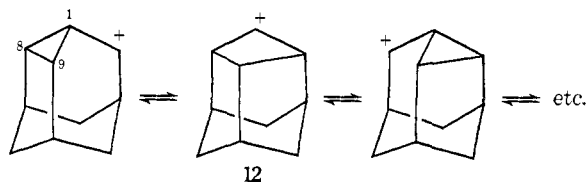


no certainty that any single formula can be utilized to represent in full the ion(s). Alternatively, the degenerate equilibration of the parent 8,9-dehydro-2-adamantyl cation may also be accounted for by an initial C₁-C₉ bond shift to give the 2,5-dehydro-4-protoadamantyl cation (**12**), followed by migration of



the C₈-C₉ bond,¹⁰ a situation very similar to the adamantyl-protoadamantyl rearrangement.¹¹

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(10) For a detailed discussion of the cyclopropylcarbinyl to cyclobutyl rearrangement see K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

(11) D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 2138 (1974), and references cited therein.

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An "Alkylcarbene" Complex of Tantalum by Intramolecular α -Hydrogen Abstraction

Sir:

In the vast majority of transition metal carbene complexes the carbene carbon bears a heteroatom substituent.¹ Only rarely does it bear a proton.² No example of an alkylcarbene (or alkylidene) complex, which contrasts sharply with these trends, has been reported. A thermally stable neopentylidene complex of tantalum has now been isolated and is described here along with the results of some preliminary studies concerning the mechanism of its formation.

The reaction of 2 mol of neopentylolithium with Ta[CH₂C(CH₃)₃]₃Cl₂³ in pentane at room temperature over a period of approximately 1 hr yields 2 mol of lithium chloride (isolated and analyzed), 1 mol of neopentane (measured and identified by gc-mass spectral methods), and a highly soluble, orange, crystalline

(1) (a) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972); (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); (c) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973); (d) C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **95**, 5833 (1973); (e) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Amer. Chem. Soc.*, **95**, 5430 (1973).

(2) B. Cetinkaya, M. F. Lappert, and K. Turner, *J. Chem. Soc., Chem. Commun.*, 851 (1972).

(3) (a) This species was prepared from TaCl₅ and 1.5 mol of Zn[CH₂C(CH₃)₃]₂ in pentane. It has also been prepared by Mowat and Wilkinson from (CH₃)₃CCH₂MgCl and TaCl₅ in diethyl ether.^{2b} (b) W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973).

compound with the formula Ta[CH₂C(CH₃)₃]₃[CHC(CH₃)₃] (**1**) in quantitative yield: ¹H nmr (τ) in C₆D₆, 8.09 (s, 1), 8.57 (s, 9), 8.85 (s, 27), 9.16 (s, 6); mass spectrum, parent ion at 464.2857 (calcd 464.2821); cryoscopic molecular weight in benzene, 472; mp (sealed capillary), 71°. *Anal.* Calcd for TaC₂₀H₄₈: C, 51.72; H, 9.33; Ta, 38.95. Found: C, 51.39; H, 9.31; Ta, 41.22. The reaction of 5 mol of (CH₃)₃CCH₂MgCl with TaCl₅ in diethyl ether also produces **1** which may be sublimed (essentially distilled) from the crude reaction mixture in ca. 50% isolated yield at 75° and <1 μ . The neopentylidene complex reacts violently with oxygen and moisture but may be stored indefinitely at room temperature in an inert atmosphere. Its reaction with 5 mol of DCl in hexane gave 3.7 mol of neopentane which was found by mass spectrometry to be a mixture of three parts of neopentane-*d*₁ and one part of neopentane-*d*₂.

Further proof of the essential structural features of **1** is provided by ¹³C nmr. In C₆D₆ the neopentylidene α -carbon is found at 250.1 ppm downfield from TMS, a shift which is at the high field end of the range of chemical shifts for α -carbon atoms in other carbenoid ligands.⁴ In the uncoupled spectrum this resonance is a doublet due to coupling to the single α -hydrogen ($J = 90$ Hz). Other resonances were similarly identified at 113.7 (neopentyl α -carbons, triplet, $J = 107$ Hz), 35.2 (neopentyl γ -carbons, quartet, $J = 124$ Hz), 34.9 (neopentylidene γ -carbons, quartet, $J = 124$ Hz), 35.3 (neopentyl β -carbons), and 47.0 ppm (neopentylidene β -carbon) downfield from TMS. It is unknown at this time whether the apparent equivalence of the neopentyl ligands in pseudo-tetrahedral **1** is due to insufficient stereochemical influence of a nonrotating neopentylidene moiety or to rotation about the metal-neopentylidene-carbon bond.

The mechanism of formation of **1** was studied by deuterium labeling techniques. The reaction of Ta[CD₂C(CH₃)₃]₃Cl₂ with 2 mol of LiCH₂C(CH₃)₃ produced 1 mol of neopentane with an isotopic distribution shown in Table I (run A).⁵ The organometallic product was labeled at the carbenoid carbon to the extent of 38%.⁶ When a deficiency of lithium reagent was used (run B) only 0.5 mol of essentially identically labeled neopentane was formed and 0.5 mol of pure Ta[CD₂C(CH₃)₃]₃Cl₂ recovered.⁷ A large excess of lithium reagent (run C) produced neopentane with a slightly higher proton content. This result is believed to be outside experimental error and may indicate an exchange of as much as 0.5 mol of -CH₂C(CH₃)₃ for -CD₂C(CH₃)₃ during the course

(4) (a) C. G. Kreiter and V. Formáček, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972); (b) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972); (c) D. J. Ciappinelli, F. A. Cotton, and L. Kruczyński, *J. Organometal. Chem.*, **50**, 171 (1973); (d) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973); (e) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, **95**, 8574 (1973).

(5) Isotopic distributions were estimated from the intensities of the peaks resulting from loss of one methyl group from neopentane. The fragmentation patterns of pure (CH₃)₃CCH₂D, (CH₃)₃CCHD₂, and (CH₃)₃CCD₃ were checked and found to be straightforward. Due to limitations of the instrument and the method of calculation, the maximum absolute error in these figures is estimated to be $\pm 3\%$.

(6) The method of determination is one of numerous and varied reactions which will be disclosed in future publications.

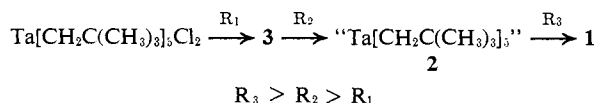
(7) Exchange of one alkyl to the extent of 10% could have been observed by ¹H nmr.

Table I. Isotopic Distribution in the Products of the Reaction of $\text{Ta}[\text{CD}_2\text{C}(\text{CH}_3)_3]_3\text{Cl}_2$ with $\text{LiCH}_2\text{C}(\text{CH}_3)_3$ in Hexane or Diethyl Ether

	$\text{Ta}[\text{CD}_2\text{C}(\text{CH}_3)_3]_3\text{Cl}_2$	$\text{LiCH}_2\text{C}(\text{CH}_3)_3$	neo- d_0	d_1	d_2	d_3	$\alpha\text{-}d^a$
A (hexane)	1	2	15	20	43	22	38
B (hexane)	1	1	11	25	41	23	
C (hexane) ^b	1	10	22	21	46	11	
Theory ^c	1	2	16	24	40	20	44
A' (ether)	1	2	17	21	43	19	42

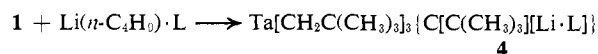
^a This notation refers to the per cent deuteration at the neopentylidene α -carbon in **1**- d_x ; theory = 56% $\text{CHC}(\text{CH}_3)_3$, 44% $\text{CDC}(\text{CH}_3)_3$. ^b Reaction between **1** and LiC_3H_7 in pentane (or benzene) is slow as judged by ^1H nmr examination of mixtures. ^c Primary deuterium isotope effect = 2.

of the reaction. These results suggest (respectively) the following: (1) neopentane is formed by abstraction of a neopentyl α -hydrogen by a second neopentyl group in a statistical manner involving *all five* neopentyl moieties with a primary deuterium isotope effect of *ca.* 2 (see theory, Table I); (2)(a) alkyl exchange between $\text{Ta}[\text{CD}_2\text{C}(\text{CH}_3)_3]_3\text{Cl}_2$ and lithium reagent or intermediate tantalum species is slow and (b) the rate of reaction of $\text{Ta}[\text{CD}_2\text{C}(\text{CH}_3)_3]_3\text{Cl}_2$ with lithium reagent is the slowest step prior to equilibration of all neopentyl groups; and (3) alkyl exchange between excess lithium reagent and *any* tantalum species is slow on the time scale of the reaction. The simplest and most reasonable postulated mechanism involves rapid formation of a penta(neopentyl) species, **2**, which then "decomposes" by elimination of neopentane to give **1**.⁸ If, for example, an intermediate, **3**, is postulated, it is necessary under the experimental conditions employed that the rate of formation of **2** (R_2) be greater than the rate of formation of **3** (R_1), and, since **2** is not the end product, $R_3 \geq R_2$, *viz.*



A description in terms of rate constants awaits a more detailed study. Although the rate of formation of **1** is apparently greater in diethyl ether the isotopic distribution (run A') remains essentially unchanged.

An α -hydrogen transfer process related to that which results in the formation of **1** can be observed within **1** itself. The reaction of **1** with $\text{Li}(n\text{-C}_4\text{H}_9)\cdot\text{L}$ ($\text{L} = \textit{inter alia}$ N,N,N',N' -tetramethylethylenediamine, 1,2-dimethoxyethane, or N,N' -dimethylpiperazine) in aliphatic hydrocarbons yields the pentane soluble lithiated species, **4**. Treatment of **4** with $\text{CF}_3\text{CO}_2\text{D}$ in



pentane at -78° yields **1**- d_1 (isolated by sublimation) deuterated to the extent of 90% at the neopentylidene α -carbon. Heating **1**- d_1 at 80° for 24 hr in C_6D_6 scrambles deuterium among the neopentylidene and neopentyl ligands. Essentially no decomposition occurs during this time period. This re-

(8) Pentamethyltantalum (R. R. Schrock and P. Meakin, *J. Amer. Chem. Soc.*, **96**, 5288 (1974)) has been isolated. Steric factors therefore probably play an important role in the "decomposition" of **2**.

sult should be compared with the more rapid hydrogen transfer process which occurs in $(\text{CH}_3)_3\text{P}(\text{CH}_2)_9$.

The findings presented here demonstrate clearly that under some conditions (1) complexes of "nonstabilized" carbenoid ligands containing an α -hydrogen, *e.g.*, alkylidenes, are stable and (2) α -hydrogen abstraction is a viable mode of "decomposition" of transition metal alkyl complexes.¹⁰

(9) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 604 (1968).

(10) See, for example, M. C. Baird, *J. Organometal. Chem.*, **64**, 289 (1974).

Richard R. Schrock

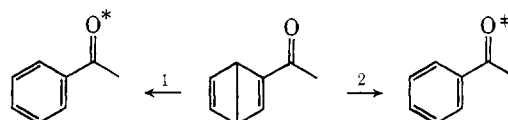
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Chemiexcitation of Acetophenone via the Nonadiabatic Thermal Rearrangement of Dewar Acetophenone

Sir:

Bicyclo[2.2.0]hexadienes have been observed to produce electronically excited state products upon thermolysis.¹ The previous studies were restricted in scope by the lack of established reactions of the benzene excited triplet state and by energetic constraints on the production of excited singlet benzene. We have pursued the investigation of this interesting family of non-adiabatic valence isomerization with the study of Dewar acetophenone (**1**),² eq 1 and 2. The Dewar aceto-



phenone-acetophenone system possesses several *important* and *fundamentally different features* from the previously studied cases: (1) both the S_1 and T_1 states of the valence isomer product correspond to n, π^* configurations; (2) both the S_1 and T_1 states of the valence isomer product possess a lower energy content than the transition state for thermal rearrangement; (3) the essential chemistry occurs (Dewar benzene to benzene) on atoms which are spatially distinct from the expected final site of chemiexcitation (the carbonyl function). Thus, a study of the thermolysis of **1** to acetophenone offers an opportunity to evaluate several intriguing aspects of a simple unimolecular chemiexcitation process.

The thermolysis of Dewar acetophenone is anticipated to release *ca.* 90 kcal/mol in activation enthalpy, and reaction enthalpy.¹ This amount of energy is sufficient³ to produce either singlet or triplet acetophenone (Figure 1). The photochemistry of acetophenone is well understood.⁴

(1) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3025 (1973).

(2) Compound **1** was prepared by the addition of cyclobutadiene (released from its iron carbonyl complex) to 3-butyne-2-one. The material was handled after distillation, in solution since attempts at purification resulted in rearrangement to acetophenone. Our samples contained acetophenone as the sole impurity detectable by nmr.

(3) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley, New York, N. Y., 1969, p 198.

(4) For example, see H. Lutz, M.-C. Duval, and E. Breheret, and L. Linqvist, *J. Phys. Chem.*, **76**, 821 (1972), and references therein.