close to the expected tetrahedral value (range 104.5–109.8°), the P(1)–Ni–P(2) angle is severely enlarged, at 117.9 (2)°. The corresponding P(1)–Th–P(2) angle is still acute [83.7 (1)°]; in fact, this value represents a decrease over the P–Th–P angle is **1**.[8] The closest contact between a methyl carbon on the Cp* ring and a phenyl carbon is 3.27 (2) Å compared to the closest methyl carbon contact between Cp* rings of 3.28 (2) Å.

If one considers the Th-phosphido bonding to be principally ionic in character, the P–Th–P angle may vary over a considerable range with only an insignificant cost in energy. Indeed the H–Th–H angle in $[\mathrm{ThCp}^*{}_2\mathrm{H}(\mu\text{-H})]_2$ is only 58 (1)°.[20] For the present complex if one imagines a structure in which the $\mathrm{ThP_2Ni}$ core is planar, the metal–phosphorus distances remain fixed at the observed values and the Th–Ni distance is increased to 3.7 Å, the calculated internal angles would be P–Th–P = 74.9°, Th–P–Ni = 91°, and P–Ni–P = 103.2°. Since the P–Th–P angle is less than the observed angle we would expect C–C contacts between Cp* and the phenyl rings to increase slightly for the hypothetical model. We conclude, therefore, that there are no structural constraints in the present structure which dictate a short Th–Ni distance, other than a direct metal–metal interaction. Nonetheless, the extent of this interaction obviously remains an open question. The problem is currently being pursued at Los Alamos via theoretical calculations, attempts to oxidize or reduce the complex, spectroscopic and magnetic measurements, and attempts to prepare a monobridged Th–Ni phosphido species.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy and in part under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy.

Supplementary Material Available: ORTEP projection and tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors for $\mathrm{Cp}^*{}_2\mathrm{Th(PPh_2)_2Ni(CO)_2}$ (4 pages). Ordering information is given on any current masthead page.

Aldol Reactions of Transition-Metal Carbene Complexes

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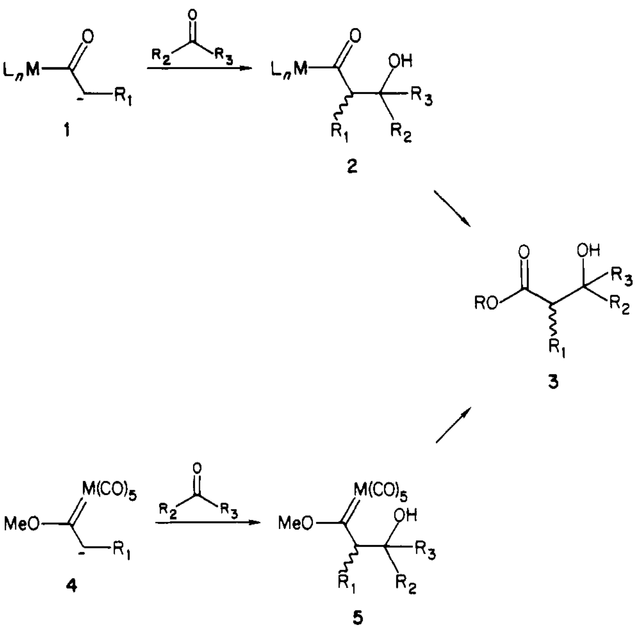
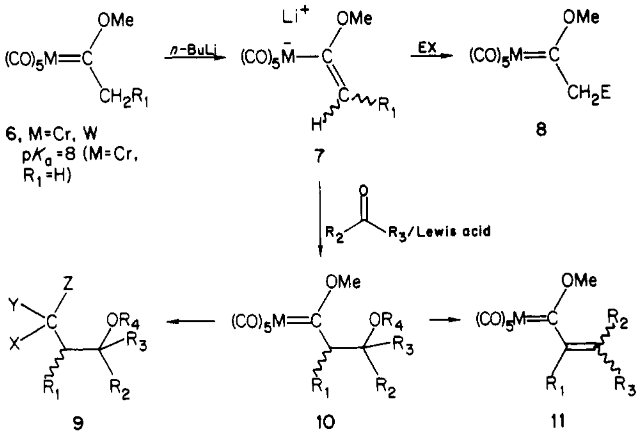
Received August 16, 1984

The enolate anions of metal acyl complexes are known to condense with carbonyl compounds to give β-hydroxy acyl complexes of the type **2**.[1,2] These complexes can serve as synthons for esters in the aldol reaction since oxidative cleavage of the metal gives rise to β-hydroxy esters. We report here the first examples of the reactions of "enolate" anions of transition-metal carbene complexes[3] with carbonyl compounds to give aldol products of the type **5** and an initial look at the stereoselectivity of these condensations and at methods for the removal of the metal from these complexes (Scheme I).

Scheme I



Scheme II



It is well established[3] that heteroatom-stabilized carbene complexes activate α-hydrogens and give anions of the type **4** upon deprotonation. The methyl group in complex **6a** (R_1 = H, M = Cr) displays tremendous thermodynamic acidity[4] (pKa = 8) and as might be anticipated the conjugate base of complex **6a** was found to be relatively unreactive with all but the most reactive of electrophiles.[3f,g,5,6] The anions **7** do not react with ketones or most aldehydes. Reactions have only been reported with three nonenolizable aldehydes from which the α,β-unsaturated complexes **11** were isolated in 20–50% yield.[6] The aldol complexes **10** were never observed from these reactions, which was attributed to an intramolecular prototropic shift which is rapid due to the greater acidity of protons α to the carbene carbon in **10** (R_4 = Li) than the proton of a hydroxyl group (Scheme II).

The inherent unreactivity of the anion **7** can be overcome by preactivating the carbonyl compound with a Lewis acid (Table I), which gives rise to the β-hydroxy carbene complex **10** (R_4 = H) as the exclusive product, a result that can be attributed to the much greater bond strengths of the boron and titanium bonds to

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(1) (a) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441–443 and references therein. (b) Davies, S. G.; Seeman, J. I. *Tetrahedron Lett* **1984**, 1845–1848 and references therein. (c) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250–5252.

(2) Aktoga, N.; Felkin, H.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1303–1304.

(3) For reviews of the chemistry of these complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron*, in press. (c) Dötz, K. H. *Pure Appl. Chem.* **1983**, 1689. (d) Casey, C. P. *React. Intermed.* **1981**, 2. (e) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (f) Casey, C. P. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1. (g) Casey, C. P. *Organomet. Chem. Libr.* **1976**, *1*, 397–421.

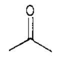
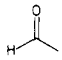
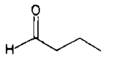
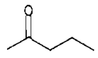
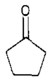
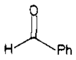
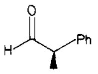
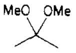
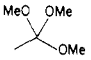
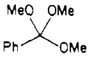
(4) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

(5) (a) Casey, C. P.; Brunsvold, W. R.; Scheck, D. M. *Inorg. Chem.* **1977**, *16*, 3059. (b) Casey, C. P.; Anderson, R. L. *J. Oganomet. Chem.* **1974**, *73*, C28.

(6) (a) Casey, C. P. *CHEMTECH* **1979**, 378. (b) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345. (c) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947. (d) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175. (e) Brunsvold, W. R. Ph.D. Thesis, University of Wisconsin, Madison, 1976. (f) Anderson, R. L. Ph.D. Thesis, University of Wisconsin, Madison, 1974.

0002-7863/85/1507-0503$01.50/0

Table I. Lewis Acid Mediated Aldol Reactions of Chromium and Tungsten Carbene Complexes

carbonyl/ acetal	complex 6			Lewis acid (equiv)	method[a]	aldols 10 & 11				% yield[b] of 10	% recovery of 6
		M	R_1				R_2,	R_3,	R_4		
	6a	Cr	H	$BF_3 \cdot Et_2O$ (20)	B	10a	CH_3	CH_3	Ac[c]	76	
				$BF_3 \cdot Et_2O$ (10)	B	10b	CH_3	CH_3	H	70	10
				$BF_3 \cdot Et_2O$ (5)	B		CH_3	CH_3	H	54	22
				$BF_3 \cdot Et_2O$ (2)	B		CH_3	CH_3	H	44	21
				$TiCl_4$ (10)	A		CH_3	CH_3	H	41	
				$TiCl_4$ (1.2)	A		CH_3	CH_3	H	27	
				Et_2AlCl (1.2)	A[d]		CH_3	CH_3	H	25	16
				$SnCl_4$ (1.2)	A		CH_3	CH_3	H	5	81
	6b	W	H	$BF_3 \cdot Et_2O$ (10)	B[e]	10c	CH_3	CH_3	H	55	16
	6a	Cr	H	$BF_3 \cdot Et_2O$ (10)	B	10d	CH_3	H	H	34	43
				$TiCl_4$ (10)	C		CH_3	H	H	77	
	6a	Cr	H	$BF_3 \cdot Et_2O$ (20)	B	10e	n-Pr	H	H	47	
				$TiCl_4$ (10)	C		n-Pr	H	H	67	
				$TiCl_4$ (2)	C		n-Pr	H	H	59	
	6a	Cr	H	$BF_3 \cdot Et_2O$ (20)	B	10f	n-Pr	CH_3	H	58	17
	6a	Cr	H	$BF_3 \cdot Et_2O$ (10)	B	10g	$-(CH_2)_4-$		H	56	
	6a	Cr	H	$BF_3 \cdot Et_2O$ (10)	B	10h	Ph	H	H	81	
	6c	Cr	CH_3	$BF_3 \cdot Et_2O$ (20)	B	10i	Ph	H	H	60[f]	
				$TiCl_4$ (2)	C		Ph	H	H	55[g]	24
	6a	Cr	H	$TiCl_4$ (2)	C	10j	CH(Me)Ph	H	H	59[h]	
	6a	Cr	H	$TiCl_4$ (10)	A	10k	CH_3	CH_3	CH_3	53	12
	6a	Cr	H	$TiCl_4$ (10)	A[i]	11l	CH_3	OCH_3	CH_3	71[j,k]	
	6a	Cr	H	$TiCl_4$ (10)	A[i]	11m	Ph	OCH_3	CH_3	65[j,l]	

[a] Method A: The anion of 6 (0.4 mmol) was generated in 15 mL of ether at −78 °C with 1 equiv of n-BuLi (10 min) and added to a solution of a 1:1 Lewis acid/carbonyl complex in 25 mL of CH_2Cl_2 at −78 °C followed by hydrolysis with a pH 7 buffer after 10–20 min. Method B: Same as method A except the Lewis acid/carbonyl complex was generated in ether at 0 °C and after addition of the anion of 6 the mixture was warmed to 25 °C for 20–60 min before hydrolysis. Method C: Same as method A except the reaction time is 1 h. [b] Yields of purified material isolated by flash chromatography on silica gel in air. [c] Reaction was quenched with excess acetic anhydride prior to hydrolysis. [d] Lewis acid/carbonyl complex formed at −78 °C and warmed to 25 °C prior to reaction. [e] Initial reaction temperature was −40 °C instead of 0 °C. [f] Ratio of anti to syn isomers is 1.0/1.8. [g] Ratio of anti/syn isomers is 6.0/1.0. [h] Ratio of syn to anti isomers is 8/1. [i] Reaction temperatures brought from −78 to 0 °C before hydrolysis. [j] Yield of elimination product 11; a different reaction product (presumably 10) is observable by TLC prior to concentration of the crude reaction mixture. [k] ≥97% E isomer. [l] 8:1 mixture of E and Z isomers.

oxygen vs. that for lithium to oxygen. The crossed aldol product **10b** can be obtained from the complex **6a**[7a] and acetone in 70% yield when the anion **7** is added to 10 equiv of a 1:1 complex of acetone and boron trifluoride etherate in ether at 0 °C.[7b,8] It was somewhat surprising that the corresponding reaction of the tungsten complex **6b** gave the aldol complex **10c**, since it has been suggested that the "enolate" anion of the tungsten complex **6b** is unstable with respect to elimination of lithium methoxide.[9,10]

The best results for ketones are obtained with boron trifluoride etherate, whereas titanium tetrachloride is the superior Lewis acid for aldehydes. In the reaction of **6a** with acetaldehyde the yield of **10a** increases from 34% to 77% upon changing from boron trifluoride etherate to titanium tetrachloride. More importantly the amount of the excess Lewis acid can be substantially reduced. The yield of **10e** drops by only 8% when the amount of excess titanium tetrachloride/aldehyde complex is reduced from 10 to 2 equiv. The preactivation of acetals and ortho esters with titanium tetrachloride[11] generates electrophiles[12] that are successful in giving condensation products **10k**, **11l**, and **11m** with the anion **7**.

The ethylchromium complex **6c** is diastereoselective in its condensation with benzaldehyde giving a 6.0/1.0 mixture in favor of the anti isomer **10i**[13] (Scheme III). The analogous condensations of both the enolate anions of metal acyls (**1**, $R_1 = CH_3$)[1b,14] and the ester enolate of methyl propionate[15] occur without any significant diasteroselectivity. The 6.0/1.0 ratio does not nec-

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(7) (a) The methylmethoxycarbene complex **6a** can be prepared in 60–70% yield in 10 g lots by using a slight modification of the following published procedure: Senoff, C. V.; Lam, G. T.; Malkiewich, C. D. *Inorg. Synth.* **1978**, *17*, 95. (b) These reactions were carried out with the procedures described in the footnotes of Table I and under an inert atmosphere with solvents that were not degassed. No significant change in the mass balance was observed when rigorously degassed solvents were used.

(8) The mass balance for these reactions is usually quite good and therefore carbyne complex formation is not a serious side reaction: Fischer, E. O.; Kleine, W.; Kreis, G.; Kreissl, F. R. *Chem. Ber.* **1978**, *111*, 3542.

(9) Levisalles, J.; Rudler, H.; Jeannin, Y.; Dahan, F. *J. Organomet. Chem.* **1979**, *178*, C8.

(10) Precaution was taken to run the reaction of the tungsten complex **6b** at a lower temperature (−40 °C).

(11) Mukaiyama, T. *Org. React.* (*N.Y.*) **1982**, *28*, 203–331.

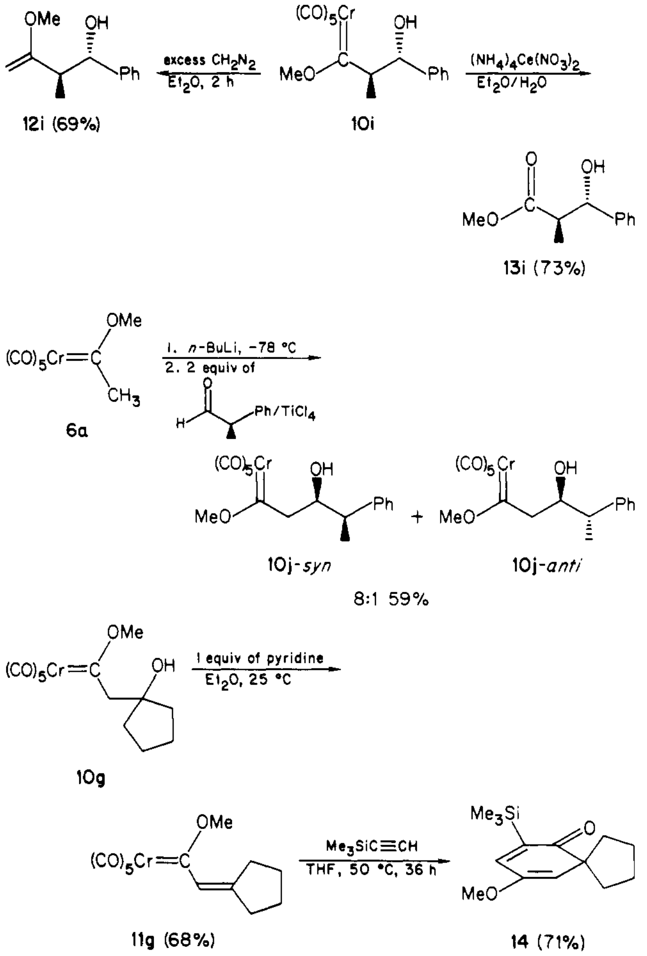
(12) (a) The reactions of the anion of **6b** with enol ethers in the presence of trifluoroacetic acid have been reported[12b] to occur via an ene reaction; however, on the basis of the experimental evidence, these reactions can also be interpreted as occurring via carbonium ion intermediates. (b) Rudler-Chauvin, M.; Rudler, H. *J. Organomet. Chem.* **1981**, *212*, 203–210.

(13) The stereochemistry of these complexes was confirmed by oxidative conversion to the known methyl esters (see supplementary material).

(14) The reactions of the enolates of cyclic metal acyls are stereoselective with some aldehydes.[1c] High diastereoselectivity with anions such as **1** (R_1 = H) have been observed with respect to a chiral metal center.[1]

(15) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–1081.

Scheme III



essarily represent a limit to the diastereoselectivity of this particular reaction, since we have not yet established whether or not there is selective formation of the "enolate" anion **7** ($R_1 = CH_3$). The anion generated from the chromium complex **6c** and *n*-butyllithium at -78 °C in ether can be precipitated with bis(triphenylphosphine)iminium chloride to give a 2.4/1.0 mixture of the isomeric salts as determined by ^{1}H NMR at ambient temperatures.[16] We are currently investigating the use of other bases and attempting to directly observe the lithium "enolates". The condensation of the methyl complex **6a** with 2-phenylpropanal gives predominantly the Cram-rule product[17] (**10j**-*syn*/**10j**-*anti*, 8:1)[13] with a higher selectivity than that observed for the reaction of the ester enolate of methyl acetate with this aldehyde.[17] The selectivity can be predicted by the model presented by Heathcock on the basis of the steric bulk of the chromium pentacarbonyl group.[17]

The β-hydroxy carbene complexes of the type **10** have considerable synthetic value since as indicated in Scheme II they could either be dehydrated to give the α,β-unsaturated complexes of the type **11**, which are intermediates of established synthetic value,[18] or the metal may be removed in a number of ways to give functionalized alcohols (such as **12i**) by employing known reactions of group 6 carbene complexes.[3,18f] For example, the purified anti isomer of **10i** can be oxidatively cleaved with cerium(IV) to give the β-hydroxy ester **13i**, and despite the acidity of the α-proton of **10i** the oxidation occurred without epimerization to the extent that the ester **13i** was found to be greater than 99.4% diastereomerically pure as determined by capillary GC. The metal can be removed from **10i** in a carbon homologation reaction with excess diazomethane to give the interesting enol ether **12i**, which is diastereomerically pure within the limits of detection by high-field ^{1}H NMR (ca. 3%).[19,18f] A dehydration of β-hydroxy complex **10g** can be effected with pyridine[20] to give a 68% yield of the exocyclic alkenyl complex **11g**, which was found to react with (trimethylsilyl)acetylene to give the spirocyclic dienone **14** in 71% yield.[18c] It is envisioned for more complex systems that this reaction will allow for the stereoselective introduction of a spirocyclic center.

The Lewis acid mediated condensation of "enolate" anions of chromium carbene complexes with carbonyl compounds described herein provides for a convenient synthesis of the synthetically versatile β-hydroxy carbene complexes.[6d] More detailed studies are under way concerning the origin of stereoselectivity of these condensations as well as on the corresponding aldol reactions of non group 6 carbene complexes.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (PHS Grant GM 33589) and from the National Science Foundation (CHE-820935). Pressure Chemical Co. is acknowledged for material support. The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

Supplementary Material Available: Spectral and physical data for all new compounds (6 pages). Ordering information is given on any current masthead page.

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[16] A similar observation has been made previously.[6f]

[17] Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667-1668.

[18] (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565-7567. (b) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293-2295. (c) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1131-1133. (d) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434-436. (e) Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732. (f) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726-6727.

[19] Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. *Tetrahedron Lett.* **1973**, 1431.

[20] A 65% yield of **11g** can be obtained by elution of **10g** from an activity I neutral alumina[6d,12b] column with hexane. These elimination reaction are slightly more efficient with β-acetoxy complexes. The complex **10a** can be converted to the isobutenyl complex[18c] in 80% yield with alumina/hexane.

Unusual Reactivity of $[Os_3Sn(\mu\text{-}H)_2(CO)_{10}R_2]$ Involving the Tin Atom and the Novel Bridging Hydride: X-ray Crystal and Molecular Structures of $[Os_3Sn(\mu\text{-}H)_2\{\mu\text{-}RC(OS){=}O(SN)\}(CO)_9R]$ and $[Os_3Sn(CO)_9\{\mu_2,\eta^1\text{-}C(CO_2Me)CH_2C{=}O(Os)OMe\}R_2]$ $[R = CH(SiMe_3)_2]$

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We recently reported[1] the structure and synthesis of $[Os_3Sn(\mu\text{-}H)_2(CO)_{10}R_2]$ (I) $[R = CH(SiMe_3)_2]$, which has the unusual feature of a hydrogen atom bridging tin and osmium. Three features of this molecule may be expected to lead to high reactivity, namely, the presence of a main-group metal, the two very bulky alkyl ligands, and the novel hydrogen bridge. We now report two reactions of I, illustrating these three points, and on the detailed molecular structures of the products.

Reaction 1 occurs essentially quantitatively on heating I in heptane, after which crystalline II can be filtered off from the

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[1] Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 609.

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