Rotational isomerism in bis(carbon dioxide) complexes of molybdenum generated by conrotatory motion of the CO2 ligands

Ernesto Carmona, Miguel A. Munoz, Pedro J. Perez, and Manuel L. Poveda

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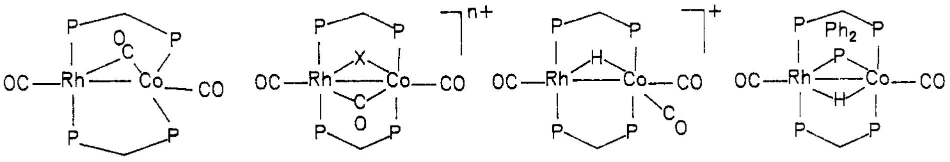
Chart I



1

3a, X=Cl, n=1

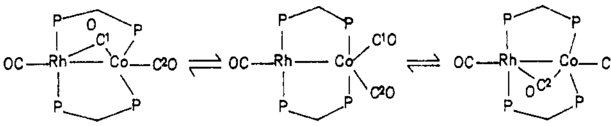
3b, X=I, n=1

3c, X=S, n=0

4

5

when M^2 = Co (2.6852 (7) Å) than when M^2 = Rh (2.739 (1) Å)[6] lead to the shorter distance $Rh^1\cdots C^1$ = 2.420 (4) Å and the more cute angle $\angle Rh^1M^2C^1$ = 62.06 (13)° for **1** compared to corresponding values of 2.533 (3) Å and 63.5 (1)° for **2**. The semibridging CO ligand in **1** is characterized by ν(CO) = 1815 cm^{-1} compared to 1835 cm^{-1} in **2**. The complex **1** is fluxional at room temperature in the sense that the two carbonyl ligands on cobalt are effectively equivalent in the ^{13}C NMR spectrum, but there is no evidence for exchange of carbonyls between metal centers as appears to occur for **2**.[6] The fluxionality, which can be frozen out at −45 °C, is illustrated in eq 1.[4,8]



(1)

Complex **1** is readily oxidized. For example, reaction with $HgCl_2$ or $CHCl_3$, followed by precipitation with $NaBPh_4$, gave **3a**, reaction with iodine and $NaBPh_4$ gave **3b**, and reaction with sulfur gave **3c**.[9] Complex *1* was protonated by HBF_4 at the Co–Rh bond to give, after precipitation with $NaBPh_4$, complex **4**. Complex **4** differs from $[Rh_2(\mu\text{-H})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]^+$ in that it has no μ-CO group.[6,10] This is consistent with the tendency of cobalt to adopt a higher coordination number than rhodium, as is also seen in the structure of **1**. Complex **4** is fluxional, since the ^1H NMR spectrum gives a singlet for the CH_2P_2 protons and the ^{13}C NMR spectrum gives a single CoCO resonance; in this case, inversion of the RhCo(μ-H) group must occur.[10]

Complex **1** reacts easily with Ph_2PH to give complex **5**, which has been characterized crystallographically.[11] The structure is shown in Figure 2. The structure is disordered with 0.5 occupancy by Co and Rh in each metal position, and so bond distances, other than d(Co–Rh) = 2.795 (3) Å, involving the metal centers are average values. Nevertheless, a peak corresponding to the expected position of the hydride ligand was observed and the position is shown in Figure 2. The Rh–Co bond in **5** (2.795 (3) Å) is significantly longer than in **1** (2.6852 (7) Å). In both **4** and **5** the RhCo(μ-H) interaction is a 3c–2e bond only and so the longer metal–metal bond is expected.

These reactions clearly illustrate that the bimetallic Rh–Co core can be stabilized by μ-dppm ligands, and the organometallic and catalytic reactivity of the complex **1** is being studied.

Acknowledgment. We thank the NSERC (Canada) for financial support.

Registry No. **1**, 125782-10-7; **3a**, 125782-11-8; **3b**, 125782-12-9; **3c**, 125782-13-0; **4**, 125801-23-2; **5**, 125782-14-1; **5**·$2C_2H_5OH$, 125782-15-2; $CHCl_3$, 67-66-3; Co, 7440-48-4; Rh, 7440-16-6.

Supplementary Material Available: Listings of crystal data, positional and thermal parameters, and bond distances and angles for **1** and positional and thermal parameters, bond distances and angles, least-squares planes, and torsion angles for **5** (29 pages); a listing of observed and calculated structure factors for **5** (25 pages). Ordering information is given on any current masthead page.

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(8) NMR data for **1**: ^{31}P, δ 31.5 [br s, *P*Co], 20.1 [dt, $^2J(PP)$ = 72 Hz, $^1J(RhP)$ = 129 Hz, *P*-Rh]; ^{13}C (−45 °C), δ 214.7 [br s, Co*C*O], 214.4 [br s, Co*C*O], 180.7 [dt, $^2J(PC)$ = 15 Hz, $^1J(RhC)$ = 71 Hz, Rh*C*O]. IR: ν(CO) 1965 (s), 1922 (s), 1815 (s) cm^{-1}.

(9) Spectroscopic data for **3a**: ^{31}P NMR, δ 46.1 [t, $^2J(PP)$ = 39 Hz, *P*Co], 26.5 [dt, $^2J(PP)$ = 39 Hz, $^1J(RhP)$ = 104 Hz, *P*Rh]; IR, ν(CO) 1986 (m), 1962 (s), 1850 (m) cm^{-1}. Spectroscopic data for **3b**: ^{31}P NMR, δ 47.9 [t, $^2J(PP)$ = 47 Hz, *P*Co], 29.3 [dt, $^2J(PP)$ = 47 Hz, $^1J(RhP)$ = 100 Hz, *P*Rh]; IR (Nujol), ν(CO) 1997 (m), 1990 (m), 1970 (s), 1849 (m) cm^{-1}. Spectroscopic data for **3c**: ^{13}C NMR, δ 197.7 [dt, $^1J(RhC)$ = 73 Hz, $^2J(PC)$ = 14 Hz, Rh*C*O], 211.0 rt, $^2J(PC)$ = 56 Hz, μ-*C*O], 222.6 [s, Co*C*O]; ^{31}P NMR, δ 25.3 [dt, $^1J(RhP)$ = 134 Hz, $^2J(PP)$ = 32 Hz, Rh*P*], 38.4 [t, $^2J(PP)$ = 32 Hz, Co*P*]; IR (Nujol), ν(CO) 1971 (s), 1958 (s), 1796 (m) cm^{-1}.

(10) Spectroscopic data for **4**: ^1H NMR, δ −13.3 [br, CoRh(μ-*H*)], 3.80 [s, CH_2P_2]; ^{31}P NMR, δ 44.8 [t, $^2J(PP)$ = 56.5 Hz, *P*Co], 25.5 [dt, $^2J(PP)$ = 56.5 Hz, $^1J(RhP)$ = 111 Hz, *P*Rh]; ^{13}C NMR, δ 206.9 [*s*, 2 C, Co*C*O], 182.0 [dt, 1 C, $^1J(RhC)$ = 60.7 Hz, $^2J(PC)$ = 14.5 Hz, Rh*C*O]; IR, ν(CO) 1981 (s), 1946 (sh), 1933 (m) cm^{-1}.

(11) Crystal data for **5**·$2C_2H_5OH$: $C_{68}H_{67}CoO_4P_5Rh$; fw 1265.00; monoclinic, space group $P2_1/c$; a = 12.241 (5) Å, b = 20.459 (4) Å, c = 25.394 (5) Å, β = 96.48 (3)°; V = 6319 (6) $Å^3$; Z = 4; calculated density 1.33 g cm^{-3}; T = 21 °C; Mo Kα radiation (λ = 0.710<<mt73 Å); μ(Mo Kα) = 6.9 cm^{-1}; unique reflections 7231 with 2θ up to 43°; Lorentz, polarization, linear decay, and a numerical absorption correction applied; R = 0.075, R_w = 0.092 for 358 variable parameters and 2464 observations with $I \geq 3\sigma(I)$. ^1H NMR data for **5**: δ −15.49 [br s, CoRh(μ-H)]. ^{31}P NMR data for **5**: δ 28.7 [m, 2 P, Rh*P*], 46.4 [m, 2 P, CoP], 213.0 [m, 1 P, μ-*P*Ph_2].

Rotational Isomerism in Bis(carbon dioxide) Complexes of Molybdenum Generated by Conrotatory Motion of the CO_2 Ligands

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Summary: The existence of rotational isomers in $(CO_2)_2$ complexes of molybdenum and their interconversion by a concerted rotation, in which the two CO_2 ligands rotate in the same direction, have been demonstrated with the aid of variable-temperature NMR studies carried out with complexes of the type *trans*-$[Mo(CO_2)_2(PMe_3)_2(P\text{-}P)]$ and *trans*-$[Mo(CO_2)_2(P\text{-}P)_2]$ (P-P = chelating diphosphine).

We have recently described the formation of *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ (**1**) and *trans*-$[Mo(CO_2)_2(PMe_3)_3(CNR)]$ (**2**), the first bis(carbon dioxide) adducts of a transition metal.[1] Although these compounds were fully

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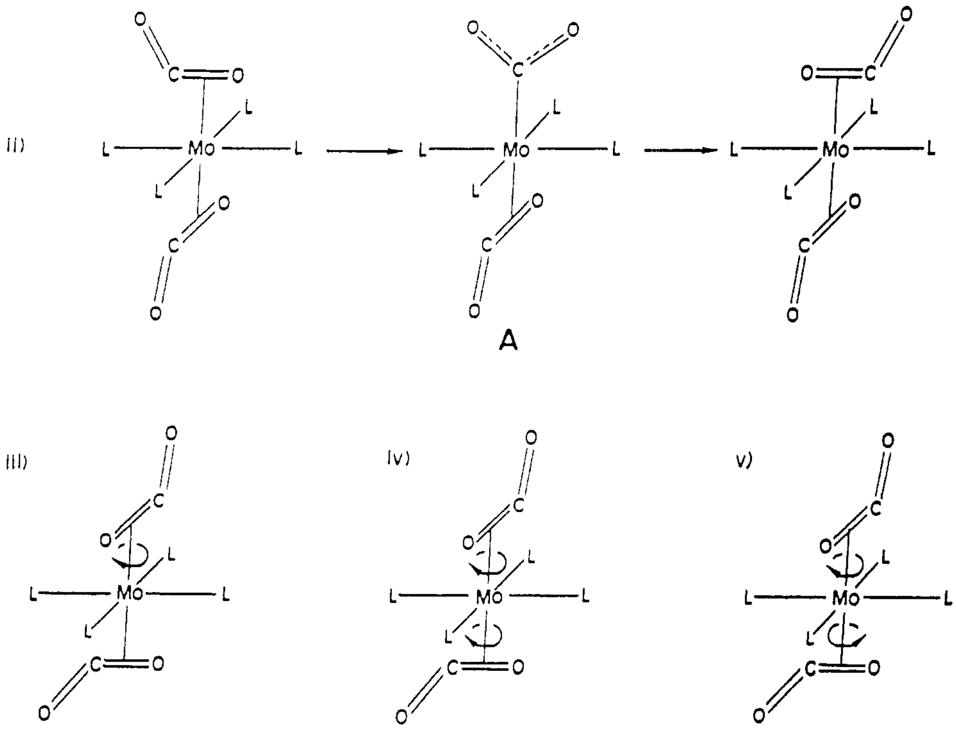
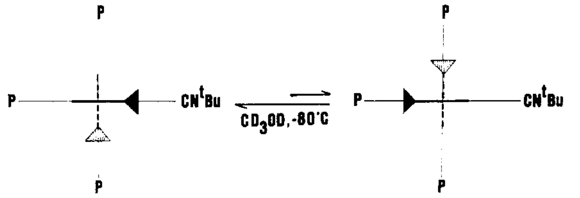
(1) Alvarez, R.; Carmona, E.; Marín, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286.

Scheme I



characterized by spectroscopy and, in some cases, by X-ray studies, they exhibit temperature-dependent NMR spectra due to a fluxional behavior that was not investigated at that time. Since a better understanding of the M–CO_2 interaction is of fundamental importance in connection with the activation of this molecule,[2] we have decided to investigate the intimate nature of the mechanism responsible for the observed fluxionality. As discussed below, this investigation has allowed the detection, for the first time, of M–CO_2 rotational isomers and has demonstrated in addition that these rotamers interconvert by a concerted rotation of the η^2-CO_2 ligands in which both molecules of CO_2 rotate in the same direction.

As already reported,[1] complex 1 gives rise to an AA′BB′ pattern in the low-temperature $^{31}P\{^1H\}$ NMR spectrum (−80 °C, 81 MHz), which transforms into a singlet in the fast exchange limit (50 °C, 32.4 MHz). For compound **2a** (R = *t*-Bu) a thermodynamic mixture of two species (ca. 4:1 ratio) that are under dynamic equilibrium can be detected by ^{31}P NMR spectroscopy. Although these are likely the rotational isomers shown in eq 1, it is worth discussing at this point all the possible fluxional processes related with the motion of the CO_2 ligands and show that the spectroscopic data are consistent with only one of them.



(1)

Five different pathways can in principle be invoked to account for the observed NMR features (Scheme I): (i) an intermolecular process implying CO_2 dissociation and reassociation, (ii) exchange of the free and coordinated oxygen atoms of one of the CO_2 ligands, (iii) independent rotation of the CO_2 ligands, (iv) concerted rotation with the two CO_2 molecules rotating in the same direction (conrotatory), and (v) concerted rotation with both molecules rotating in opposite directions (disrotatory).

Although some of these pathways can be disregarded on the basis of data already available,[1] in order to ascertain the precise motion of the CO_2 ligands, the new complexes *trans*-$[Mo(CO_2)_2(PMe_3)_2(P\text{-}P)]$ (**3**) and *trans*-$[Mo(CO_2)_2(P\text{-}P)_2]$ (**4**) (P-P = $Me_2PCH_2CH_2PMe_2$ (dmpe), **3a** and **4a**; P-P = $Et_2PCH_2CH_2PEt_2$ (depe), **3b** and **4b**; P-P = $Me_2PCH_2PMe_2$ (dmpm) **3c** have been synthesized. The routes shown in eq 2 and 3 take advantage of the strength

$$\underset{\mathbf{1}}{trans\text{-}[Mo(CO_2)_2(PMe_3)_4]} \xrightarrow{\text{P-P, 20 °C, 1 h}} \underset{\mathbf{3}}{trans\text{-}[Mo(CO_2)_2(PMe_3)_2(P\text{-}P)]} + 2PMe_3 \quad (2)$$

$$\underset{\mathbf{1}}{trans\text{-}[Mo(CO_2)_2(PMe_3)_4]} \xrightarrow{\text{2P-P, 60 °C, 3 h}} \underset{\mathbf{4}}{trans\text{-}[Mo(CO_2)_2(P\text{-}P)_2]} + 4PMe_3 \quad (3)$$

of the Mo–η^2-CO_2 linkages and provide complexes **3** and **4** in essentially quantitative yield (by NMR spectroscopy). The new compounds[3] exhibit enhanced thermal stability, and in particular *complexes* **4** *can be heated in solution up to 150 °C without noticeable decomposition.*

Of the above mechanisms, pathway i can be disregarded since the ^{31}P–$^{13}CO_2$ coupling is maintained for these complexes in the fast exchange limit; in addition, no $^{13}CO_2$–$^{12}CO_2$ exchange can be detected when solutions of

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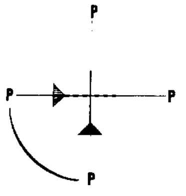
(2) (a) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (b) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661.

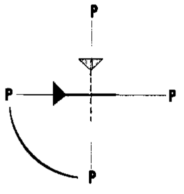
(3) All new compounds were fully characterized by microanalysis and spectroscopic data. As a representative example, data are presented for *trans*-$[Mo(CO_2)_2(PMe_3)_2(dmpm)]$ (**3c**). Anal. Calcd for $C_{13}H_{32}MoO_4P_4$: C, 33.1; H: 6.8. Found: C, 32.8; H, 6.6. IR spectrum (Nujol mull): ν_{CO_2} 1670 s, 1155 m, 1100 m cm^{-1}. $^{31}P\{^1H\}$ NMR (81 MHz, CD_3OD, −90 °C): Only one rotamer observed, AMNX system δ 22.2, 3.8 (P_A, P_M, dmpm), −1.0, −18.8 (P_N, P_X, 2PMe$_3$); J_{AM} = 15.5 Hz, J_{AN} = 16.5 Hz, J_{AX} = 157 Hz, J_{MN} = 157 Hz, J_{MX} = 25 Hz, $J_{NX} \simeq 0$. ^1H NMR (200 MHz, CD_3OD, 40 °C): δ 1.41 (d, $^2J_{HP}$ = 7.8 Hz, 18 H, 2PMe$_3$), 1.48 (d, 6 H, $^2J_{HP}$ = 8.0 Hz, 2 Me, dmpm), 1.61 (d, 6 H, $^2J_{HP}$ = 8.4 Hz, 2 Me, dmpm), 3.54 (tt, 2 H, $^2J_{HP}$ = 10.0, $^4J_{HP}$ = 1.1 Hz, PCH_2P).

the CO_2 complexes are exposed to $^{13}CO_2$. A reasonable pathway for route ii could involve the intermediacy of an η^1-CO_2 complex[4] of structure A (Scheme I), corresponding to a 16-electron species in which η^1-CO_2 acts as a Lewis acid.[5] This is a very unfavorable electronic situation[6] and, very likely, inaccessible at normal temperatures. Moreover, this mechanism implies the inequivalence of the two CO_2 ligands in compounds **2** in the high-temperature limit, in disagreement with the observation of a single resonance (triplet of doublets, $^2J(CP_1) \simeq 20$ Hz, $^2J(CP_2) \simeq 10$ Hz) in their $^{13}C\{^1H\}$ NMR spectra.[1]

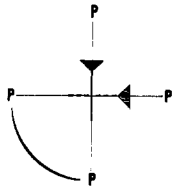
For compounds **3**, the three different rotamers B–D (and their corresponding enantiomers) can exist, and they are indeed observed in the low-temperature (−80 °C, 81 MHz) $^{31}P\{^1H\}$ NMR spectrum of **3a**. At higher temperatures, interconversion of the isomers is fast on the NMR time scale, as shown by the observation of an AA′XX′ pattern in the fast exchange limit (60 °C, 81 MHz). Since the independent rotation would involve at some stage a transition state or intermediate that would introduce an effective plane of symmetry, the observation of two different resonances for the methyl groups of the chelating diphosphine ligands in the ^1H NMR spectra of **3a** and **3c** recorded at 60 °C clearly argues against this pathway.



B

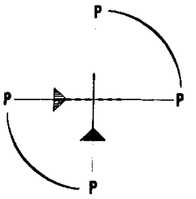


C

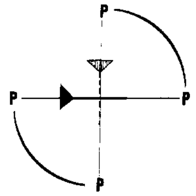


D

Similar observations with reference to compounds **4** can be used to discard the disrotatory motion (pathway v). Two rotamers, E and F, can exist for these complexes, and indeed both can be detected by ^{31}P NMR spectroscopy. Thus, the $^{31}P\{^1H\}$ NMR spectra of **4a** and **4b** show, at −20 °C, two AA′XX′ patterns assigned to the corresponding rotamers with structures E and F. At 20 °C, these sets of resonances convert into two very broad features that give rise to a broad singlet ($\Delta\nu \simeq 14$ Hz) at 110 °C (toluene) and finally transform into a sharp singlet ($\Delta\nu \simeq 3$–4 Hz) at 150 °C in mesitylene. Therefore, in the high-temperature limit, fast interconversion of rotamers E and F takes place. This is in disagreement with the disrotatory movement but is in excellent accord with the conrotatory mechanism, since the former would convert rotamer E into itself or its enantiomer (consider, for example, a 360° rotation of the CO_2 ligands, carried out in four 90° steps) while the latter interconverts rotamers E and F. At variance with the disrotatory motion, which would proceed through transition states or intermediates that possess either an effective plane of symmetry containing the MoP_4 unit or a center of inversion, the interconversion of E and F by the conrotatory mechanism does not introduce any additional elements of symmetry. Hence, two resonances are expected for the methyl protons of the diphosphine ligands of compound **4a** in the fast exchange limit, in excellent agreement with the experimental results.



E



F

In conclusion, we have convincingly demonstrated the existence of rotational isomerism in $(CO_2)_2$ adducts, *trans*-$[Mo(CO_2)_2L_xL'_{4-x}]$, and shown that the observed rotamers interconvert by a concerted motion of the CO_2 ligands in which both molecules of carbon dioxide rotate synchronously in the same direction. These experimental observations are in accord with recent theoretical calculations by Sânchez-Marcos et al. that had predicted this behavior. This study concluded[7] that the more stable conformations have the CO_2 ligands mutually perpendicular while the conformers with eclipsed CO_2 groups have much higher energies (about 70 kcal mol^{-1}). Finally, since the conrotatory motion of the CO_2 ligands does not interchange enantiomeric structures, the isolation of optically active carbon dioxide complexes of this type seems feasible. Work aimed at this purpose is currently under way in our laboratory.

Acknowledgment. We thank the Direcciôn General de Política Científica for financial support.

Supplementary Material Available: Representative variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of complexes **3a**, **3c**, and **4a** (3 pages). Ordering information is given on any current masthead page.

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[4] As pointed out by one reviewer, the exchange of the free and coordinated oxygen atoms of the CO_2 ligands does not necessarily require the intermediacy of an η^1-CO_2 complex. It should be noted, however, that the nature of the intermediate or transition state associated with this mechanism does not alter the conclusions reached with respect to its feasibility.

[5] Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *103*, 5914.

[6] Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

[7] Sânchez-Marcos, E.; Caballol, R. Trinquier, G.; Bartherlat, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 2373.

Ligand Influences on the State of Cluster Aggregation. Ligand-Dependent Formation of Cluster Complexes with $[PtRu_2]_n$ (n = 1–3) Metal Groupings

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Summary: The reaction of $Pt(COD)_2$ with $Ru(CO)_5$ at 25 °C produced the hexanuclear metal complex $[PtRu_2(CO)_9]_2$ (**1**) in 31% yield, which consists of an open cluster containing two ruthenium atoms bonded to two platinum atoms followed by two additional ruthenium atoms. Compound **1** reacted with dppe by a symmetrical cleavage of the molecule to yield $PtRu_2(CO)_8(dppe)$ (**2**). The reaction of **1** with PhC_2Ph produced the higher cluster $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$ (**3**) in 30% yield. Compound **3** consists of a Pt_3Ru_3 octahedron with three ruthenium atoms capping triangular faces. It also contains three triply bridging PhC_2Ph ligands.

In recent studies, we have demonstrated the effects of bridging sulfido ligands on promoting the agglomeration[1]

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[1] (a) Adams, R. D.; Babin, J. E.; Wolfe, T. A. *Polyhedron* **1989**, *8*, 1123. (b) Adams, R. D.; Mannig, D.; Segmüller, B. E. *Organometallics* **1983**, *2*, 149. (c) Adams, R. D.; Hor, T. S. A. *Organometallics* **1984**, *3*, 1915.

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