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Aryl(pentachlorophenyl)nickel(II) Complexes. Lack of Free Rotation about Tolyl–Nickel Bonds and Lack of "Ortho Effect" in Carbonylation

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A series of complexes of the type *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$ (where R = aryl) was prepared. Their ^1H NMR spectra indicate that both R = *o*-tolyl and *m*-tolyl groups are oriented perpendicularly to the nickel coordination plane. Reaction of carbon monoxide with these complexes gave, under mild conditions, $R(C_6Cl_5)CO$ for R = aryl groups including *o*-tolyl but not for 2-furyl and its analogues. The *o*-tolyl complex was exceptionally stable toward thermal reductive elimination in tetrachloroethylene under air. Factors affecting the relative reactivities of these complexes are discussed, based mainly on the early explanation for the so-called "ortho effect".

Introduction

Since the initial discovery of σ-bonded alkyl and aryl transition metal complexes, the criteria for their stability have evolved considerably. In organonickel chemistry, complexes of types *trans*-$X(R)Ni(PR'_3)_2$ and *trans*-$R_2Ni(PR'_3)_2$ (X = anionic ligand such as halogen; R' = alkyl or aryl) have been shown to have considerable stability when R is an ortho-substituted aryl group.[1-3] This so-called "ortho effect"[2] has been accounted for originally by Chatt and Shaw[1] by a combination of steric and electronic factors, but the detailed evidence seems to be quite scanty, especially for those nickel complexes with an ortho-unsubstituted aryl group.[3]

The pentachlorophenyl group is of interest in organonickel chemistry not only because of the great overall stability of pentachlorophenyl–nickel bond but also because of its ability to stabilize the nickel–carbon bond trans to the group. In fact, MacKinnon and West have shown that the pentachlorophenyl–nickel bond in *trans*-$Cl(C_6Cl_5)Ni(PPh_3)_2$ (X = halogen) is thermally stable up to 240 °C, although above 160 °C at 10^{-2} mm pressure the triphenylphosphine sublimes from the complexes,[4] and Rausch and Tibbetts have reported that, in spite of the repeated failures by Chatt and Shaw to isolate methylnickel complexes of the type *trans*-$X(CH_3)Ni(PR_3)_2$ (X = halogen),[1] the pentachlorophenyl analogue ($X = C_6Cl_5$) is stable enough to be isolated and characterized.[5] In contrast, some facile decompositions of pentachlorophenylnickel complexes have been reported recently. We have observed previously the formation of pentachlorobenzene as a by-product in the reaction of *trans*-$Cl(C_6Cl_5)Ni(PPhMe_2)_2$, **1**, and crotylmagnesium chloride, which probably resulted from the β-hydrogen elimination of an intermediate followed by the reductive elimination of the resulting nickel hydride.[6] Coronas et al. have also reported the formation of pentachlorobenzene by the reaction of *trans*-$Cl(C_6Cl_5)Ni(PPh_3)_2$ and an excess of KCN[7] and the formation of hexachlorobenzene by the reaction of $Cl(C_6Cl_5)Ni(dpe)$ and molecular chlorine,[8] but they have not presented any explanation for these reactions.

In connection with our current research program on pentachlorophenylnickel complexes,[6,9] we have now studied the preparation and the spectral and chemical properties of a series of nickel complexes of the type *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$, **2**, with an aim to obtain information about the steric and/or electronic effects of the aryl (R) group. We have also obtained additional examples of the facile decomposition of pentachlorophenylnickel complexes.

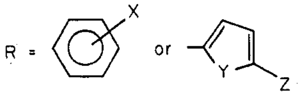
Experimental Section

The starting material, *trans*-$Cl(C_6Cl_5)Ni(PPhMe_2)_2$, **1**, was prepared as described previously.[9] IR spectra were recorded on a Hitachi 225 spectrophotometer or on a JASCO Model IR-G spectrophotometer over the range 4000–500 cm^{-1} and on a Hitachi EPI-L spectrophotometer over the range 700–200 cm^{-1} using Nujol mulls. ^1H NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to TMS as an internal standard. Electronic spectra were measured on a Hitachi two-wavelength double-beam spectrophotometer, Model 356. Mass spectra were measured on a Hitachi mass spectrometer, Model RMU-6E.

Preparations of *trans*-Aryl(pentachlorophenyl)bis(dimethylphenylphosphine)nickel(II) Complexes, *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$, 2 [R = (a) C_6H_5, (b) *o*-$CH_3C_6H_4$, (c), *m*-$CH_3C_6H_4$, (d) *p*-$CH_3C_6H_4$, (e) *p*-ClC_6H_4, (f) *p*-$CH_3OC_6H_4$, (g) 2-furyl, (h) 5-methyl-2-furyl, (i) 2-thienyl]. These complexes **2a–i** were prepared essentially by the same procedures, so only representative examples are described. Percentage yields, melting points, and analytical data as well as ^1H NMR and electronic spectral data are summarized in Table I.

An ethereal solution of phenyllithium was prepared from bromobenzene (0.43 ml, 4.1 mmol) and a 15% *n*-pentane solution of *n*-butyllithium (2.48 ml, 4.0 mmol) in 10 ml of dry diethyl ether. The two reagents were mixed at 0 °C under a nitrogen atmosphere and the solution was stirred at room temperature for 1 h. The phenyllithium solution was cooled on an ice bath and a benzene (10 ml) solution of **1** (0.620 g, 1.0 mmol) was added. The mixture was stirred

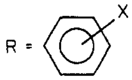
Table I. Analytical and Spectral[a] Data for *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$



Complexes		Yield,		% C		% H			
No.	X or Y, Z	%	Mp, °C	Calcd	Found	Calcd	Found	τ(P–CH_3), ppm	λ_{max},[b] nm
2a	H	70	152-153	50.84	50.66	4.11	4.08	8.78 t	(360)
2b	CH_3-*o*	48	146-148	51.57	51.37	4.33	4.33	8.80 t, 8.75 t[c]	(370)
2c	CH_3-*m*	52	131-132	51.57	51.51	4.33	4.40	8.83 t, 8.77 t[c]	(363)
2d	CH_3-*p*	74	169-170	51.57	51.48	4.33	4.25	8.81 t[c]	(365)
2e	Cl-*p*	69	193 dec	48.33	48.26	3.77	3.74	8.78 t	(355)
2f	OCH_3-*p*	67	160-161	50.37	50.40	4.23	4.18	8.81 t[d]	(365)
2g	O, H	58	147-148	47.94	47.84	3.87	3.95	8.73 t	375
2h	O, CH_3	81	123-124	48.74	48.71	4.09	4.09	8.88 t[c]	
2i	S, H	60	143-144	46.79	46.77	3.78	3.82	8.72 t	382

[a] CH_2Cl_2 solution. [b] The spectra exhibited very intense bands in the ultraviolet region tailing toward the visible region, and those bands in parentheses are of shoulder character. The total ϵ values were less than 10^3. [c] τ(C–CH_3) values were 7.96 s, 8.02 s, 7.86 s, and 7.87 s for **2b**, **2c**, **2d**, and **2h**, respectively. [d] The τ(O–CH_3) value was 6.37 s.

Table II. Analytical and Spectral Data for $R(C_6Cl_5)CO$



Compounds		Yield,[a]		% C		% H		ν(C=O),[b]	$\tau(CH_3)$,[c]
No.	X	%	Mp, °C	Calcd	Found	Calcd	Found	cm^{-1}	ppm
3a	H	26	150-151	44.05	44.15	1.42	1.29	1676	
3b	CH_3-*o*	34	163-164	45.63	45.37	1.91	1.65	1685	7.30 s
3c	CH_3-*m*	37	154-155	45.63	45.61	1.91	1.81	1650	7.61 s
3d	CH_3-*p*	31	164-165	45.63	45.54	1.91	1.75	1638	7.56 s
3e	Cl-*p*	27	202-203	40.15	39.88	1.04	0.94	1660	
3f	OCH_3-*p*	29	190-192	43.74	43.67	1.84	1.72	1638	6.11 s

[a] After purification. [b] Nujol mull. [c] CH_2Cl_2 solution.

for 1 h at room temperature and then warmed to gentle reflux. The solvent was removed under a reduced pressure and the residue was extracted with hot ethanol. The extract was filtered in air while hot, and the filtrate was cooled in a refrigerator to give yellow crystals of **2a**.

An ethereal solution of *o*-tolyllithium was prepared from *o*-bromotoluene and a 15% *n*-pentane solution of *n*-butyllithium in diethyl ether in the same manner as described above. The reaction with **1** was also conducted using the same procedure as above. The resulting residue, after removal of the solvent, was extracted with three 1-ml portions of dichloromethane. The extracts were chromatographed on a 10-cm column of Florisil utilizing dichloromethane as the eluent. The yellow-brown fraction was collected and the solvent was removed under a reduced pressure. The residue was recrystallized from ethanol to give yellow-brown crystals of **2b**.

An ethereal solution of 2-furyllithium was prepared from furan (0.15 ml, 2.1 mmol) and a 15% *n*-pentane solution of *n*-butyllithium (1.24 ml, 2.0 mmol) in 10 ml of dry diethyl ether and was treated with a benzene (10 ml) solution of **1** (0.620 g, 1.0 mmol) in the same manner as used for **2a** to give orange-yellow crystals of **2g**.

The preparative procedures for complexes **2c–f** were similar to that employed for **2a**, and those for complexes **2h** and **2i** were similar to that employed for **2g**, except that the resulting residue, after removal of the reaction solvents, was extracted with acetone in the cases of **2d** and **2e**.

The complexes **2a–i** thus prepared are yellow to orange crystalline solids and indefinitely stable in the solid state under air. They are soluble in dichloromethane, benzene, tetrachloroethylene, and hot acetone. The IR spectra of all the complexes show characteristic bands due to pentachlorophenyl group near 1320 (s), 1290 (s), 1230 (m), 1100 (w), and 630 (m) cm^{-1} and those due to dimethylphenylphosphine at 940 (m), 910 (s), 490 (s), and 430 (m) cm^{-1}.

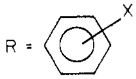
Reactions of *trans*-Aryl(pentachlorophenyl)bis(dimethylphenylphosphine)nickel(II) Complexes, 2a–i with Carbon Monoxide. A suspension of complex **2d** (0.200 g, 0.30 mmol) in 20 ml of acetone was stirred at room temperature for 12 h under carbon monoxide at atmospheric pressure to give a light yellow solution. The carbon monoxide atmosphere was replaced by air and the solution was stirred at room temperature again for 12 h to oxidize the nickel(0) species expected to be formed.[10] The solvent was then evaporated under a reduced pressure, and the residue was treated with diethyl ether–water. The ether layer was separated and then evaporated to leave a white solid, which was recrystallized from ethanol to give colorless crystals of *p*-tolyl pentachlorophenyl ketone, *p*-$CH_3C_6H_4(C_6Cl_5)CO$, **3d**.

Complexes **2a–c**, **2e**, and **2f** were treated similarly with carbon monoxide to give the corresponding aryl pentachlorophenyl ketones, $R(C_6Cl_5)CO$, **3a–c**, **3e**, and **3f**, respectively, as colorless crystals, but the complexes **2g–i** were recovered unchanged even after a 48-h reaction period. Percentage yields, melting points, and analytical data as well as IR and ^1H NMR spectral data are summarized in Table II. The mass spectra were also measured for these ketones and the results were consistent with the proposed formulations.

Reactions of *trans*-Aryl(pentachlorophenyl)bis(dimethylphenylphosphine)nickel(II) Complexes, 2a–f, in Tetrachloroethylene under Air. A solution of complex **2d** (0.300 g, 0.45 mmol) in 6 ml of tetrachloroethylene was heated on boiling water bath for 12 h under air. The solvent was removed under a reduced pressure and the residue was extracted with 1 ml of dichloromethane. The extract was chromatographed on a 10-cm column of Florisil utilizing dichloromethane as the eluent. A colorless to light yellow fraction and a yellow-brown fraction were collected separately. The solvent was removed and each residue was recrystallized from ethanol to give colorless crystals of *p*-$CH_3C_6H_4C_6Cl_5$, **4d**, from the former fraction and orange-brown crystals of *trans*-$Cl(CCl_2{=}CCl)Ni(PPhMe_2)_2$, **5** (mp 123 °C), from the latter fraction. Anal. Calcd for **5**, $NiC_{18}H_{22}P_2Cl_4$: C, 43.17; H, 4.43. Found: C, 42.94; H, 4.43. The ^1H NMR spectrum ($CCl_2{=}CCl_2$ solution) showed the P–CH_3 resonances at τ 8.39 (t) and 8.45 (t) with J_P = 8 Hz, respectively.

Complexes **2a–c**, **2e**, and **2f** were treated similarly in tetrachloroethylene to give the corresponding biphenyl, RC_6Cl_5, **4a**, **4c**, **4e**, and **4f**, and complex **5**, except for complex **2b**, which was recovered unchanged even after heating for 48 h.

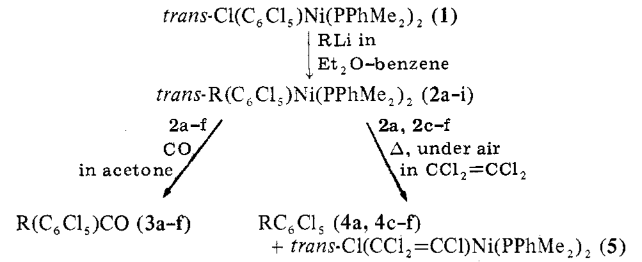
Table III. Analytical and Spectral Data for RC_6Cl_5



Compounds		Yield,[a] %	Mp, °C	% C		% H		$\tau(CH_3)$,[b] ppm
No.	X			Calcd	Found	Calcd	Found	
4a	H	27 (31)	122-124	44.15	44.05	1.54	1.54	
4c	CH_3-*m*	34 (28)	115-116	45.86	45.63	2.07	1.89	7.64 s
4d	CH_3-*p*	73 (35)	184-185	45.86	45.69	2.07	1.91	7.59 s
4e	Cl-*p*	21 (30)	158-160	39.94	39.68	1.12	1.14	
4f	OCH_3-*p*	63 (32)	120-121	43.80	43.81	1.98	1.87	6.21 s

[a] Yield of complex **5** is shown in parentheses. [b] In $CCl_2{=}CCl_2$ solution.

Scheme I



R: a, C_6H_5; b, *o*-$CH_3C_6H_4$; c, *m*-$CH_3C_6H_4$; d, *p*-$CH_3C_6H_4$; e, *p*-ClC_6H_4; f, *p*-$CH_3OC_6H_4$; g, 2-furyl; h, 5-methyl-2-furyl; i, 2-thienyl

Percentage yields, melting points, and analytical data as well as ^{1}H NMR spectral data for RC_6Cl_5 are summarized in Table III. The mass spectra were also measured and the results were consistent with the proposed formulations. Percentage yields for complex **5** are also shown in Table III.

Determination of the Relative Rates of Reductive Elimination. A solution of two complexes **2a** and **2d** (0.30 mmol, respectively) in 10 ml of tetrachloroethylene was heated on a boiling water bath for 5 min and then was stirred at room temperature for 12 h under carbon monoxide at atmospheric pressure to decompose the unreacted starting complexes to $R(C_6Cl_5)CO$. The resultant solution was analyzed by gas chromatography on a 1-m column of SE 30 at 240 °C using a Hitachi gas chromatograph, Model 164, and nitrogen as the carrier gas. Another solution containing three complexes **2d–f** was also treated in a similar manner as above. The relative amounts of formation for **4a** and **4d–f** were 1.09, 1.50, 1.00, and 1.66, respectively. The following respective retention times had been observed separately: **4a**, 235 s; **4d**, 295 s; **4e**, 379 s; **4f**, 442 s; **3a**, 393 s; **3d**, 536 s; **3e**, 602 s; **3f**, 826 s.

Results and Discussion

The preparation and reactions of complexes **2a–i** are summarized in Scheme I. Although the chlorine atom bonded to nickel in *trans*-$Cl(C_6Cl_5)Ni(PPh_2Me)_2$ has been reported to be very inert to σ-aryl substitution,[5,11] complex **1**, which has less bulky tertiary phosphines, reacts with a variety of aryllithiums in diethyl ether–benzene to yield complexes of type **2**, which are stable under normal conditions. The ^{1}H NMR spectra of these complexes in the region of phosphine methyl protons were examined to establish the configuration of the complexes; the data are shown in Table I. The single 1:2:1 triplet pattern observed for **2a** is typical of a trans square-planar configuration,[12] and the double 1:2:1 triplet pattern observed for **2b** is indicative that this complex has a trans configuration with the *o*-tolyl group oriented perpendicularly to the nickel coordination plane, in agreement with the observation by Moss and Shaw[13] for several complexes of type *trans*-X(*o*-tol)$Ni(PPhMe_2)_2$. Of interest is the observation of analogous double triplet pattern for complex **2c**, indicating that the *m*-tolyl group bonded to nickel is also oriented perpendicularly to the nickel coordination plane in disagreement with the early expectation.[1,2] Due to the symmetry of the aryl group in **2a** and **2d–f**, it is not possible to elucidate about the orientation of the aryl group, but the qualitative similarity of their phosphine methyl chemical shift values and electronic spectra (vide infra) to those of **2b** and **2c** seems to indicate their perpendicular orientation. The observation of single triplet patterns in the ^{1}H NMR spectra of **2g–i** is probably due to the presence of rapid free rotation about the nickel–2-furyl, –5-methyl-2-furyl, and –2-thienyl bonds. These spectra did not change appreciably even at –80 °C in dichloromethane.

One of the early explanations for the so-called ortho effect[2] is that the presence of ortho substituents prevents free rotation of the aryl group and compels it to interact with the nickel d_{xy} orbital, thereby increasing ΔE, the value of the energy difference between the highest filled (d_{xy}) and the lowest unfilled (σ^*, predominantly $d_{x^2-y^2}$) orbitals. This explanation implies an assumption that ortho-unsubstituted aryl groups would rotate about the nickel–aryl bond and thus interact at various times with the metal d_{xz} or d_{yz} and d_{xy} orbitals. Table I includes such ΔE values in terms of λ_{max} observed for complexes **2a–i** in the electronic spectra[14] and shows that the energy for *o*-tolyl complex **2b** is rather the lowest among the three tolylnickel complexes **2b–d**, although the energy differences are quite small. Additional conclusions drawn from these electronic spectra data include the fact that the para-substituted phenyl groups in **2d–f**, as well as **2a**, are also oriented perpendicularly, if the ΔE value would vary significantly to lower energy on their rotations.

From these ^{1}H NMR and electronic spectral results we propose that there are enough nonbonding steric repulsions even between the two ortho protons in the phenyl group and the dimethylphenylphosphine ligands to hinder the free rotation. We have obtained analogous ^{1}H NMR and electronic spectral data for a series of isoelectronic complexes, *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]^+ClO_4^-$, where L is a substituted pyridine.[15]

The alternative explanation for the ortho effect is based on a kinetic reason. Due to the lack of free rotation about the nickel–aryl bond, the ortho substituent remains in a position where it can most effectively hinder the attack of reagents at the metal atom,[1,2] although some ambiguities still remain for the attack from the opposite site of a mono ortho substituent. Nevertheless, this kinetic explanation seems to be more plausible in relation to the facts collected by Fahey that experimentally determined carbon–nickel bond distances were of normal σ-bond lengths,[16] that an unsubstituted phenylnickel complex, $Cl(C_6H_5)Ni(P(n\text{-}Bu)_3)_2$, could be recovered in 90% yield after 12 h at 130–150 °C in decalin solution under nitrogen,[17] and that x-ray photoelectron binding energies in *trans*-$X(Y)Ni(PEt_3)_2$ (X, Y = alkyl, alkenyl, aryl, halogens) could be correlated with partial ionic character of each nickel–carbon σ bond.[18] To test such a steric effect of an ortho substituent toward incoming reagents, complexes **2a–i** were treated first with carbon monoxide, since its insertion into a transition metal–carbon bond has widely been known.[19]

Unexpectedly, the *o*-tolylnickel complex **2b** underwent facile reaction in a solution of acetone with carbon monoxide at 1 atm and room temperature to yield a ketone **3b**. Complexes **2a** and **2c–f** reacted in a similar manner to yield corresponding ketones, while complexes **2g–i** were recovered unreacted even after a prolonged reaction period. Attempts to isolate the aroylnickel intermediate expected to be formed during these reactions have been unsuccessful, although such studies are still under investigation.

We next studied the air stability of complexes **2a–i**. While this work was in progress, Morrell and Kochi have shown that molecular oxygen enhances the reductive elimination of aryl(methyl)nickel(II) species by a mechanism in which the reaction is promoted by prior electron transfer from the complex to the oxygen.[20] We also observed an analogous effect of molecular oxygen for some of our complexes. Complex **2d**, for example, is stable in tetrachloroethylene at 100 °C in an evacuated glass tube, but under air it reacts to give the coupling product *p*-$CH_3C_6H_4C_6Cl_5$, **4d**, and *trans*-$Cl(CCl_2{=}CCl)Ni(PPhMe_2)_2$, **5**. The ^1H NMR spectrum of the reaction mixture in the carbon methyl and phosphine methyl proton regions showed the absence of any other reaction products. Complexes **2a**, **2c**, **2e**, and **2f** reacted in a similar manner, while the *o*-tolylnickel complex **2b** was recovered unchanged even after a prolonged heating under the same conditions. Complexes **2g–i** are less reactive than **2d**, although the ^1H NMR spectrum of a solution of **2h** heated for a much longer period (48 h) showed the presence of several reaction products; we have not yet succeeded in their separation. Due to the heterogeneous nature of these reactions, only the relative reactivities were studied by a conventional method for complexes containing a para-substituted phenyl group, **2a** and **2d–f**. Although no drastic difference in reactivity is observed (see Experimental Section), the observed trend of **2f** (OCH_3) > **2d** (CH_3) > **2a** (H) $\gtrsim$ **2e** (Cl) is consistent with the mechanism by Morrell and Kochi.[20]

In our present work the unique stability of the *o*-tolylnickel complex **2b** toward thermal reductive elimination under air may be attributed to a kinetic ortho effect, while its facile reactivity with carbon monoxide is astonishing. A mechanism containing initial dissociation of a phosphine to form a tricoordinated intermediate may be precluded from the fact that this complex in solution is considerably stable even at 100 °C under air.[21] Since the sizes of molecular oxygen and carbon monoxide are almost comparable, the lack of an ortho effect in the carbonylation is probably due to the difference in the interaction modes between these two reagents at the intermediate or transition state. Our results are tentatively explained by assuming that carbon monoxide interacts with nickel in a *head-on* manner, while molecular oxygen reacts in a *side-on* manner, the latter mode being affected more by steric repulsion. The different reactivities between complexes **2a–f** and **2g–i** toward carbon monoxide may be attributed to an electronic effect, and the lack of reactivity of complexes **2g–i** is consistent with a mechanism in which carbon monoxide also acts as an electrophilic reagent.

Hidai et al.[22] measured the thermal decomposition point under nitrogen for several arylnickel complexes of the type *trans*-$Cl(R)Ni(PPh_3)_2$. The effect of substituent in the aryl group on the stability is almost consistent with that observed for our complexes **2a–f** under air. Without any kinetic data, our tentative explanation is that their thermal decomposition may contain a bimolecular reaction path to give a biaryl,[23] which is affected by the kinetic ortho effect.

Acknowledgment. We acknowledge very helpful discussions with Professor M. D. Rausch.

Registry No. **1**, 15526-04-2; **2a**, 60949-79-3; **2b**, 60949-80-6; **2c**, 60949-81-7; **2d**, 60949-82-8; **2e**, 60949-83-9; **2f**, 60949-84-0; **2g**, 60949-85-1; **2h**, 60949-86-2; **2i**, 60949-87-3; **3a**, 25201-62-1; **3b**, 60921-32-6; **3c**, 60921-33-7; **3d**, 60921-34-8; **3e**, 60921-35-9; **3f**, 60921-36-0; **4a**, 25429-29-2; **4c**, 60921-37-1; **4d**, 37853-49-9; **4e**, 41411-63-6; **4f**, 60921-38-2; **5**, 60949-88-4.

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