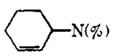
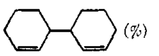
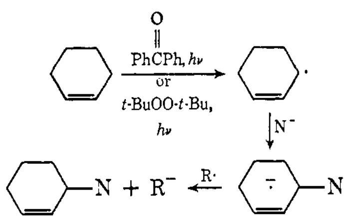
Table I. Yields of Products and Conversion Levels for the Reaction of Cyclohexenyl Radical with Various Nucleophiles

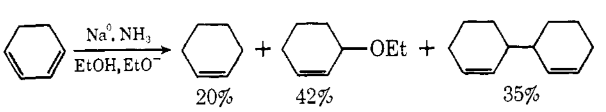
Nucleophile (N^-)	 N(%)	 (%)	Conversion
EtO^{-a}	60	0	16
EtO^{-b}	78	3	30
N_3^{-a}	71	0	8
N_3^{-b}	77[c]	12	24
AcO^{-a}	25	72	42

Cyclohexenyl radical produced by irradiation of *t*-BuOH solution of cyclohexene, NaN, and [a] benzophenone or [b] di-*tert*-butyl peroxide. [c] This yield was determined by isolation; all others, as well as conversion levels, were by glc.

taining di-*tert*-butyl peroxide and the nucleophile. In the former, benzophenone triplets abstract allylic hydrogen and in the latter this is effected by *tert*-butoxy radicals from the photodissociation of the peroxide. A Pyrex filter was used in all experiments to ensure that direct excitation of alkene and/or adduct did not occur. No attempt has yet been made to optimize yields; instead a standard set of conditions was adopted for making comparisons in which the ratio cyclohexene/nucleophile/radical precursor was maintained 1/1/1. The results are summarized as follows and in Table I.



One experiment was performed using a third approach to generating 3-cyclohexenyl radical, the reduction of 1,3-cyclohexadiene by sodium in ammonia using inverse addition.[6] Results shown were at 32% conversion of cyclohexadiene.



There is at present no evidence for the radical ion shown in the reaction scheme. The only reasonable alternative is a transition state in which an electron is ejected to solvent, but this seems less likely because the π bond of the adduct should "solvate" the electron more effectively than will *tert*-butyl alcohol. This point will be clarified as the study is extended to even simpler radicals.

The small variations in yield in reactions involving ethoxide and azide ions are probably not significant; both nucleophiles seem to be rather efficient radical scavengers as evidenced by the small amounts of dimer produced. By contrast, acetate ion is known to be a relatively poor nucleophile and it is observed in this reaction to compete rather poorly with the dimerization reaction.

(6) D. Y. Myers, R. R. Grabbe, and P. D. Gardner, *Tetrahedron Lett.*, 533 (1973).

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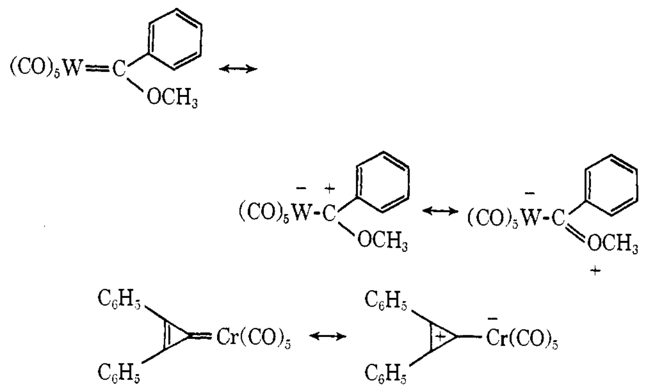
(Diphenylcarbene)pentacarbonyltungsten(0)

Sir:

Stable transition metal carbene complexes[1] generally have at least one heteroatom (O, N, S) directly bonded to the carbene carbon atom.[2-5] The heteroatom serves to stabilize the complex by electron donation to the electron deficient carbene carbon atom. The resulting partial double bonding between the heteroatom and the carbene carbon atom is manifested by a shortening of the carbon-heteroatom bond and by a substantial rotational barrier about the carbon-heteroatom bond.[1]



The only well-documented reports of carbene complexes not substituted with heteroatoms are (2,3-diphenylcyclopropenylidene)chromium and -palladium compounds;[6,7] the high stability of these complexes is undoubtedly related to the aromaticity of the diphenylcyclopropenium cation.

Heteroatom substituted carbene complexes are often thermally stable to over 100° [1] and have been found to act as methylene transfer agents only toward α,β-unsaturated esters and vinyl ethers.[8] We began studies

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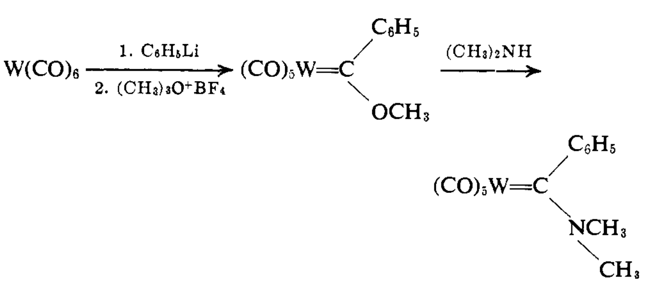
(1) For recent reviews of transition metal-carbene complexes see D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 575 (1972); F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 243 (1972).

(2) At least partially, this is a consequence of the available synthetic methods. Oxygen-substituted carbene complexes are usually prepared by reaction of a metal carbonyl with an organolithium reagent followed by O-alkylation of the resulting acyl anion.[3] The corresponding nitrogen[4] and sulfur[5] substituted carbene complexes are derived from the oxygen substituted carbene complexes by displacement reactions.



(3) E. O. Fischer and A. Massböl, *Chem. Ber.*, **100**, 2445 (1967).

(4) U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, **89**, 7141 (1967); J. A. Connor and E. O. Fischer, *Chem. Commun.*, 1024 (1967).

(5) E. O. Fischer, M. Leupold, C. G. Kreiter, and J. Müller, *Chem. Ber.*, **105**, 150 (1972).

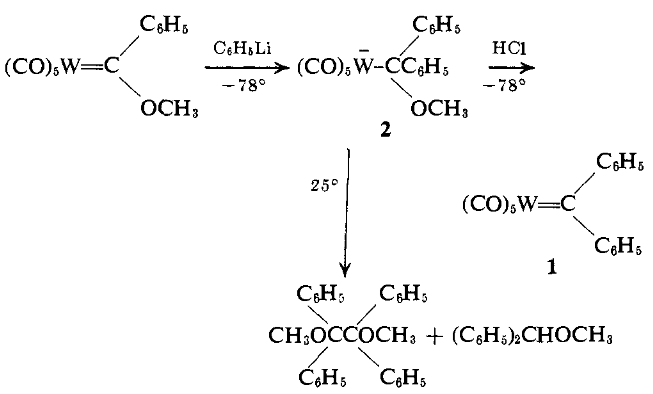
(6) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, 7, 950 (1968); *J. Organometal. Chem.*, **22**, C9 (1970).

(7) The synthesis of a diphenylcarbene complex of rhodium from the reaction of diphenylketene with $[RhCl(CO)_2]_2$ has been reported but the available spectral data and method of synthesis do not allow unambiguous assignment of the structures of the diphenylcarbene complexes: P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 993 (1972).

(8) K. H. Dötz and E. O. Fischer, *Chem. Ber.*, **105**, 1356 (1972); **105**, 3966 (1972).

of the preparation of diphenylcarbene complexes since we felt that these complexes would be less stable and potentially more reactive in methylene transfer reactions than heteroatom substituted carbene complexes. Here we report the synthesis, isolation, and surprising thermal stability of (diphenylcarbene)pentacarbonyltungsten(0) (**1**).

The reaction of phenyllithium with a phenylmethoxycarbene complex provides a straightforward route to a diphenylcarbene complex. Fischer and Riedmuller[9] have reported that reaction of phenyllithium with (phenylmethoxycarbene)pentacarbonylchromium(0) in ether at 0° gives 1,2-dimethoxy-1,1,2,2-tetraphenylethane in addition to other products. Similarly we have found that addition of phenyllithium to a red solution of (phenylmethoxycarbene)pentacarbonyltungsten(0) in ether at −78° produces a homogeneous brown solution which, on warming to room temperature, undergoes decomposition to give 1,2-dimethoxy-1,1,2,2-tetraphenylethane (19%) and benzhydryl methyl ether (20%). The formation of these products can be rationalized in terms of the decomposition of the tetrahedral adduct **2**.



To convert the presumed adduct **2** to the diphenylcarbene complex **1**, 1 equiv of HCl in ether was added to the brown solution of **2** at −78°. An immediate dramatic color change to dark red indicated that a reaction had occurred. Column chromatography (silica gel–pentane) followed by recrystallization of a fast moving band from pentane at −78° gave a 50% yield of (diphenylcarbene)pentacarbonyltungsten(0) (**1**) as a black solid, mp 65–66°. The structure of **1** was assigned on the basis of spectral data: ir (heptane) 2077 (s), 1965 (sh), 1959 (s) cm^{-1}; nmr (CS$_2$) δ 7.10, multiplet; uv (hexane) 232 mμ (46,500), 485 (10,400). A small parent ion was observed at *m/e* 490 in the mass spectrum; the exact mass of the larger M–CO peak was observed at *m/e* 462.0058, in good agreement with *m/e* of 462.0088 expected for C$_{17}$H$_{10}$O$_4$W.

Anal. Calcd for C$_{18}$H$_{10}$O$_5$W: C, 44.11; H, 2.05; W, 37.51. Found: C, 43.94; H, 2.11; W, 37.69.

The diphenylcarbene complex **1** was further characterized by chemical reactions. Ceric ammonium nitrate, a reagent known to convert metal–carbene complexes to the corresponding carbonyl compounds,[10] reacted with **1** in ether at room temperature to give benzophenone (58%). Methylenetriphenylphosphorane, a reagent which reacts with metal–carbene complexes to produce the corresponding methylene compound,[10] reacted with **1** in ether at room temperature to give 1,1-diphenylethylene in high yield.

The diphenylcarbene complex **1** is more thermally labile than (phenylmethoxycarbene)pentacarbonyltungsten. Thermal decomposition of **1** in heptane was complete in less than 2 hours at 100° and gave W(CO)$_6$ (19%), tetraphenylethylene (35%), and diphenylmethane (10%). Decomposition of **1** in cyclohexene gave increased amounts of diphenylmethane (30%) and decreased amounts of tetraphenylethylene (13%); no 1,1-diphenylnorcarane was detected under these conditions.

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[9] E. O. Fischer and S. Riedmuller, unpublished results quoted by E. O. Fischer, *Pure Appl. Chem.*, 30, 353 (1972).

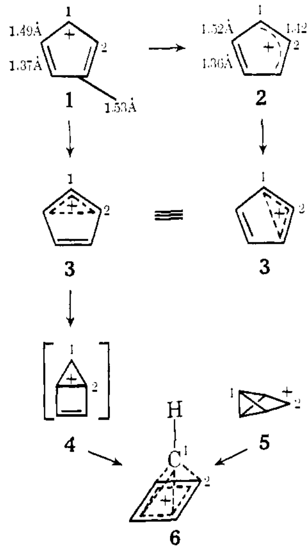
[10] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **94**, 6543 (1972).

CNDO Calculations on Isomeric (CH)$_5^+$ Cations

Sir:

Stohrer and Hoffmann[1] have posed the intriguing possibility that the most stable structure for the (CH)$_5^+$ cation is not any of the conventional forms, **1–5**, but rather may be a square pyramid, **6**. Furthermore, it was suggested that **6** might be "the unique stable structure in this system," *i.e.*, **1–5** might rearrange without activation to **6** (Scheme I).[1] Experimental interest has quickened,[2-4] but definitive answers are not

Scheme I



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[1] W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

[2] Reviews: R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970); R. Leone, J. C. Barborak, and P. v. R. Schleyer in "Carbonium Ions," Vol. 4, G. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, N. Y., 1973, Chapter 33, p 1837 ff.

[3] R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972); M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *ibid.*, **95**, 3017 (1973).

[4] S. Masamune, M. Sakai, and H. Ona, *ibid.*, **94**, 8955 (1972);