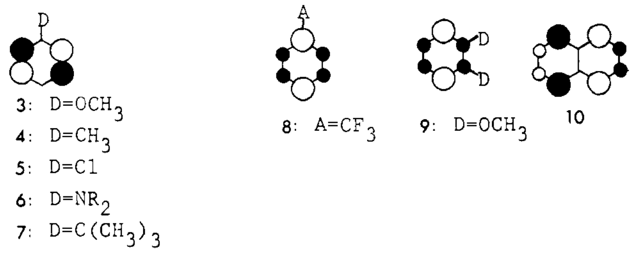
3: D=OCH_3
4: D=CH_3
5: D=Cl
6: D=NR_2
7: D=$C(CH_3)_3$
8: A=CF_3
9: D=OCH_3
10

Figure 1. Estimated LUMO coefficients for substituted arenes.

Another view of the pathway would focus on HOMO-LUMO interactions, presumably HOMO (carbanion) and LUMO (arene complex).[7] The site of attack would correlate with the magnitude of the orbital coefficients at the arene atoms in LUMO (complex). Unfortunately, neither ESR data nor detailed calculations are available to specify the coefficient distribution for the arene complexes studied here. Nevertheless, we find a *useful* correlation of regioselectivity with LUMO coefficients estimated for the *free arene ligand*, ignoring any perturbation in coefficient distribution due to the $Cr(CO)_3$ unit. Structures **3–11** (Figure 1) display the estimated relative magnitude of LUMO coefficients;[10,11] the correlation with position of anion attack is quite good. Obviously, it is based on a superficial analysis of orbital interactions (ignoring the metal!) and does not necessarily reveal information about the actual mechanism. But it is simple to apply and may have some predictive value.

Discrepancies are also obvious: anisole and aniline (where ortho is not favored), and *tert*-butylbenzene (where para is favored). We are seeking a better understanding of polar effects and conformational effects in **1**, which may allow these to fit into a more refined rule for regioselectivity.[13]

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(4) In each example in Table I, the carbanion was generated at −78 °C in tetrahydrofuran (or THF–HMPA mixtures) and the arene complex was added. After the mixture had been stirred at 0 °C under argon for 0.2–1.0 h, excess iodine was added and the resulting substituted arenes were isolated. The product ratios were determined by quantitative GLC, the products were identified by comparison of spectral and GLC data with samples synthesized by standard methods, and the yields were determined by weighing the distillation fraction containing the product isomers (and nothing else). The chromium complexes were prepared by the standard method of heating the arene with chromium hexacarbonyl in dioxane for several days.

(5) M. F. Semmelhack and H. T. Hall, Jr., *J. Am. Chem. Soc.*, **96**, 7092 (1974).

(6) The trimethylsilyl substituent is attached efficiently by ortho metalation of π-anisolechromium tricarbonyl and quenching with chlorotrimethylsilane: M. F. Semmelhack, J. Bisaha, and M. Czarny, submitted for publication.

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(11) These diagrams are based on simple Hückel molecular orbitals (HMO) with substituent perturbation.[10c] The patterns of LUMO coefficients from ESR spectra of radical anions are generally in line with these pictures. We assume that the LUMO for chlorobenzene will be similar to that for arenes with resonance donor substituents, and that LUMO for *o*-dimethoxybenzene is similar to LUMO for *o*-xylene (large coefficients adjacent to the substituents).[12]

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(13) We are pleased to acknowledge financial support from the National Science Foundation and discussions with Roald Hoffmann, Tom Albright, and Barry Carpenter.

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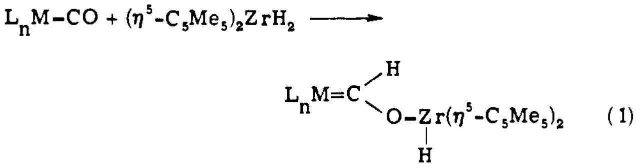
Reduction of Coordinated Carbon Monoxide to "Zirconoxy" Carbenes with Permethylzirconocene Dihydride

Sir:

We have reported the stoichiometric reduction of carbon monoxide by alkyl and hydride derivatives of bis(pentamethylcyclopentadienyl)zirconium(IV).[1,2] Most of our observations may be interpreted in terms of a sequence involving coordination of CO to the 16-electron species $(\eta^5\text{-}C_5Me_5)_2ZrR_2$ (R = H, alkyl), followed by rapid intramolecular migratory insertion of CO into either a Zr–H or Zr–C bond to generate η^2-formyl or acyl species.[2,3] The final product types observed were rationalized on the basis of an oxy carbenoid reactivity imparted to the carbonyl carbon as a result of its η^2 coordination mode.

A possible exception to this general scheme is the reaction of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**1**) which leads over several hours under H_2 (1 atm) at 25 °C to a nearly quantitative yield of $[(\eta^5\text{-}C_5Me_5)_2ZrH]_2(\mu\text{-}OCH{=}CHO)$ (**2c**).[2,4] Since **2c** is not among the products formed in reactions of **1** with free carbon monoxide,[4] we wondered whether **1** could serve to transfer hydride directly to CO which is coordinated to another zirconium, or, more generally, to carbonyl ligands of other transition metal complexes (eq 1). Consideration of



$$L_nM\text{-}CO + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \longrightarrow L_nM{=}C\begin{matrix}\diagup H\\ \diagdown O\text{-}\underset{\displaystyle H}{\underset{|}{Zr}}(\eta^5\text{-}C_5Me_5)_2\end{matrix} \qquad (1)$$

this possibility appears warranted in any case, since the hydrogen ligands of **1** are distinctly hydridic, comparable with trialkylborohydride in reactivity. The latter has recently been shown to convert a number of metal carbonyls to the corresponding formyl anions.[5-7]

In view of the large number of stable carbene complexes of molybdenum and tungsten reported, we have carried out a study of the reactions of **1** with $(\eta^5\text{-}C_5H_5)_2M(CO)$ (M = Mo, W) in hopes of observing directly the product of the proposed reaction type (eq 1). $(\eta^5\text{-}C_5H_5)_2W(CO)$[8] (**3**) does indeed react smoothly with 1 equiv of **1** in toluene solution at −80 °C to yield $(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**4**)[9] which may be isolated as red-brown crystals in 95% yield (eq 2). When this

$$(\eta^5\text{-}C_5H_5)_2W(CO) + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \longrightarrow (\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 \qquad (2)$$

reaction was carried out in a sealed NMR tube (benzene-d_6) with a molar ratio of **1**:**3** of 0.77:1.00, the spectrum shown in Figure 1 was obtained. The inequivalence of the two $(\eta^5\text{-}C_5H_5)$ rings for **4** may be attributed to a π interaction of the carbon p orbital with the filled b_2 orbital in the equatorial plane of the $(\eta^5\text{-}C_5H_5)_2W$ moiety thus firmly locking the "zirconoxy" carbene ligand with its hydrogen directed toward one cyclopentadienyl ligand and oxygen toward the other. A similar

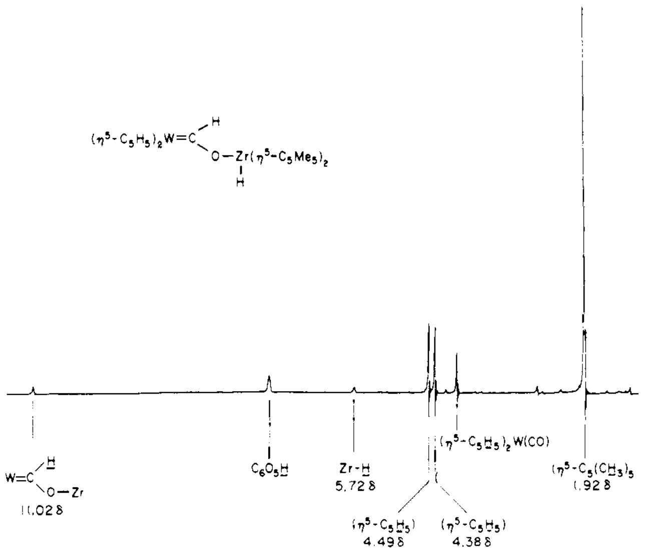


Figure 1. ^1H NMR spectrum (benzene-d_6) for product mixture from reaction 2.

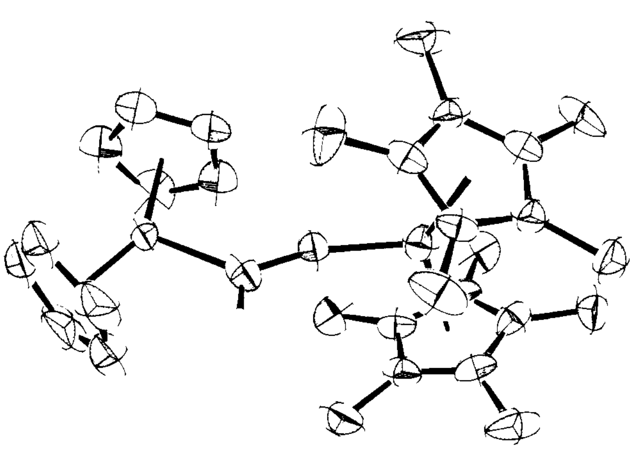


Figure 2. Molecular configuration of $(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$.

geometry has been observed for the carbene complexes $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Ta(CH_2)(CH_3)$ and $(\eta^5\text{-}C_5H_5)_2Ta(CHPh)(CH_2Ph)$.[10,11] The position of the carbene hydrogen resonance is comparable with those found in the tantalum alkylidenes (δ 10.22 and 11.03, respectively),[10,11] but rather surprisingly the W=CHO resonance is observed as a barely resolved doublet due to coupling with Zr-H ($^4J_{HH} = 1.0$ Hz) as confirmed by decoupling experiments. The latter appears as a rather broad signal at δ 5.72.

This structure for **4** was confirmed by diffraction X-ray methods. Single crystals of $(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(\eta^5\text{-}C_5Me_5)_2$ obtained from toluene solution are monoclinic (space group $P2_1/n$) with $a = 10.178$ (3), $b = 35.611$ (14, $c = 8.293$ (2) Å; $\beta = 109.93$ (2)°; $Z = 4$. Two sets of diffraction data ($hk\bar{l}$, hkl, $\bar{h}\bar{k}l$, and $\bar{h}\bar{k}\bar{l}$ octants), each containing 5080 independent reflections with $1.5° < 2\theta < 50°$, were collected on a Syntex P2$_1$ automated diffractometer using graphite-monochromated Mo Kα radiation and ω scans 1° wide. Using anisotropic thermal parameters for all nonhydrogen atoms, least-squares refinement on 3890 averaged, independent reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ has yielded an R index of 0.053 with goodness of fit of 2.16.[12,13] The cyclopentadienyl ring centroids and carbene carbon are coplanar in a roughly trigonal arrangement around tungsten (Figures 2 and 3). The pentamethylcyclopentadienyl ring centroids and oxygen comprise three fourths of the usual pseudotetrahedral arrangement about zirconium; the (as yet unrefined) hydride ligand undoubtedly occupies the fourth coordination site. All cyclopentadienyl and pentamethylcyclopentadienyl ligands are coordinated in a conventional *pentahapto* mode (W—C distances, 2.28 (2)–2.31 (2) Å; Zr—C distances, 2.50 (2)–2.58 (2) Å) with normal R(1)-W-R(2) and R(3)-Zr-R(4) angles (Figure 3). The W=C bond distance (2.005 (13) Å) is short when compared with the corresponding distances for $(CO)_5W{=}CPh_2$ (2.14 (2) Å)[14] and $(CO)_5Mo{=}C(OC_2H_5)(SiPh_3)$ (2.15 (2) Å).[15] The C—O bond distance is at the long end of the range found for alkoxy substituted carbenes.[16,17] Both of these features suggest a moderately strong W=C π bond and a reduced C—O π interaction. The greater π basicity of the tungstenocene moiety (relative to $[(CO)_5W]$)[18] and the π acidity of the Zr(IV) substituent are undoubtedly important factors.

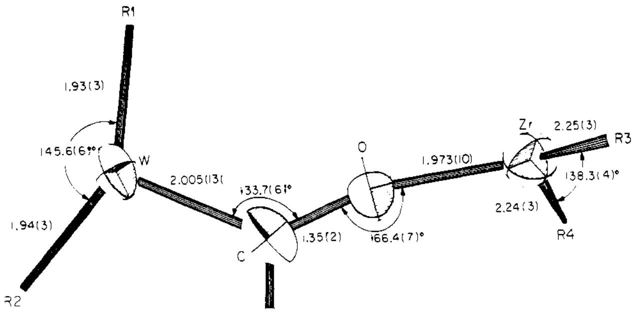


Figure 3. Skeletal view of **4**.

4 exhibits remarkable thermal stability; toluene solutions are unchanged after hours at 150 °C (NMR). When treated with 1 atm of H_2 at 170 °C over a 48-h period, $(\eta^5\text{-}C_5H_5)_2WH_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ are obtained in ~50% yield (eq 3). A fivefold excess of ethylene reacts smoothly with

$$(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 + 2H_2 \xrightarrow{170°} (\eta^5\text{-}C_5H_5)_2WH_2 + (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) \quad (3)$$

4 in a sealed NMR tube at 70 °C to afford only the corresponding ethyl derivative (**5**);[19] there is no evidence of addition to the zirconoxy carbene moiety (eq 4).

$$(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 + C_2H_4 \longrightarrow (\eta^5\text{-}C_5H_5)_2W{=}CHOZr(CH_2CH_3)(\eta^5\text{-}C_5Me_5)_2 \quad (4)$$

$(\eta^5\text{-}C_5H_5)_2Mo(CO)$[20] and $(\eta^5\text{-}C_5H_5)_2Cr(CO)$[21] undergo similar reactions with **1** to yield $(\eta^5\text{-}C_5H_5)_2Mo{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**6**)[22] and $(\eta^5\text{-}C_5H_5)_2Cr{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**7**),[23] respectively. **6** is comparable with **4** in stability. **7** may be isolated as red-orange crystals, but decomposes in solution over a period of several minutes at room temperature.

This reaction type was extended to the niobium carbonyl derivative $(\eta^5\text{-}C_5H_5)_2Nb(H)(CO)$.[24] Once again a rapid reaction is observed with **1** at −80 °C to generate the zirconoxy carbene complex $(\eta^5\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**8**)[25] in nearly quantitative yield (NMR) (eq 5).[26]

$$(\eta^5\text{-}C_5H_5)_2Nb(H)(CO) + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \longrightarrow (\eta^5\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 \quad (5)$$

Interestingly structure **8** would formally result from α C-H abstraction from its tautomer $(\eta^5\text{-}C_5H_5)_2Nb{—}CH_2OZr(H)(\eta^5\text{-}C_5Me_5)_2$. This tautomer could in fact be trapped at 25 °C by addition of CO (1 atm) providing $(\eta^5\text{-}C_5H_5)_2(CO)Nb{—}CH_2OZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**9**)[27] in 95% yield (eq 6). **8** also undergoes a smooth reaction with H_2 (1 atm) at 25 °C to yield

$$(\eta^5\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 + CO \longrightarrow (\eta^5\text{-}C_5H_5)_2(CO)Nb{-}CH_2OZr(H)(\eta^5\text{-}C_5Me_5)_2 \quad (6)$$

$$(\eta^5\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 + 2H_2 \xrightarrow{25^\circ} (\eta^5\text{-}C_5H_5)_2NbH_3 + (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) \quad (7)$$

$(\eta^5\text{-}C_5H_5)_2NbH_3$ and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (eq 7).[28] The facility of reaction 7 vis-à-vis reaction 3 may be attributed to the availability of a tautomerization pathway for **8** which generates a formal 16-electron Nb(III) species capable of oxidatively adding H_2.

These new results bring into question the occurrence of an *intra*molecular hydride transfer for the rearrangement of $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ to $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH)$. We are presently extending our studies of this reaction type to the zirconium carbonyl systems as well as to group 8 transition metal carbonyls.

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(8) Obtained by Na/Hg reduction of $(\eta^5\text{-}C_5H_5)_2WCl_2$ under 1 atm of CO as described by J. L. Thomas, *J. Am. Chem. Soc.*, **95**, 1838 (1973).

(9) Calcd for $C_{31}H_{42}OWZr$: C, 52.76; H, 6.00; W, 26.05; Zr, 12.93. Found: C, 52.48; H, 6.14; W, 26.31; Zr, 12.70. IR (Nujol mull): ν(ZrH) 1560 cm^{-1}, ν(CO) 1190 cm^{-1}.

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(12) Goodness of fit = $[\Sigma w\,(F_o^2 - s^2F_c^2)/(N - P)]^{1/2}$, where $N = 3890$ reflections $> 3\sigma$, and the number of parameters $P = 314$. Refinement with full data yielded $R = 0.075$, and goodness of fit = 1.61, where $N = 4495$ and $P = 314$.

(13) Refinement was by least-squares minimization of $\Sigma w(F_o^2 - s^2F_c^2)^2$ where $1/s$ is the scale factor for F_o and $w = 1/\sigma^2(F_o^2)$. Complete structural information will be available in a forthcoming article.

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(18) This increased π basicity is demonstrated by the reduced ν(CO) for $(\eta^5\text{-}C_5H_5)_2W(CO)$ (1865 cm^{-1}) relative to ν(CO) for $W(CO)_6$ (~1980 cm^{-1}).

(19) NMR (benzene-d_6): $[\eta^5\text{-}C_5H_5]$, s, δ 4.39 (5 H), and s, δ 4.41 (5 H); CHO, s, δ 11.12 (1 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ 1.84 (30 H); $ZrCH_2CH_3$, q, δ 0.83 (2 H); $ZrCH_2CH_3$, t, δ 1.44 (3 H) ($^3J = 8$ Hz).

(20) Prepared by photolysis of $(\eta^5\text{-}C_5H_5)_2MoH_2$ under CO (1 atm): G. L. Geoffroy, M. G. Bradley, and R. Bierantozzi, *Adv. Chem. Ser.*, **No. 167**, 181 (1978).

(21) K. L. T. Wong and H. H. Brintzinger, *J. Am. Chem. Soc.*, **97**, 5743 (1975).

(22) Calcd for $C_{31}H_{42}OMoZr$: C, 60.27; H, 6.85; Mo, 15.53; Zr, 14.76. Found: C, 60.09; H, 6.76; Mo, 15.44; Zr, 14.60. NMR (benzene-d_6): $[\eta^5\text{-}C_5H_5]$, s, δ 4.50 (5 H), and s, δ 4.53 (5 H); CHO, s, δ 11.17 (1 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ 1.92 (30 H); ZrH, s, δ 5.80 (1 H). IR (Nujol mull): ν(ZrH) 1543 cm^{-1}, ν(CO) 1160 cm^{-1}.

(23) NMR (toluene-d_8) at −3 °C: $[\eta^5\text{-}C_5H_5]$, s, δ 4.12 (5 H), and s, δ 4.24 (5 H); CHO, s, δ 13.27 (1 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ 1.93 (30 H); ZrH, s, δ 5.94 (1 H).

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(25) Calcd for $C_{31}H_{43}ONbZr$: C, 60.46; H, 7.04. Found: C, 58.76; H, 6.80. ^{1}H NMR (benzene-d_6): $[\eta^5\text{-}C_5H_5]$, s, δ 5.02 (10 H); NbH, s, δ −3.14 (1 H); CHO, s, δ 11.63 (1 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ 1.99 (30 H); ZrH, s, δ 5.70. ^{13}C NMR (benzene-d_6): $[\eta^5\text{-}C_5H_5]$, d, δ 92.8 ($^1J_{CH} = 143$ Hz), and d, δ 90.9 ($^1J_{CH} = 143$ Hz); CHO, d, δ 265.5 ($^1J_{CH} = 136$ Hz); $[\eta^5\text{-}C_5(CH_3)]$, s, δ 116.9, and s, δ 116.4; $[\eta^5\text{-}C_5(CH_3)_5]$, q, δ 7.80 ($^1J_{CH} = 130$ Hz). IR (Nujol mull): ν(ZrH) 1567 cm^{-1}; ν(NbH) 1701 cm^{-1}, ν(CO) 1192 cm^{-1} (ν(^{13}CO) 1150 cm^{-1}).

(26) Whereas there could be some ambiquity concerning the origin of the hydrogen which was transferred to the carbonyl group in reaction 5, treatment of $(\eta^5\text{-}C_5H_5)_2Nb(H)(CO)$ with $[\eta^5\text{-}C_5(CD_3)_5]_2ZrD_2$ yields $(\eta^5\text{-}C_5H_5)_2(H)Nb{=}CDOZr(D)[\eta^5\text{-}C_5(CD_3)_5]_2$. Thus, as in all other cases, this hydrogen originates at zirconium.

(27) Calcd for $C_{32}H_{43}O_2NbZr$: C, 59.70; H, 6.58; Zr, 14.17. Found: C, 59.36; H, 6.94; Zr, 14.33. NMR (benzene-d_6): $[\eta^5\text{-}C_5H_5]$, s, δ 4.72 (10 H); OCH_2 and ZrH, s, δ 5.23 (3 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ, 2.01 (30 H). IR (Nujol mull): ν(ZrH) 1553 cm^{-1}; ν(CO) 1126 cm^{-1}; ν(C≡O) 1898 cm^{-1}.

(28) Treatment of $(\eta^5\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta^5\text{-}C_5ME_5)_2$with excess D_2 (1 atm) yielded a mixture of $(\eta^5\text{-}C_5Me_5)_2Zr(H)_n(D)_{1-n}(OCH_mD_{3-m})$ (n = 0, 1; m = 0, 1, 2, 3), suggesting that scrambling of the carbene hydrogen with the D_2 atmosphere occurs during reaction 7.

(29) Fannie and John Hertz Foundation Fellow.

(30) Alfred P. Sloan Fellow, 1976–1978, and Camille and Henry Dreyfus Teacher-Scholar, 1977–1982.

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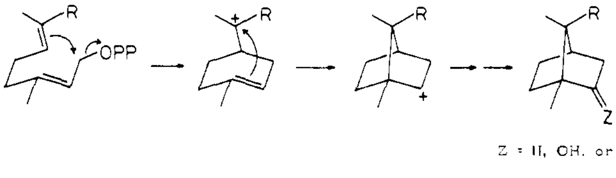
Intramolecular Dibromo Ketone–Iron Carbonyl Reaction in Terpene Synthesis

Sir:

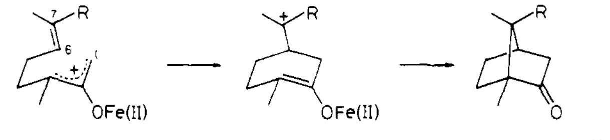
The iron carbonyl promoted cyclocoupling reaction of polybromo ketones and unsaturated substrates provides a powerful tool for the synthesis of five- and seven-membered carbocycles.[1] Trapping of the reactive 2-oxyallyl-iron(II) species with 1,3-dienes in a [3 + 4] manner produces 4-cycloheptenones efficiently, whereas [3 + 2] cycloaddition across an olefinic linkage gives cyclopentanone derivatives. The intramolecular version of such transformations, if feasible, would allow direct, highly ordered construction of polycyclic frameworks from open-chain systems. Reported herein is a new entry to polycyclic terpenes utilizing this strategy.

Possible [3 + 2] type cyclization was inspired by a biogenetic hypothesis. The carbon skeleton of mono- and sesquiterpenes having a bicyclo[2.2.1]heptane system can be derived from acyclic terpene precursors formally by carbocation-olefin cyclization (eq 1)[2] and this biogenetic formulation prompted



(1)

Z = H, OH, or O



(2)

us to examine the chemical sequence involving an oxyallyl-iron(II) intermediate (eq 2) which could open a new route to camphor and campherenone[3,4] starting from geraniol (or nerol) and farnesol, respectively.

This plan has worked indeed well. When a mixture of the dibromo ketone **1** (obtained from geraniol) and $Fe_2(CO)_9$ (1:1.2 mol ratio) in benzene was heated in a pressure bottle at