles (deg): Re–C1 2.072(4), Re–C2 2.076(4), Re–C3 2.014(4), Re–C4 1.980(4), Re–C5 1.95(1), Re–Br 2.484(1), C1–Re–C3 174.6(1), C2–Re–C4 173.0(2). b) Molecular structure of *trans,mer*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$. Selected bond lengths (Å) and angles (deg) for one of two independent molecules: Re–Br1 2.495(2), Re–C1 2.062(4), Re–C2 2.050(4), Re–C3 2.04(1), C1–Re–C2 180, C1–Re1–C3 91.9(4), C3–Re1–Br 85.4(4). More bond lengths and angles are given in the Supporting Information.

The *cis* coordination of the two bulky isocyanides causes a considerable steric stress inside the molecule. This is manifested by a marked distortion of the octahedral coordination sphere as can best be seen at the C1–Re–C3 and C2–Re–C4 angles of 174.6(1) and 173.0(2)°, respectively. Indeed, *cis*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$ can be regarded as a ‘kinetic product’, since a prolonged heating of this compound in toluene results in isomerization and the final formation of *trans*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$. The *trans* product is also formed, when the reaction between $[\text{Re}(\text{CO})_5\text{Br}]$ and $\text{CNAr}^{\text{Dipp}2}$ is performed in boiling toluene. The lowering of the steric stress by the *trans* coordination of the bulky $\text{CNAr}^{\text{Dipp}2}$ ligands brings the three carbonyl ligands in the energetically less favored meridional arrangement. Similar observations have been made before for the lighter homologues of rhenium: technetium and manganese;^{23,24} but also for molybdenum(0) complexes, where during reactions of *fac*-

$[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ with $\text{CNAr}^{\text{Dipp}2}$ also a *fac/mer* isomerization of the carbonyl ligands and formation of *trans*- $[\text{Mo}(\text{CO})_3(\text{NCMe})(\text{CNAr}^{\text{Dipp}2})_2]$ was observed.¹⁸ These findings may be related to the frequent observation that reactions on 3d and 4d metal ions proceed faster than on their 5d counterparts.^{25–27} Thus, *cis*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$ can be regarded as an intermediate of the reaction of $[\text{Re}(\text{CO})_5\text{Br}]$ with $\text{CNAr}^{\text{Dipp}2}$, which finally gives the stable *trans* isomer.

The IR spectrum of *trans*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$ exhibits two $\nu(\text{C}=\text{O})$ bands at 1986 and 1922 cm^{-1} and a $\nu(\text{C}\equiv\text{N})$ absorption at 2121 cm^{-1} . Two doublets around 1 ppm are found for the methyl protons in the ^1H NMR spectrum of the *trans* complex indicating magnetic equivalence of the two isocyanide ligands. The low solubility of the compound in all common solvents prevented from the acquisition of a ^{13}C NMR spectrum with sufficient quality, but an X-ray diffraction study confirms the octahedral coordination of Re with the two encumbering $\text{CNAr}^{\text{Dipp}2}$ ligands occupying *trans* positions to each other (Fig. 1b). The Re–C (isocyanide) bond lengths are slightly shorter in the *trans* isomer, which is in accordance to the stronger *trans* influence of CO. The three CO and the Br ligands are statistically disordered over the four equatorial coordination positions.

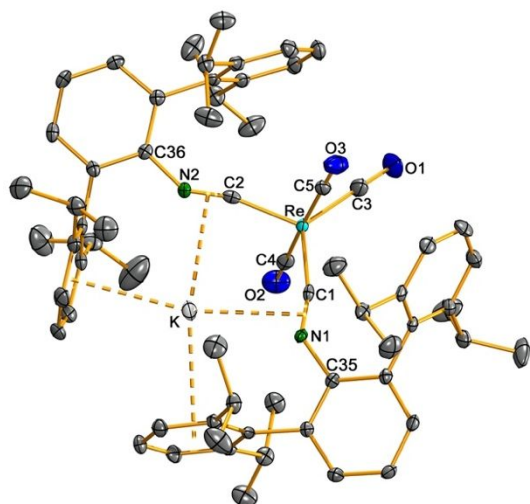
It has been shown that reduction of *m*-terphenyl isocyanide complexes of transition metals such as manganese, cobalt or iron may result in the formation of fairly stable products with highly reduced metal species having remarkable chemical properties.^{28–33} The isolation of highly reduced species also succeeded with the compounds of this study. Prolonged stirring of *cis,fac*- $[\text{Re}(\text{CO})_3\text{Br}(\text{CNAr}^{\text{Dipp}2})_2]$ with sodium amalgam in THF produces a deep purple solution from which a dark purple solid can be isolated. Most parts of its IR spectrum are practically identical with the spectrum of the starting material, but the isocyanide band is shifted to a value of 2083 cm^{-1} and three carbonyl bands are found at 1966, 1948 and 1913 cm^{-1} (Fig. 2). The observations suggest the formation of the neutral complex $[\text{Re}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$, in which the formal



oxidation state of rhenium is zero. This assumption is confirmed by the detection of a

Figure 2. Triple bond regions of the IR spectra (inset) of *cis*-[Re(CO)₃Br(CNAr^{Dipp2})₂], [Re⁰(CO)₃(CNAr^{Dipp2})₂] and K[Re⁻¹(CO)₃(CNAr^{Dipp2})₂], and frozen solution X-band EPR spectrum of [Re⁰(CO)₃(CNAr^{Dipp2})₂] in THF ($g_x = 2.1386$, $g_y = 2.0585$, $g_z = 2.0203$, $A^{Tc}_x = 32 \cdot 10^{-4} \text{ cm}^{-1}$, $A^{Tc}_y = 20 \cdot 10^{-4} \text{ cm}^{-1}$, $A^{Tc}_z = 404 \cdot 10^{-4} \text{ cm}^{-1}$).³⁷

well-resolved EPR spectrum (Fig. 2). It reflects essentially axial symmetry with a marked rhombic component. A large coupling of $404 \cdot 10^{-4} \text{ cm}^{-1}$ of the unpaired electron with the nuclear spins of ^{185,187}Re ($I = 5/2$) is resolved in the parallel part of the spectrum, while it is small and less resolved in the other spectral components. ^{185,187}Re hyperfine couplings of similar size have been found in the parallel part of the spectrum of the low-temperature EPR spectrum of [Re(CO)₃(tricyclohexylphosphine)₂],^{34,35} another monomeric rhenium(0) species of appreciable stability.⁸ Those in related spin-trapped Re(0) species, however, are significantly smaller.³⁶ These findings confirm a mainly metal-centered unpaired electron in



[Re(CO)₃(CNAr^{Dipp2})₂].

Figure 3. Molecular structure of K[Re(CO)₃(CNAr^{Dipp2})₂]. Selected bond lengths (Å) and angles (deg): Re-C1 1.936(2), Re-C2 1.942(2), Re-C3 1.970(3), Re-C5 1.986(3), C1-N1 1.227(3), C2-N2 1.218(3); C1-Re-C2 113.1(1), C2-Re-C3 = 120.7(1), C3-Re-C5 87.4(1), C3-Re-C4 88.8(1), C4-Re-C5 176.2(1), C1-N1-C35 135.1(2), C2-N2-C36 141.2(2).

Remarkably, the reaction of [Re(CO)₃Br(CNAr^{Dipp2})₂] with KC₈ in THF produces a dark red solution, from which another reduction product could be obtained. This experimental result illustrates nicely the difference in reductive powers of Na/Hg and KC₈, which has been described earlier.^{38–40} The IR spectrum of the isolated red solid presents a broad isocyanide $\nu(\text{C}\equiv\text{N})$ band at 1912 cm^{-1} and broad, less resolved CO bands with two maxima around 1800 cm^{-1} (see Fig. 2). The strong red-shift of the CN band (ca. 100 cm^{-1}) is in agreement with the findings for the analogous manganese complex. It suggests a strong π -back donation from the Re center and supports the formation of a rhenium(-I) species.³⁰ The ¹H NMR spectrum of the compound in benzene shows only two doublets for two sets of non-equivalent methyl groups in the region from 1.0 to 1.3 ppm. This is consistent with the presence of a symmetric five-coordinate complex having two isocyanide ligands in an equivalent magnetic

environment. An X-ray structural analysis (Fig. 3) reveals the formation of the salt K[Re(CO)₃(CNAr^{Dipp2})₂] as a contact ion pair, in which the five-coordinate rhenium monoanion has a trigonal bipyramidal coordination geometry with apical CO ligands. The K⁺ counter ion is embedded in an organic cavity, where it is coordinated by two aromatic rings and the π -systems of the two C \equiv N groups. Notably, the isocyanide C-N bond distances in K[Re(CO)₃(CNAr^{Dipp2})₂] (1.227(3) Å and 1.218(3) Å) are significantly longer than those found for free CNAr^{Dipp2} (1.1577(18) Å) and the formally Re(I) bromide complexes *cis, fac*-[Re(CO)₃Br(CNAr^{Dipp2})₂] (1.155(4), 1.558(4) Å) and of *trans, mer*-[Re(CO)₃Br(CNAr^{Dipp2})₂] (1.147(5) – 1.159(3) Å). This

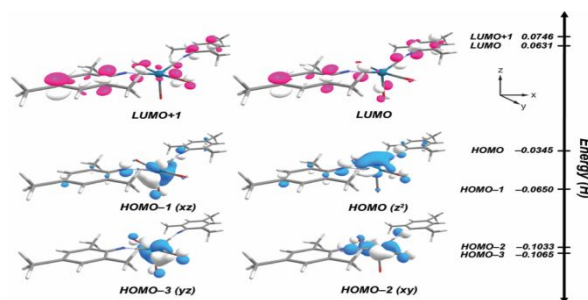


Figure 4. Calculated frontier molecular orbitals for the model complex [Re(CO)₃(CNMes)₂]⁻ at the B3LYP/ZORA-def2-TZVP DFT level.⁴¹

elongation is suggestive of strong π -backbonding interactions from the reduced Re center to the isocyanide π^* orbitals and is consistent with the presence of an electron rich, d⁸ metal center. Indeed, the isocyanide C-N bond distances in K[Re(CO)₃(CNAr^{Dipp2})₂] are also longer than those in the related manganese(-I) complexes [K(18-crown-6)][Mn(CO)₂(CNAr^{Mes2})₃] ($\text{Ar}^{\text{Mes2}} = 2,6\text{-(2,4,6-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$) and [Na(NCMe)₃][Mn(CO)₃(CNAr^{Dipp2})₂],²² which reflects the greater electron-releasing character of 5d metals relative to 3d metals.

DFT calculations (B3LYP/ZORA-def2-TZVP) on the model complex [Re(CO)₃(CNMes)₂]⁻ (Mes = 2,4,6-Me₃C₆H₂) further support the assignment of K[Re(CO)₃(CNAr^{Dipp2})₂] as a rhenium-centered metalloanion. The optimized structure of [Re(CO)₃(CNMes)₂]⁻ is in good agreement with the crystal structure of K[Re(CO)₃(CNAr^{Dipp2})₂], despite the absence of the K⁺ counterion. As shown in Fig. 4, the four highest-lying filled molecular orbitals are Re-based and portray a classical d⁸ configuration with significant π -backbonding interactions to both the isocyanide and carbonyl ligands. Of particular note is the HOMO calculated for [Re(CO)₃(CNMes)₂]⁻, which is predominantly Re dz² in character, but is also engaged in π -backbonding interactions to both the CNMes and CO units. A similar orbital interaction was calculated for the SOMO of the neutral zero-valent manganese complex, Mn(CO)₃(CNAr^{Dipp2})₂,²⁹ and accounted for delocalization of unpaired spin density from the Mn center to the supporting ligands. However, in the case of [Re(CO)₃(CNMes)₂]⁻, and by extension K[Re(CO)₃(CNAr^{Dipp2})₂], the presence of an additional electron results in a closed-shell configuration. Furthermore, unlike [Re(CO)₃(bipy)]⁻, in which the bipy ligand possesses low-lying π^* orbitals, but is not an effective π -acid,¹² the strong backbonding interactions from Re to the isocyanide ligands in

K[Re(CO)₃(CNAr^{Dipp2})₂] result in a redox-innocent ligand manifold thereby further promoting localization of electron density on the Re center.

In conclusion, we have synthesized mixed carbonyl/isocyanide complexes with rhenium in the formal oxidation states “+1”, “0” and “-1”, showing that encumbering *m*-terphenyl isocyanides are well suitable for the stabilization of such highly reduced rhenium compounds and that a careful choice of the reductant allows a selective one- or two-electron reduction.

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Conflicts of interest

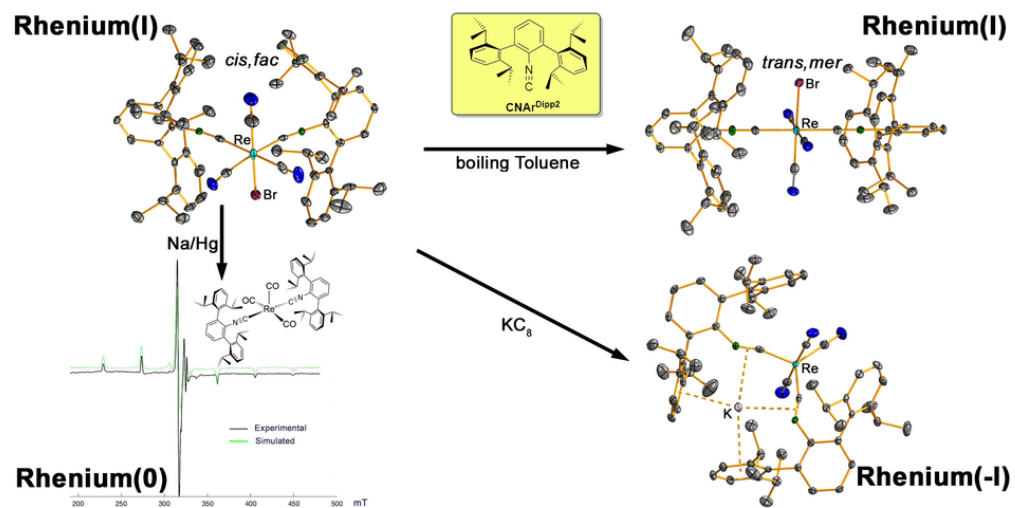
There are no conflicts to declare.

Notes and references

§ In contrast to that of [Re(CO)₃(CNAr^{Dipp2})₂], where linewidth considerations and the simulation confirm only small couplings between 20 and 30 · 10⁻⁴ cm⁻¹, the frozen solution EPR spectrum of the phosphine complex shows a remarkably large ^{185,187}Re couplings of approximately 80 · 10⁻⁴ cm⁻¹ in the perpendicular part.

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Mixed isocyanide/carbonyl complexes with rhenium in the oxidation states “+1”, “0” and “-1” were prepared assisted by a sterically encumbered.



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