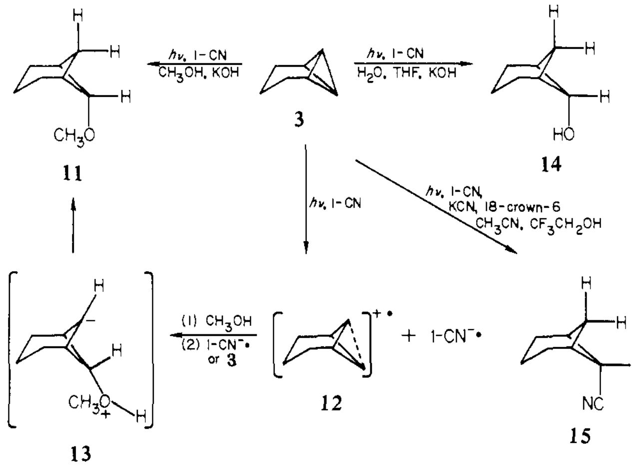
and 1-cyanonaphthalene as a photosensitizer. Under these conditions, irradiation of **3** with a 450-W, medium-pressure Hanovia lamp through Vycor for 20 h gave a quantitative yield of **11** (by VPC analysis vs. an internal standard). The structure of **11** was established through comparison with an authentic sample synthesized according to the literature procedure.[10]



The facile addition of methanol to **3** under photosensitized conditions suggested the intermediacy of a highly polar intermediate. Whether this intermediate is a highly polarized complex (charge-transfer complex or exciplex) or an ion pair resulting from electron transfer cannot be established on the basis of the presently available data. In view of the correlation between the log k_q for naphthalene fluorescence quenching by highly strained hydrocarbons and the oxidation half-wave potential for these same hydrocarbons, we will utilize the concept of ion-pair formation for the sake of mechanistic discussions in this communication. Electron transfer from **3** to excited state 1-cyanonaphthalene (1-CN) could produce **12** and 1-CN^{-}·. This is reasonable in view of the excited-state reduction potential of 1.83 V for 1-CN. The cation radical, **12**, would be expected to be extremely reactive, but structurally stable.[11] Addition of methanol to **12** would produce a new cation radical which could accept an electron back either from 1-CN^{-}· or from a second molecule of starting material[12] to produce **13** or a related precursor of **11**. Utilization of methanol-*O-d* as solvent resulted in 100% incorporation of one deuterium, which indicated that the source of the hydrogen which was added to **3** was the hydroxyl proton.

The clean photosensitized addition of methanol to **3** prompted us to investigate the use of other nucleophiles. When 10% aqueous tetrahydrofuran containing 0.1% potassium hydroxide was used as solvent, **14** was obtained in 90% (VPC yield vs. an internal standard, isolated yield 50%).[13] When the irradiation was carried out on a 40:1 acetonitrile 2,2,2-trifluoroethanol solution of **3**, 1-CN,[14] potassium cyanide, and 18-crown-6, **15** was obtained in 91% yield, mp 31–32 °C.[6] The structure of **15** was established on the basis of comparison of its ^{1}H NMR and ^{13}C NMR spectra with those of **11** and **14**.

In summary, we have demonstrated that the quenching of fluorescence by *saturated* hydrocarbons can result in productive and interesting photochemical conversion of these hydrocarbons. To our knowledge, the addition reactions described above represent the first examples of photosensitized additions of nucleophiles to hydrocarbons in the absence of activating aryl substituents or other π systems attached directly to the hydrocarbon skeleton.[15] As part of our studies of the oxidation of strained hydrocarbons,[2] we have measured the oxidative half-wave potentials of approximately 40 compounds which would be predicted to quench fluorescence of various naphthalene and anthracene derivatives. It is anticipated that many of these compounds will undergo interesting and useful photosensitized reactions. We are continuing to explore this area.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231, which supported this investigation.

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(8) The potassium hydroxide was added to avoid any acid-catalyzed side reaction of **3**, which is extremely acid sensitive. In the absence of base, the photosensitized reaction gave a mixture of **11** and 2-methoxybicyclo[4.1.0]heptane (the normal product of acid-catalyzed addition of methanol to **3**).[9] Control experiments established that the fluorescence of 1-cyanonaphthalene was not quenched under our reaction conditions in the absence of **3**. This ruled out electron transfer from methoxide to the sensitizer, followed by attack of the methoxyl radical on **3**.

(9) Wiberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571.

(10) Müller, E. *Tetrahedron Lett.* **1973**, *1201*, 1203. Müller, E. *Chem. Ber.* **1975**, *108*, 1401.

(11) Theoretical calculations indicate that the cation radical generated by removal of an electron from bicyclo[1.1.0]butane should maintain a structure which is very similar to the parent hydrocarbon. Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793.

(12) The latter possibility would require the involvement of a photoinduced chain reaction. The observation of a quantum yield of 0.22 for product formation and a quantum yield of 0.89 for fluorescence quenching of 3×10^{-2} – 3×10^{-3} M 1-CN in methanol containing 10^{-1} M **3** suggests the absence of a chain reaction but does not rigorously exclude such a possibility. Clearly, only a small portion of the fluorescence quenching leads to the chemical transformation of **3**. A photoinduced chain reaction has been observed in a related system by Mukai and co-workers.[3]

(13) The structure of **14** was established through comparison with an independently synthesized authentic sample.[10] The sample of **14** prepared photochemically had mp 124–126 °C (lit.[10] mp 109–124 °C). The sharp melting point is attributed to the excellent stereochemical purity of the photosensitized addition.

(14) The log k_q for the fluorescence quenching of 1-CN by **3** in acetonitrile was 10.06. Under these conditions the process appeared to be diffusion controlled.

(15) In some respects the additions to saturated C–C bonds described in this communication are reminiscent of the sensitized additions of various nucleophiles to the double bond of 1-phenylalkenes studies by Arnold and co-workers: Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407. Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535. See also: Arnold, D. R.; Humphreys, R. W. R. *Ibid.* **1979**, *101*, 2743.

Synthesis and Characterization of "Long-Chain" Alkylidene-Bridged Hetero Bimetallic Complexes

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Received March 16, 1981
Revised Manuscript Received June 16, 1981

Alkylidene-bridged binuclear complexes of transition metals are currently undergoing active study as models for intermediates in the Fischer–Tropsch process[1] or olefin metathesis[2] or as reagents for alkylidene transfer. Early interest in this field derived from observations of reactions between Cp_2TiCl_2 and trimethylaluminum.[3] A major advance in this area occurred when Tebbe and co-workers isolated, identified, and characterized a series of compounds of general structure **1** from this type of reaction (reaction 1).[4] It was noted that such compounds could participate

$$Cp_2TiCl_2 + 2\,AlMe_3 \longrightarrow Cp_2Ti\overset{CH_2}{\underset{Cl}{\lessgtr}}Al(CH_3)_2$$

1

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(1) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *Ibid.* **1979**, *101*, 4128. Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *Ibid.* **1980**, *102*, 1752. Herrman, W. A.; Plank, J.; Ziegler, M. L.; Balbach, B. *Ibid.* **1980**, *102*, 5906. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(2) Garnier, F.; Krausz, P. *J. Mol. Catal.* **1980**, *8*, 91. Rudler, H. *Ibid.* **1980**, *8*, 53.

(3) Heins, E.; Hinck, H.; Kaminsky, W.; Oppermann, G.; Raulinat, P.; Sinn, H. *Makromol. Chem.* **1970**, *134*, 1.

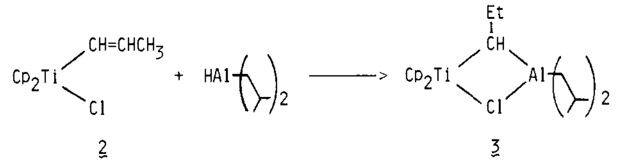
0002-7863/81/1503-4979$01.25/0

Table I. ^{1}H NMR Chemical Shifts of α Proton in **4a**,**b** and **7a–e**

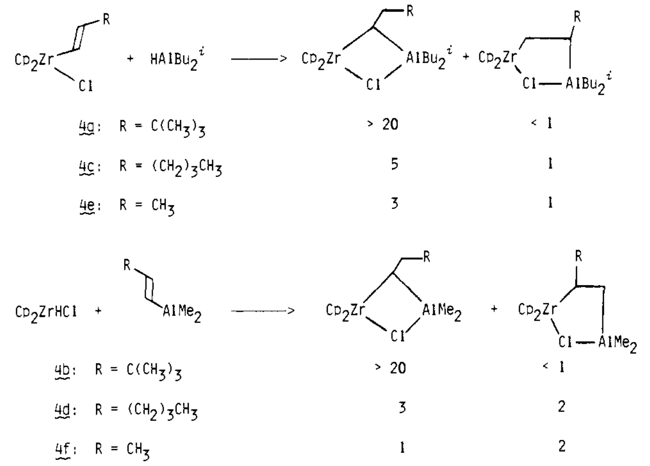
complex	bridging ligand, X	chemical shift, ppm
4a	Cl	6.97
4b	Cl	6.96
7a	OMe	6.65
7b	SEt	6.61
7c	NEt_2	6.84
7d	PPh_2	6.48
7e	$CH_2C(CH_3)_3$	8.60

in olefin metathesis and that the bridging methylene ligand could be transferred to a ketone or ester to give olefinic products. The use of compounds such as **1** to elucidate olefin metathesis pathways has now been noted[5] and compound **1** has been developed as a useful synthetic reagent for the organic chemist[6] as a result of its ability to react as an active "Wittig-type" reagent which, for example, can convert esters or lactones into vinylic ethers in high yield. The family of alkylidene-bridged complexes **1** has thus far been limited to species containing the bridging *methylene* unit. This limitation arises presumably as a result of the synthesis of **1** which likely proceeds via an α-elimination reaction from an intermediary alkyl complex; when β hydrogens are present in the organoaluminum reagent, alternative products are formed. For example, the reaction between Cp_2TiCl_2 and triethylaluminum leads to a product containing the bridging cyclopentadienyl group.[7] We have now discovered a new method for preparing analogues of **1** in which structural variation is possible in the alkylidene unit and wish to report our observations.

Alkylidene-bridged complexes of titanium and aluminum are obtained by addition of an organoaluminum hydride[8] to the double bond of an alkenyltitanium complex as follows: A solution of dicyclopentadienylpropenylchlorotitanium[9] (**2**) (0.2 M in toluene-d_8), at −40 °C is treated with 1 equiv of diisobutylaluminum hydride (also as a 0.2 M toluene-d_8 solution). The reaction mixture is allowed to warm to room temperature over a 30-min period. The product has not yet been isolated but has been identified spectroscopically. A signal at δ 9.9 in the ^{1}H NMR spectrum[10] and model studies involving isolable zirconium analogues (vide infra) suggests that a propylidene-bridged titanium aluminum complex **3** has been formed (reaction 2). Some broadening of lines in the proton NMR spectrum of **3**, probably due to the presence of Ti(III) byproducts,[11] precludes detailed spectral elucidation of **3**. [Treatment of this species as an unisolated entity with cyclohexanone according to the method developed by Evans[6] gives propylidenecyclohexane[12] in 50% yield[13] based on **3** (measured by NMR internal standard); preliminary results show that **3** also converts methyl benzoate into the corresponding vinyl ether.[12]]



With its lower tendency to form reduced valence state paramagnetic species, it was of interest to obtain zirconium analogues of **3** for structure elucidation by NMR analysis. Indeed, we find that zirconium analogues (**4**) of **3** can be obtained readily by either of two routes: the addition of an organoaluminum hydride to an alkenylzirconium complex[14] or the addition of Cp_2ZrHCl[14] to the double bond of an organoaluminum alkenyl[15] (reaction 3). In both cases the direction of addition to the double bond, indicated by ^{1}H NMR analysis, is apparently dependent on the steric bulk of the substituents on the double bond. Thus the reaction of a benzene solution of diisobutylneohexenylaluminum with a benzene suspension of Cp_2ZrHCl (at room temperature) gives, after filtration, one major compound (>95% by ^{1}H NMR spectroscopy). Dimethyl-*n*-hexenylaluminum reacts with Cp_2ZrHCl to give a mixture of addition products formed in a ratio of 3:2, the major isomer corresponding to the alkylidene-bridged species. The regioselectivity for the alkylidene species is greater when the hydride is supplied by the aluminum reagent. The reaction of diisobutylaluminum hydride with the *n*-hexenylzirconium complex gives a 5:1 mixture of products with the alkylidene-bridged species predominating.



In the ^{1}H NMR spectrum[16] of **4a** the chemical shifts of the two diastereotopic β protons are separated by 0.4 ppm and give rise, along with the α proton, to an ABX pattern, confirmed by decoupling experiments. The nonequivalent cyclopentadienyl ligands appear as two singlets separated by 3.6 Hz (at 90 MHz). The chemical shift of the α proton occurs at δ 7.02, considerably upfield of both the methylene protons found in **1**, which appear at δ 8.27,[4] and the α proton of **2** (vide supra). In the ^{13}C NMR spectrum the signal for the carbenoid carbon appears at 151 ppm ($^1J_{CH}$ = 107 Hz), also upfield of that found for other bridged alkylidene complexes (cf. $\delta_{^{13}C}$ 188 for **1**[4]). Complex **4b**, which has been isolated as red-brown crystals from toluene–hexane, displayed similar ^{1}H and ^{13}C NMR spectra.[16]

Tebbe has reported that replacement of the bridging chloride ligand or the entire dialkylaluminum chloride unit by other groups markedly affects the reactivity of the methylene species **1**.[5a,11] The reactivity of the carbenoid species increases toward olefin metathesis, for example, as the apparent strength of the carbon–aluminum (or replacement atom) bond decreases. Paralleling this

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(4) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(5) (a) Tebbe, R. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876.

(6) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

(7) Tebbe, F. N.; Guggenberger, L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 227.

(8) A similar procedure was used to prepare geminal dialuminoalkanes. See: Zweifel, G.; Steele, R. B. *Tetrahedron Lett.* **1966**, 6021.

(9) Waters, J. A.; Mortimer, G. A. *J. Organomet. Chem.* **1970**, *22*, 417.

(10) ^{1}H NMR chemical shift with reference to δ 7.00 (toluene-d_8) on 100-MHz XL-100.

(11) Tebbe, F. N., personal communication.

(12) The organic products were isolated by preparative GC and identified by GM/MS and ^{1}H NMR spectroscopy by comparison of their spectra with independently synthesized samples.

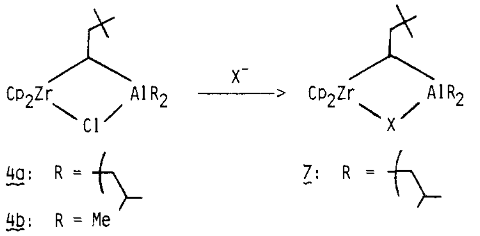
(13) The yields were determined by GLC.

(14) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

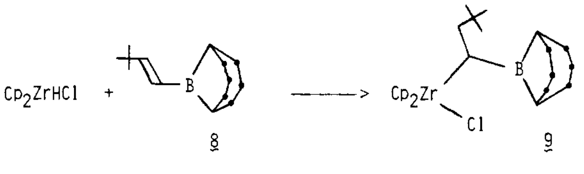
(15) Carr, D. B.; Ph.D. Dissertation, Princeton University, Princeton, NJ, 1978.

(16) NMR spectra in C_6D_6: ^{1}H NMR with reference to δ 7.15 (C_6D_5H) and ^{13}C NMR with reference to δ 128 (C_6D_6). **4a**: δ 6.97 (d of d, J = 4.0, 11.4 Hz, 1 H), 5.78 (s, 5 H), 5.74 (s, 5 H), 3.18 (d of d, J = 11.4, 14.9 Hz, 1 H), 2.79 (d of d, J = 4.0, 14.9 Hz, 1 H), 2.15 (septet, J = 6.4 Hz, 2 H), 1.22 (d, J = 6.4 Hz, 12 H), 0.85 (s, 9 H), 0.40 (m, 4 H). **4b**: δ 6.96 (d of d, J = 5.6, 8.9 Hz, 1 H), 5.74 (s, 5 H), 5.71 (s, 5 H), 3.07 (d of d, J = 8.9, 15.0 Hz, 1 H), 2.84 (d of d, J = 5.6, 15.0 Hz, 1 H), 0.87 (s, 9 H), −0.28 (s, 6 H). The spectra were recorded at ambient temperature (37 °C) on 90-MHz instruments (JEOL FX90-Q or Perkin-Elmer R32).

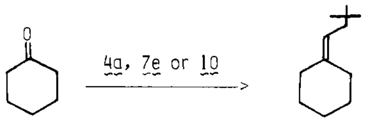
altered reactivity was the observation by proton NMR analysis that the more reactive the species, the further downfield were chemical shifts of the alkylidene protons. To prepare a series of analogues of **4**, therefore, was of interest for these zirconium species. Indeed, we find that addition of 1 equiv of either sodium methoxide, sodium thioethoxide, lithium diethylamide, lithium diphenylphosphide, or neopentyllithium to **4a** in benzene (followed by removal of the alkali metal chloride by filtration) gave a series of new complexes (reaction 4). The ^{1}H NMR spectra for **7a–e** (Table I) showed absorptions for the newly incorporated anionic ligands and, as well, a shift of the signal for the carbenoid proton, suggesting that **7a–e** are simple ligand metathesis analogues of the starting material. In the neopentyl complex (**7e**), the chemical shift of the α proton is comparable to that observed for the titanium–aluminum alkylidene complexes. As well, the chemical shift for the alkylidene carbon is shifted downfield to 191 ppm.



The mode of synthesis of the zirconium–aluminum compounds utilizing Cp$_2$ZrHCl is compatible with other alkenyl metal starting materials. For example, the addition of Cp$_2$ZrHCl to neohexenylborane **8**[17] gives a new complex **9** (reaction 5). [Its yellow color is typical of dicyclopentadienylalkylchlorozirconium species rather than the red bridging-alkylidene complexes.] The signal for the α proton appears in the ^{1}H NMR as a doublet of doublets centered at δ 3.16. Cp$_2$ZrHCl also adds to dineohexenylzinc[18] to give a bridging-alkylidene complex, **10**. Th α proton appears at δ 6.94 in the ^{1}H NMR spectrum.



Preliminary studies show that the alkylidene-bridged zirconium systems react with ketones to give "Wittig" products, although in low yield (20%). For example, both the aluminum species, **4a** and **7e**, and the zinc complex, **10**, convert cyclohexanone into neohexylidenecyclohexane[12] (reaction 6). We are currently exploring methods for activation of these readily prepared zirconium-based complexes with regard to their ultimate utilization as synthetic reagents. We are also examining means to improve titanium-based reagent systems.



Acknowledgment. We acknowledge support for this research provided by the National Institutes of Health (Grant HL-22612) and by the National Science Foundation (Grant CHE-79-00996). We also acknowledge Dr. F. N. Tebbe for many helpful comments and criticisms. F.W.H. acknowledges support from Halcon Research and Development Corporation for a partial fellowship.

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(17) Prepared by the addition of 9-borabicyclononane to 3,3-dimethyl-1-butyne.

(18) Prepared by the transmetalation reaction of dicyclopentadienylchloroneohexenylzirconium with ZnCl$_2$ in CH$_2$Cl$_2$.[15]

Bis(triphenylphosphine)iminium Nitrite. A Mild, Versatile Nitrosylating Reagent

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The majority of known metal clusters contain carbon monoxide as the predominant ligand, and with few exceptions, these clusters are sterically and electronically saturated. This fact, which certainly leads to their stability, unfortunately renders these clusters much less active as homogeneous catalysts under mild conditions. Thermolysis to achieve activation often results in disruption of the cluster since the metal–carbonyl bonds are stronger than the metal–metal bonds.[1] Substitution of an appropriate number of nitric oxide ligands for carbon monoxide is one possible method of bypassing this problem.

As part of our study of nitrosyl carbonyl clusters, we are exploring various synthetic methods for converting existing metal carbonyls into nitrosyl carbonyl compounds. The use of sodium nitrite as a nitrosylating reagent in the absence of acid has been restricted to only a few reactions.[2-6] The prototypal example, reported by Hieber and Beutner,[2] is the synthesis of [Fe(CO)$_3$(NO)]$^-$ (eq 1), which until now has been the only known nitrosyl carbonylmetalate.

$$\mathrm{Fe(CO)_5 + NaNO_2 + NaOCH_3 \xrightarrow[100\ ^\circ C]{CH_3OH,\ 1\ h} Na[Fe(CO)_3(NO)] + CO + Na(CH_3OCO_2)} \quad (1)$$

Recent attempts to extend this reaction to Mo(CO)$_6$ in order to form [Mo(CO)$_4$(NO)]$^-$ resulted instead in the incorporation of methoxide into the product forming (PPN)$_3$[Na[Mo$_3$(CO)$_6$(NO)$_3$(η_2-OCH$_3$)$_3$(η_3-O)]$_2$].[5] To avoid such complications, we have prepared bis(triphenylphosphine)iminium nitrite (PPNNO$_2$) using the method of Martinsen and Songstad[7] and have discovered that in dipolar aprotic solvents it is indeed a mild and versatile nitrosylating reagent. This has allowed us to greatly improve the synthesis of three well-known nitrosyl carbonyl complexes and readily synthesize three new compounds including the second example of a nitrosyl carbonylmetalate.

When 1 equiv of Fe(CO)$_5$ is added to a dried and deoxygenated THF solution of PPNNO$_2$, rapid evolution of gas, identified as CO$_2$ and CO, is observed as the PPNNO$_2$ completely dissolves. After 10 min the solvent is removed from the bright yellow solution, yielding yellow crystals of PPN[Fe(CO)$_3$(NO)] in virtually quantitative yield. This procedure can be contrasted with previous methods using NaNO$_2$ in hydroxylic solvents (eq 1) to produce the air-sensitive sodium salt Na[Fe(CO)$_3$(NO)] followed by metathesis with PPNCl to give PPN[Fe(CO)$_3$(NO)]. The yield of this method, which requires approximately 2 days to complete, is 50%.[8]

The reactions of PPNNO$_2$ with cationic metal carbonyls are also rapid. One equivalent of PPNNO$_2$ reacts with [Fe(CO)$_2$(PPh$_3$)$_2$(NO)](PF$_6$) at room temperature in acetonitrile to give the known dinitrosyl Fe(CO)(PPh$_3$)(NO)$_2$.[9] The reaction exhibits high selectivity in that none of the known Fe(PPh$_3$)$_2$(NO)$_2$ is observed, and considering the ease by which the starting cation

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