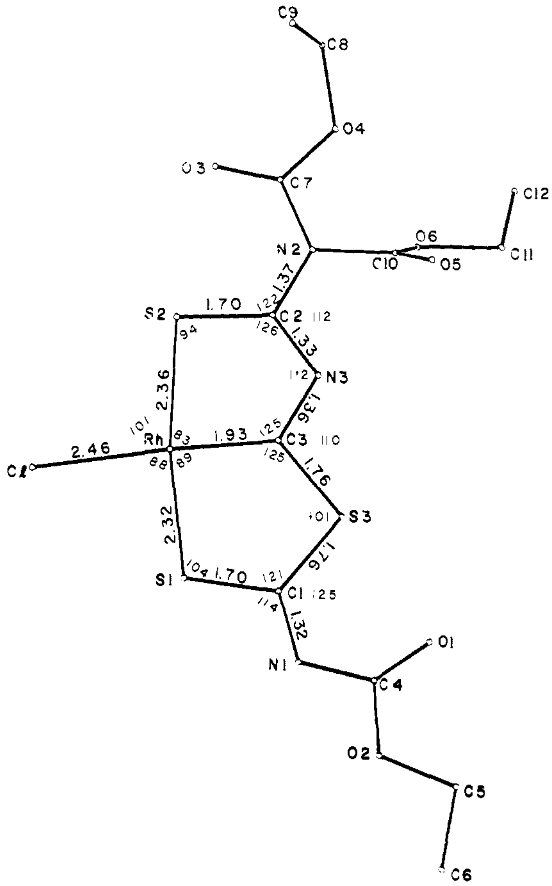


Figure 1. A drawing of molecule B of $RhCl(PPh_3)_2(EtOCONCS)_3$, viewed in the isothiocyanate ligand plane. The PPh_3 groups approximately above and below the Rh atom have been omitted for the sake of clarity. As judged by agreement between the two independent molecules in the asymmetric unit, the estimated standard deviations on bond distances are 0.01-0.02 Å and on bond angles are 0.3-1.0°.

the resultant 401 variables (isotropic model) by full-matrix least-squares methods has converged to values of 0.072 and 0.091 for the conventional R and R_w indices, respectively. (See paragraph at end of paper regarding supplementary material.)

The two independent nonsolvent molecules in the asymmetric unit differ somewhat in conformations of their terminal groups; they are otherwise equivalent. In Figure 1 we show a projection of molecule B onto the ligand plane. The trans PPh_3 groups in axial positions, approximately above and below the Rh atom, have been omitted for the sake of clarity. The Rh atom has a slightly distorted octahedral coordination with trans PPh_3 groups. The four equatorial sites are occupied by the chloro ligand and by the tridentate ligand $(EtOCONCS)_3$. Two former EtOCONCS molecules can be thought of as C(6)-C(5)-O(2)-C(4)O(1)-N(1)-C(1)-S(1) and C(9)-C(8)-O(4)-C(7)O(3)-N(2)-C(2)-S(2); the two fragments of the third EtOCONCS molecule consist of C(12)-C(11)-O(6)-C(10)O(5) attached to N(2) and of N(3)-C(3)-S(3) joining C(2) and C(1) to form a fused system of two five-membered rings. The tridentate ligand is attached to Rh through two S linkages (S(1) and S(2)) and one carbene C linkage (C(3)). The fused ring system closely resembles that found earlier for $(PhCONCS)_2$ attached to Rh(III),[1,2] with the exception that an O atom in that system has been replaced by S(2). With the exception of the geometrical changes brought about by this substitution, the geometries of the two ring systems are very similar. In particular, the present ring system is again essentially planar with some evidence for delocalization of bonding. The Rh(III)-C(3) (carbene) bond is again 1.93 Å, and the carbene again exerts a large trans influence on the trans chloro ligand.

Without mechanistic studies one can only speculate on the differing reactivity patterns of EtOCONCS and PhCONCS toward $RhCl(PPh_3)_3$. Presumably the reactions proceed along different but equally remarkable pathways, in part because of the differing basicities of R in the RCONCS groups.

Acknowledgment. This work was supported by the Ministry of Education of Japan and by the U.S. National Science Foundation.

Supplementary Material Available: Atomic parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. Cowie, J. A. Ibers, Y. Ishii, K. Itoh, I. Matsuda, and F. Ueda, *J. Am. Chem. Soc.*, **97**, 4748 (1975).
(2) M. Cowie and J. A. Ibers, *Inorg. Chem.*, in press.
(3) Data collection methods are similar to those described in earlier publications. See, for example, P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

Yoshio Ishii, Kenji Itoh, Isamu Matsuda, Fujio Ueda
Department of Synthetic Chemistry
Faculty of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464, Japan

James A. Ibers*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received January 5, 1976

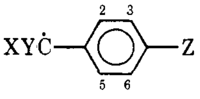
An Electron Spin Resonance Study of the Radical Anions Derived from Metal Carbene Complexes of Chromium, Molybdenum, and Tungsten

Sir:

A decade after the initial work by Fischer and Maasböl,[1] there still exists an active interest in transition metal carbene complexes,[2] particularly as regards their electronic structure, the mechanisms of their reactions, and their use in organic synthesis. ^{13}C NMR[3] and chemical studies[4] have suggested an M^{-}-C^{+} ylide nature for complexes of the type $(CO)_5MC(X)Y$ (M = Cr, Mo, W) in which the carbene carbon bound to the metal is best viewed as a carbocation stabilized by electron donation from the metal and from hetero substituents. Recent MO calculations[5] validate this picture and reveal that the LUMO in a representative complex is localized primarily on the carbene atom and is considerably more stable than the next lowest unoccupied MO. By analogy with carbonium ions,[6] these complexes should therefore readily undergo one-electron reduction to the corresponding carbon-centered radicals. We wish to report that a variety of reducing agents indeed produce such anionic organometallic radical species. We also present evidence suggesting that these novel species may be the reactive intermediates in the reactions of carbene complexes with strongly nucleophilic reagents via a single-electron transfer mechanism.

A dilute (~0.001 M) solution of (phenylmethoxycarbene)pentacarbonylchromium in THF/HMPA[7] (2:1 v/v) treated briefly at −78° in an inert atmosphere with Na/K alloy dispersed in THF gives rise to an intense and highly resolved ESR spectrum (Figure 1) which persists indefinitely at low temperatures (<−50°) but decays with increasing rates as the temperature is raised. A computer simulation

Table I. ESR Parameters for the Organometallic Radicals i and Their Analogues



i

X	Y	Z	Temp, °C	⟨*g*⟩	Isotropic Hyperfine Splittings, G *a*(X)[a]	*a*$_Y$(H)	*a*(H_2)	*a*(H_3)	*a*(H_5)	*a*(H_6)	*a*$_Z$(H)
H[b]	OH	H	−38	2.0031	14.89	1.18	5.15	1.66	1.55	4.59	5.92
H	OCH_3	H	−110	2.0030	15.24	1.51	5.04	1.51	1.51	4.52	5.75
$(CO)_5Cr^-$	OCH_3	H	−75	2.0032	3.65	0.843	4.464	1.419	1.320	4.216	5.550
$(CO)_5Mo^-$	OCH_3	CH_3	−32	2.0037	3.33	1.29	4.47	1.41	1.29	4.06	5.60
$(CO)_5W^-$	OCH_3	H	−62	2.0053	6.76	1.34	4.35	1.34	1.34	4.05	5.49
$(CO)_5W^-$	OCH_3	CH_3	−66	2.0054	6.78	1.31	4.25	1.31	1.31	3.89	5.34
H[c]	C_6H_5	H	−40		14.7		3.7	1.35			4.2
$(CO)_5W^-$	C_6H_5	H	−65	2.0064	8.29		2.57	1.01			2.86
$(CO)_5W^-$	C_6H_4	CH_3	−73	2.0062			2.58	1.05			2.99

[a] The low field metal isotope satellite lines are broader than the corresponding high field lines. [b] R. Wilson, *J. Chem. Soc. B*, 84 (1968). [c] Reference 14.

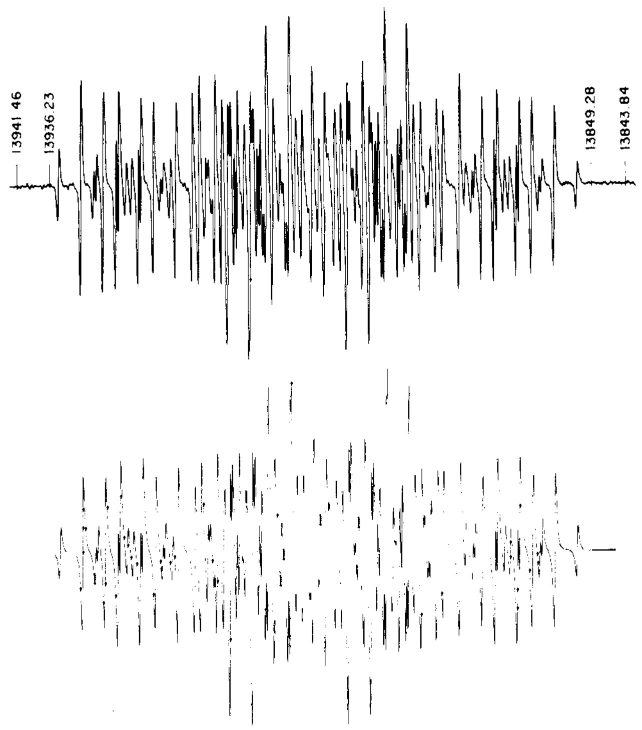


Figure 1. Experimental and calculated ESR spectra of $(CO)_5Cr^-$-$\dot{C}(OCH_3)C_6H_5$ formed by reduction of the neutral carbene complex with (π-C_5H_5)$Fe(CO)_2Na$ in THF/HMPA at −78°.

confirms the presence of five distinct doublets due to the phenyl protons and of a quartet due to the methyl protons (Table I). At higher amplification, satellite quartets belonging to the ^{53}Cr nucleus can easily be detected. This paramagnetic species is clearly the radical anion I resulting by one-electron reduction of the chromium carbene complex.

$$(CO)_5Cr^- \text{-} C^+(OCH_3)C_6H_5 \xrightarrow[Na/K]{+e} (CO)_5Cr^- \text{-} \dot{C}(OCH_3)C_6H_5$$

I

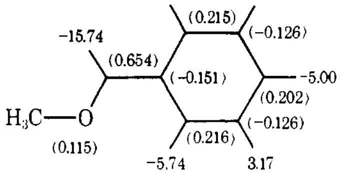
The foregoing data establish the following points: (a) the high intensity of the ESR signals indicate that reduction to the anion is extensive, (b) the unpaired electron resides predominantly on the organic moiety of the molecule (cf. *g* value, small ^{53}Cr splitting, and narrow line widths of 75 mG), (c) the rotation of the phenyl group is slow on the ESR time scale.

A better picture of the unpaired electron distribution in this radical anion emerges by consideration of the α-methoxy benzyl radical in which the α proton formally replaces the negatively charged $(CO)_5Cr$ fragment. This radical was generated by photolysis of a cyclopropane solution of benzyl methyl ether containing di-*tert*-butyl peroxide[8] (Table I).

$$C_6H_5CH_2OCH_3 \xrightarrow[\text{[-H·]}]{t\text{-BuO·}} H\text{-}\dot{C}(OCH_3)C_6H_5$$

The inequivalence of one pair of phenyl protons again implies a static phenyl group on the ESR time scale. A comparison of the ESR splittings for these radicals indicates only a minor perturbation of the unpaired electron distribution by the $(CO)_5Cr$ fragment in the organometallic radical relative to its organic analogue. Using the aromatic proton couplings as a relative measure of the unpaired spin density on the phenyl groups, it is tempting to identify the *average* decrease of about 7% in their magnitudes for the organometallic radical with the unpaired electron density reaching the $Cr(CO)_5$ group.

The proton hyperfine couplings (gauss) as well as the π spin densities for the oxygen and carbon centers (values in parentheses) for an unoptimized geometry[9] of the methoxybenzyl radical calculated by the INDO method[10] are given below. The agreement is sufficiently good to make the calculated π spin distribution, i.e., 65.4% on the central carbon, 22.9% on the coplanar phenyl group, and 11.5% on oxygen, an acceptable approximation. Judging by the proton splittings, a similar unpaired electron distribution pertains to the chromium radical anion with a small allowance for the spin density on the $(CO)_5Cr$ group. MO calculations were also carried out for the chromium carbene radical anion itself.[11] They predict that the singly occupied MO is distributed 4.3% on the metal, 31.0% on the carbene carbon, 42.3% on the phenyl group, and 13.4% on oxygen. These calculations agree with the ESR results in predicting a mostly ligand character for the singly occupied MO. It should also be noted that the ESR results require a coplanar



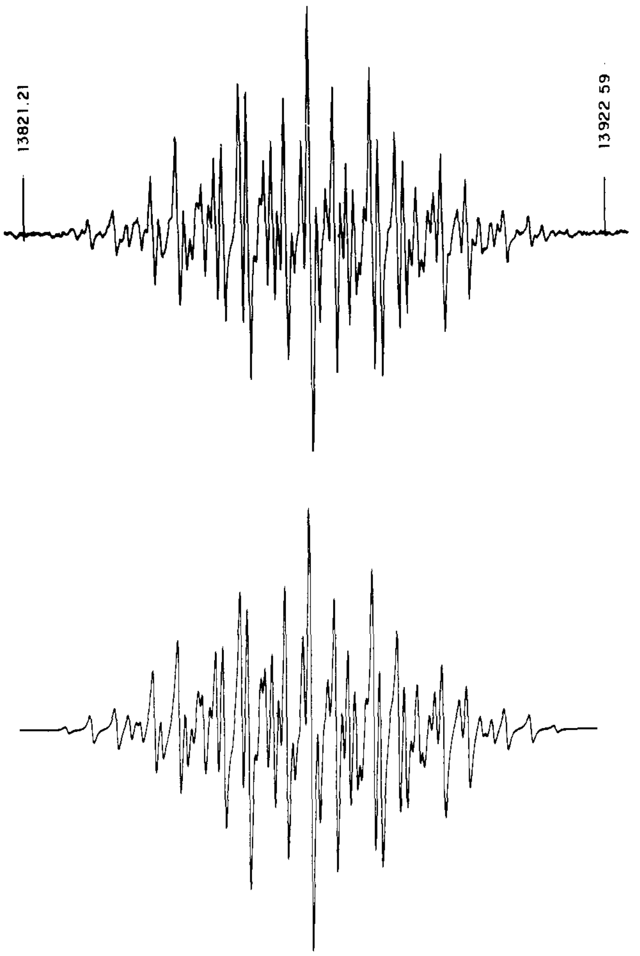


Figure 2. Experimental and calculated ESR spectra of $(\mathrm{CO})_5\bar{\mathrm{W}}$-$\dot{\mathrm{C}}(\mathrm{C_6H_5})_2$ formed by reduction of the neutral carbene complex with *tert*-butyllithium in THF at −78°.

arrangement of the phenyl group in contrast to the structure of the neutral carbene complex.[12]

Low-temperature reduction with Na/K alloy of analogous molybdenum and tungsten methoxyarylcarbenes as well as of (diphenylcarbene)pentacarbonyltungsten (Figure 2) also yielded the corresponding radical anions (Table I).

$$\underset{}{(\mathrm{CO})_5\mathrm{W}^- \text{-} \mathrm{C}^+(\mathrm{C_6H_5})_2} \xrightarrow{+e} \underset{\mathrm{II}}{(\mathrm{CO})_5\mathrm{W}^- \text{-} \dot{\mathrm{C}}(\mathrm{C_6H_5})_2}$$

The decreasing phenyl proton splittings for the carbene radical anions of the heavier metals indicate an increasing spin delocalization over the organometallic fragment (about 10% for the tungsten methoxyphenyl radical). The tungsten diphenylcarbene radical anion can be compared with the diphenylmethyl radical[14] (Table I). The average reduction of the aromatic proton splittings for the tungsten species of about 29% indicates the largest spin delocalization over the metal group in this series which is consistent with the largest g value and the largest $^{183}\mathrm{W}$ splitting (Table I).[15]

Reduction of the carbene complexes was also accomplished with typical one-electron reducing agents such as sodium naphthalide in THF and with $\mathrm{C_5H_5Fe(CO)_2}^-$ and $\mathrm{Mn(CO)_5}^-$, which are not generally regarded as one-electron donors. In these reactions, single electron transfer (SET) necessarily leads to the formation of the corresponding transition metal radicals [$\mathrm{C_5H_5\dot{F}e(CO)_2}$ and $\mathrm{\dot{M}n(CO)_5}$] which are too short lived to be observed directly.[16] Radicals I and II are also formed by reaction with triphenyl- and trimethylmethylidenephosphoranes manifestly by a SET mechanism.[17]

$$(\mathrm{CO})_5\bar{\mathrm{W}}\text{-}\mathrm{C}^+(\mathrm{C_6H_5})_2 + \bar{\mathrm{C}}\mathrm{H_2}\text{-}\mathrm{P}^+(\mathrm{C_6H_5})_3 \rightarrow \underset{\mathrm{II}}{(\mathrm{CO})_5\bar{\mathrm{W}}\text{-}\dot{\mathrm{C}}(\mathrm{C_6H_5})_2} + \underset{\mathrm{III}}{\dot{\mathrm{C}}\mathrm{H_2}\text{-}\mathrm{P}^+(\mathrm{C_6H_5})_3}$$

The collapse of the resulting radical ion pair presumably leads to the betaine-like intermediate previously postulated.[18] Radical cations such as III are not observed in these static experiments but can be detected by flow and photochemical ESR techniques.[19]

Phenyllithium and *tert*-butyllithium can also produce high concentrations of the radical anions of Table I in THF solutions at low temperatures.[20,21] If these reactions with chromium methoxyphenylcarbene are carried out at room temperature by mixing the reactants in the ESR cavity, an additional broad line (ΔH = 3 G, g = 2.014) can be observed under flow conditions. We attribute this line to the transient $(\mathrm{CO})_5\mathrm{Cr}\cdot^-$ species which can dimerize to yield the diamagnetic $(\mathrm{CO})_{10}\mathrm{Cr_2}^{2-}$ dianion. This species arises most likely by homolysis of the metal–carbon bond of the adduct IV[22] which can be formed either by nucleophilic attack *or by recombination of the radical pair* resulting from a single electron transfer from the lithium reagent. The formation of the substituted ethane V in the above reaction[23] is also consistent with a radical mechanism.

$$(\mathrm{CO})_5\mathrm{Cr}^-\text{-}\mathrm{C}^+(\mathrm{OCH_3})\mathrm{C_6H_5} \xrightarrow{\mathrm{C_6H_5Li}} \underset{\mathrm{IV}}{(\mathrm{CO})_5\mathrm{Cr}^-\text{-}\mathrm{C}(\mathrm{OCH_3})(\mathrm{C_6H_5})_2}$$

$$(\mathrm{CO})_5\mathrm{Cr}^-\text{-}\mathrm{C}(\mathrm{OCH_3})(\mathrm{C_6H_5})_2 \rightarrow (\mathrm{CO})_5\mathrm{Cr}\cdot^- + \dot{\mathrm{C}}(\mathrm{OCH_3})(\mathrm{C_6H_5})_2$$

$$2\dot{\mathrm{C}}(\mathrm{OCH_3})(\mathrm{C_6H_5})_2 \rightarrow \underset{\mathrm{V}}{(\mathrm{C_6H_5})_2(\mathrm{CH_3O})\mathrm{C}\text{-}\mathrm{C}(\mathrm{OCH_3})(\mathrm{C_6H_5})_2}$$

Acknowledgment. We are grateful to Professor R. R. Schrock for samples of methylidenephosphoranes and to Messrs. B. F. Gordon and J. J. O'Reilly for technical assistance.

References and Notes

(1) E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, **1**, 580 (1964).

(2) For reviews see (a) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972); (b) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973).

(3) (a) C. G. Kreiter and V. Formacek, *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) C. J. Ciapanelli, F. A. Cotton, and L. Kruczynski, *J. Organomet. 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).

(4) A. Davidson and D. L. Reger, *J. Am. Chem. Soc.*, **94**, 9237 (1972).

(5) T. F. Block, R. F. Fenske, and C. P. Casey, *J. Am. Chem. Soc.*, **98**, 441 (1976).

(6) K. Okamoto, Y. Matsui, and H. Shingu, *Bull. Chem. Soc. Jpn*, **38**, 153 (1965); **42**, 3249 (1969).

(7) Mixtures of THF and hexamethylphosphoramide were found to afford spectra of greatly enhanced resolution compared to THF.

(8) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **93**, 846 (1971).

(9) l(CC) = 1.39 Å, l(CO) = 1.37 Å, $l(\mathrm{OCH_3})$ = 1.42 Å, l(CH) = 1.09 Å, trigonal and tetrahedral angles.

(10) (a) J. A. Pople, D. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968). (b) We obtained a copy of the program CNINDO from the Quantum Chemical Program Exchange, Indiana University.

(11) The geometry of I was that reported for $(\mathrm{CO})_5\mathrm{CrC(OCH_3)C_6H_5}$[12] with the exception that the phenyl ring was placed in the same plane as the Cr atom and the $\mathrm{OCH_3}$ group. Calculations on the open shell system were carried out using reported procedures (J. L. Petersen, D. L. Lichtenberger, R. F. Fenske, and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6433 (1975)).

(12) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 642 (1968).

(13) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).

(14) A. R. Bassindale, A. J. Bowles, A. Hudson, R. A. Jackson, K. Schreiner, and A. Berndt, *Tetrahedron Lett.*, 3185 (1973).

(15) A part of this reduction may also be attributed to structural and torsional changes involving the phenyl groups. Torsional vibrations of substantial

amplitude for the phenyl groups in these radical anions are indicated by the appreciable temperature dependence of the aromatic proton splittings. It should be noted that the ^{183}W splitting has increased by 22.6% relative to tungsten methoxyphenyl radical anion.
(16) P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975). A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *Chem. Commun.*, 966 (1974).
(17) Easy donation of an electron from the electron pair at the ylidic carbon atom of trimethylmethylidenephosphorane is consistent with its remarkably low first ionization potential of 6.87 eV. K. A. Ostoja Starzewski, T. T. Dieck, and H. Bock, *J. Organomet. Chem.*, **65**, 311 (1974).
(18) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **94**, 6543 (1972).
(19) P. J. Krusic, manuscript in preparation.
(20) The spectrum of the radical anion $(CO)_5W^-\dot{C}Ph_2$ formed by reaction with phenyllithium becomes undetectable on warming the sample to 0°. Continued warming to ~50° produces a new intense spectrum composed of exceedingly narrow lines ($\Delta H \sim$ 50 mG). The complexity of this spectrum so far prevented its analysis.
(21) The redox properties of organolithium reagents are well recognized. Cf., for example, (a) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964); (b) G. A. Russell and D. W. Lamson, *ibid.*, **91**, 3967 (1969); (c) H. Fischer, *J. Phys. Chem.*, **73**, 3834 (1969).
(22) Alkylpentacarbonyltungsten anions have been reported recently. C. P. Casey, S. W. Polichnowski, and R. L. Anderson, *J. Am. Chem. Soc.*, **97**, 7375 (1975).
(23) E. O. Fischer and S. Riedmuller, unpublished results quoted by E. O. Fischer, *Pure Appl. Chem.*, **30**, 353 (1972).

P. J. Krusic,* U. Klabunde
Contribution No. 2341
Central Research and Development Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

C. P. Casey, T. F. Block
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received December 15, 1975

Squalene Synthetase. Differentiation between the Two Substrate Binding Sites by a Substrate Analogue[1]

Sir:

Squalene (**1a**) is synthesized biologically from two farnesyl pyrophosphate (**2a**) residues via intermediate **3a**.[2,3] Squalene synthetase, the membrane-bound enzyme which catalyzes this complex transformation in the presence of NADPH and Mg^{2+}, has recently been solubilized from yeast.[4,5] Kinetic studies indicate that, in forming **3a**, the pyrophosphate moiety of the farnesyl residue which is bound first to the enzyme is released before the second farnesyl unit is bound.[4] Little beyond this is known, however, about the enzyme mechanism or the active site topology.[2-4] We now report our studies with 2-methyl farnesyl pyrophosphate (**2b**), a substrate analogue, which for the first time demonstrates a difference in the tolerance to substrate variation of the two farnesyl pyrophosphate binding sites.[6]

Wittig condensation of geranyl acetone with diethyl-1-carboethoxyethyl phosphonate yielded ethyl 2-methyl-farnesoate (84%, *E*:*Z* ratio by GLC 54:46).[7,8] The *E,E* isomer, isolated by spinning-band distillation, was reduced with $LiAlH_4$, and the alcohol was pyrophosphorylated to give **2b**.[8,9] The structure of **2b** was confirmed by quantitative phosphorus analysis[10] and by regeneration of 2-methyl farnesol on treatment with bacterial alkaline phosphatase.[11] Substitution of ^3H-$LiAlH_4$ into the synthetic sequence gave [1-^{3}H]**2b** (sp act. 0.5 mCi/mmol).

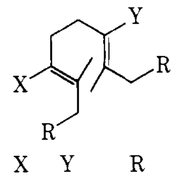
Standard incubations in this study contained the following (concentration units): substrate(s), 20 μM; $MgCl_2$, 10 mM, NADPH, 1.6 mM; NH_4OH, 0.8 mM; protein, 1.34 mg/ml;[12] and potassium phosphate buffer (pH 7.5), 50 mM. Incubations (37°, 1-10 min) were terminated with ethanol and the hydrocarbon products, extracted with petroleum ether, were chromatographed on silica gel or neutral alumina before liquid scintillation counting or structural studies.

Incubation of [^{3}H]**2b** gave a radiolabeled product which behaved like squalene on silica gel TLC (hexane, R_f 0.37). Its formation was absolutely dependent on the presence of NADPH and active enzyme, while it was stimulated by addition of unlabeled **2a** to the incubation. GLC analysis showed approximately equal amounts of radioactivity associated with two peaks, one coincident with endogenous squalene (system A, 232 °C, 7.6 min; system B, 260 °C, 14.8 min) and the other at longer retention time (system A, 232 °C, 10.0 min; system B, 260 °C, 19.35 min).[13] Both peaks were formed whether the incubation was supplemented with unlabeled **2a** or not. Control experiments showed that squalene, and probably **2a**, were present in small amounts in the enzyme preparation.

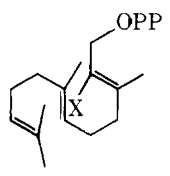
Unambiguous chemical routes were used to prepare the all-*E* isomers of 11,14-dimethylsqualene (**1b**)[14] and 11-methylsqualene (**1c**).[17] The GLC retention time of authentic **1b** (system A, 232 °C, 13.3 min) did not correspond to either labeled peak in the biosynthetic sample, while authentic **1c** had the same retention time as the slower radioactive peak. The identity of this second GLC peak as **1c** was firmly established by GLC-mass spectrometry,[20] since the fragmentation patterns of both samples were identical.[21]

Monomethylsqualene (**1c**) can be formed by distinct pathways in which **2b** replaces **2a** in either the first or second catalytic step. These two alternatives are distinguishable, since a proton is exchanged on the first but not the second farnesyl residue.[2,4] Deuterated **1c**, prepared by incubation of approximately equimolar amounts of 1-dideuterio-**2a**[22] and unlabeled **2b**, was analyzed by GLC-mass spectrometry.[20] The parent ion and all fragment ions retaining the central carbons were shifted upward by one (not two) mass units relative to the corresponding peaks in the spectrum of unlabeled **1c**.[21] This implies that only **2a** is acceptable at the first site and, therefore, **2b** can only replace the second farnesyl moiety.

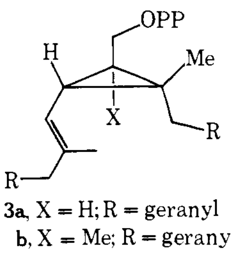
The inability of **2b** to function as a first substrate in synthesis of **1c** can result from failure to form a Michaelis complex, or, if bound, failure to meet catalytic requirements. To investigate if **2b** is bound at the first substrate site, this analogue was evaluated as an inhibitor of squalene biosynthesis from [1-^{3}H]**2a** (sp act. 6 mCi/mmol).[22] Standard 2-min incubations were carried out in which the concentration of [1-^{3}H]**2a** was varied from 1.25 to 5.00 μM in



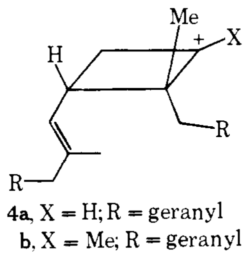
	X	Y	R
1a,	H	H	geranyl
b,	Me	Me	geranyl
c,	Me	H	geranyl



2a, X = H
b, X = Me



3a, X = H; R = geranyl
b, X = Me; R = geranyl



4a, X = H; R = geranyl
b, X = Me; R = geranyl

R = geranyl = $(CH_3)_2C{=}CHCH_2CH_2(CH_3)C{=}CHCH_2$-