The presence of the free (unbonded) formyl group is clearly indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4**,[16] which exhibit peaks at δ 7.46 and 173.75 for the formyl hydrogen and carbon, respectively. The infrared spectrum shows a characteristic C=O stretch at 1599 cm^{-1}. At room temperature, compound **4** undergoes a fluxional process that exchanges the three phosphine ligands, causing the $^{31}P\{^1H\}$ NMR signal to appear as a singlet at 25 °C. However, as the compound is cooled to −80 °C, the exchange process is stopped, and the $^{31}P\{^1H\}$ NMR spectrum decoalesces to three well-separated doublet of doublet patterns. This fluxional process probably involves $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ interconversions of the oxapentadienyl ligand.

When compound **4** is refluxed in acetone, it gradually (over a period of 24 h) undergoes metal-centered activation of the aldehydic (formyl) C-H bond to produce the iridacyclopentenone complex $(\overline{IrCH_2CH{=}CHC{=}O})(PMe_3)_3(H)$ (**5**; Scheme III).[17,18] This conversion of **4** to **5** probably involves the 16e η^1-oxapentadienyl species (A, Scheme III) as the key intermediate. The X-ray crystal structure of **5**,[19] shown in Figure 2, exhibits an essentially planar five-membered ring (mean deviation of the ring atoms and oxygen 0.052 Å). The coordination geometry is octahedral, but unlike **2**, the phosphines adopt a *fac* arrangement. As a result, all three phosphines are inequivalent and give rise to three separate signals in the $^{31}P\{^1H\}$ NMR spectrum.[20] The hydride ligand resides trans to a phosphine ligand and exhibits a characteristically strong trans H-P coupling (J_{H-P} = 128.9 Hz).

In summary, we have demonstrated that metallaoxacyclohexadiene ("metallapyran") and metallacyclopentenone complexes can be synthesized via metal-centered activation of C-H bonds in (oxapentadienyl)metal precursors. The reaction chemistry of these novel metallacycles is currently under investigation in our laboratories and will be reported in a future communication.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8520680 and CHE-9003159) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of $IrCl_3 \cdot 3H_2O$ from Johnson Matthey, Inc., is gratefully acknowledged. Washington University's X-ray Crystallography Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456). The High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Note Added in Proof. Recently, we have discovered that iridaoxacyclohexadiene complex **2** is converted to the iridacyclopentenone complex *fac*-$(\overline{IrCH_2CH{=}CHC{=}O})(PEt_3)_3(H)$ upon stirring in benzene at 22 °C for 3 days.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for **2** and **5** and an ORTEP drawing showing the positions of disordered atoms in **2** (9 pages); tables of observed and calculated structure factor amplitudes for **2** and **5** (39 pages). Ordering information is given on any current masthead page.

(16) Spectroscopic data for **4** (carbon atoms in the chain are numbered by starting at the end opposite oxygen): ^1H NMR (C_6D_6, 22 °C, 300 MHz) δ 7.46 (d, J_{H-H} = 8.7 Hz, 1, H4), 4.32 (m, H2), 4.10 (m, H3), 1.16 (s, 28, PMe_3's), 0.71 (m, 2, H1's); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, 75 MHz) δ 173.7 (s, C4), 62.2 (d, J_{C-P} = 2.7 Hz, C3), 53.1 (s, C2), 22.8 (filled-in d, J_{C-P} = 33.8 Hz, PMe_3's), 17.3 (q, J_{C-P} = 8.3 Hz, C1); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C, 121 MHz, referenced to H_3PO_4) δ −54.3 (s). At low temperature, this singlet decoalesces to three dd patterns: $^{31}P\{^1H\}$ NMR ($C(O)(CD_3)_2$, −80 °C, 121 MHz) δ −45.5 (dd, J_{P-P} = 43.9, 15.1 Hz, 1), −51.1 (dd, J_{P-P} = 23.1, 15.1 Hz, 1), −55.5 (dd, J_{P-P} = 43.9, 23.1 Hz, 1). IR (toluene, 22 °C): 1599 cm^{-1} (C=O stretch).

(17) Synthesis of **5**: An acetone solution of **4** (0.12 g, 0.24 mmol) was refluxed under nitrogen for 24 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum. The resulting residue was extracted with pentane and filtered. The pentane extract was reduced in volume, treated with several drops of acetone, and cooled to −30 °C to produce very light yellow crystals of **5**, yield 0.096 g, 80%. Anal. Calcd for $C_{13}H_{32}IrOP_2$: C, 31.89; H, 6.60. Found: C, 32.04; H, 6.66.

(18) The conversion of **4** to **5** also occurs at room temperature in acetone solution, but *very slowly*.

(19) Crystal data for **5**: yellow prism, 0.20 × 0.34 × 0.58 mm; monoclinic, space group *Cc*, a = 16.165 (4) Å, b = 9.468 (3) Å, c = 13.990 (3) Å, β = 115.35 (2)°, V = 1935.0 (9) Å^3, Z = 4, d_{calcd} = 1.680 g/cm^3, μ = 71.10 cm^{-1}; Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation, 22 °C, $\theta/2\theta$ scanning technique; 4440 unique reflections with $3.5 < 2\theta < 55°$ collected, 3726 reflections with $I > 3\sigma(I)$ used in refinement; semiempirical absorption correction (ψ scans); R = 4.58%, R_w = 5.64%, GOF = 1.54, data-to-parameter ratio 23.1:1. The location of the hydride ligand was inferred from the positions of the heavy atoms in the molecule. In Figure 2, it was placed at an idealized position with Ir-H = 1.75 Å and angle P2-Ir-H = 180°.

(20) Spectroscopic data for **5** (carbon atoms in the chain are numbered by starting at the end opposite oxygen): ^1H NMR (C_6D_6, 22 °C, 300 MHz) δ 7.36 (br m, 1, H2), 6.18 (s, 1, H3), 2.91 (br d, J = 19.8 Hz, 1, H1), 1.86 (br m, 1, H1), 1.48 (d, J_{H-P} = 8.3 Hz, 9, PMe_3), 1.07 (d, J_{H-P} = 7.1 Hz, 9, PMe_3), 0.99 (d, J_{H-P} = 7.9 Hz, 9, PMe_3), −11.19 (dt, J_{H-P} = 128.9, 19.1 Hz, 1, Ir-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, 75 MHz) δ 161.6 (d, J_{C-P} = 5.9 Hz, C2), 152.1 (d, J_{C-P} = 24.0 Hz, C3), 21.9 (overlapping d's, PMe_3's), 17.6 (d, J_{C-P} = 23.2 Hz, PMe_3), 10.2 (dt, J_{C-P} = 65.5, 4.3 Hz, C1) (the quaternary carbon C4 was not observed); $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C, 121 MHz, referenced to H_3PO_4) δ −51.2 (m, 1), −55.1 (m, 1), −61.9 (m, 1).

$Co_2(CO)_8$-Catalyzed Reaction of Cyclic Ortho Esters with a Hydrosilane and Carbon Monoxide. Novel Method for Homologation of 1,2-, 1,3-, and 1,4-Diols

Naoto Chatani, Yasuteru Kajikawa, Hideaki Nishimura, and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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Summary: In the presence of $Co_2(CO)_8$, the reaction of cyclic ortho esters with a hydrosilane and carbon monoxide resulted in the incorporation of carbon monoxide to give diols having one additional carbon atom. The reaction proceeded under mild reaction conditions (0-25 °C, 1 atm of CO).

Recently, we reported the $Co_2(CO)_8$-catalyzed reaction of epoxides with a hydrosilane and carbon monoxide giving disilyl ethers of 1,3-diol derivatives as a result of incorporation of carbon monoxide.[1] The catalytic reaction can be regarded as a new method for the conversion of 1,2-diols to 1,3-diols, since a 1,2-diol has the same oxidation level

(1) (a) Murai, T.; Kato, S.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 6093. (b) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N., Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938.

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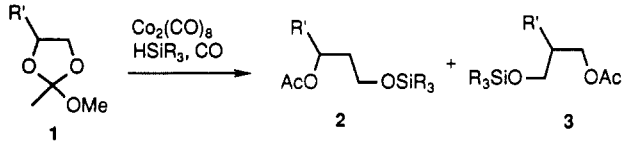
Table I. $Co_2(CO)_8$-Catalyzed Reaction of Five-Membered Cyclic Ortho Esters 1 with a Hydrosilane and Carbon Monoxide[a]

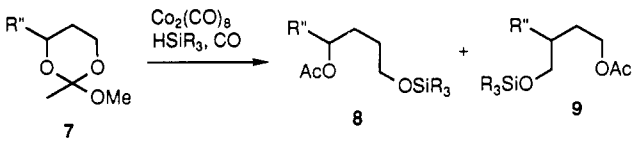


1 2 3

compd	R'	hydrosilane	solvent	temp/°C	time/days	yield/% (2:3)[b]
1a	H	$HSiEt_2Me$	C_6H_6	25	1	94
1b	Me	$HSiEt_2Me$	C_6H_6	25	1	57 (91:9)
1c	Bu	$HSiEt_2Me$	C_6H_6	25	2	69 (95:5)
1c	Bu	$HSiMe_3$	C_6H_6	25	3	72 (94:6)
1c	Bu	$HSiMe_3$	n-C_6H_{14}	25	3	70 (94:6)
1d	$ClCH_2$	$HSiMe_3$	n-C_6H_{14}	25	5	32 (100:0)
1e	$MeOCH_2$	$HSiMe_3$	n-C_6H_{14}	0	4	41 (100:0)
1f	Ph	$HSiMe_3$	C_6H_6	25	2	45 (0:100)
1f	Ph	$HSiMe_3$	n-C_6H_{14}	25	3	56 (0:100)

[a] Reaction conditions: ortho ester (2.5 mmol), $HSiR_3$ ($R_3 = Me_3$, 25 mmol; $R_3 = Et_2Me$, 12.5 mmol), $Co_2(CO)_8$ (0.1 mmol, 34 mg), and solvent (5 mL) under CO (1 atm). [b] GLC yields based on the substrates. Ratios of 2 and 3 are in parentheses.

Table II. $CO_2(CO)_8$-Catalyzed Reaction of Six-Membered Cyclic Ortho Esters 7 with a Hydrosilane and Carbon Monoxide[a]

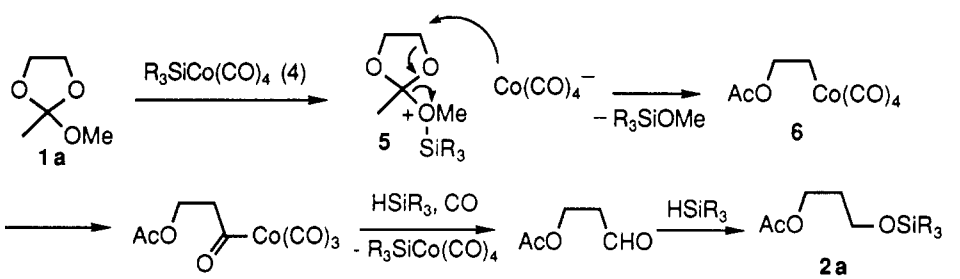


7 8 9

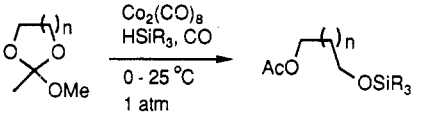
compd	R"	hydrosilane	solvent	temp/°C	time/days	yield/% (8:9)[b]
7a	H	$HSiMe_3$	C_6H_6	25	1	89
7a	H	$HSiEt_2Me$	C_6H_6	25	1	61
7b	Me	$HSiEt_2Me$	C_6H_6	35	1	34 (90:10)
7b	Me	$HSiMe_3$	C_6H_6	10	2	50 (94:6)
7b	Me	$HSiMe_3$	n-C_6H_{14}	10	4	55 (91:9)

[a] Reaction conditions: ortho ester (2.5 mmol), $HSiR_2$ ($R_3 = Me_3$, 25 mmol; $R_3 = Et_2Me$, 12.5 mmol), $Co_2(CO)_8$ (0.1 mmol, 34 mg), and solvent (5 mL) under CO (1 atm). [b] GLC yields based on the substrates. Ratios of 8 and 9 are in parentheses.

Scheme I



with an epoxide. To expand the scope of the catalytic reaction, we have examined the reaction of some other 1,2-diol equivalents such as ethylene carbonate,[2] ethylene glycol cyclic sulfate,[3] and an ortho ester, 2-methyl-methoxy-1,3-dioxolane (**1a**). Among these 1,2-diol equivalents, only the cyclic ortho ester **1a** is found to react with $HSiEt_2Me$ and CO in the presence of $Co_2(CO)_8$ to afford 1,3-propanediol derivative **2a**. Described below is a new $CO_2(CO)_8$-catalyzed reaction of a hydrosilane and carbon monoxide[1,4] with cyclic ortho esters (eq 1), which are readily derivable from diols.[5] The reaction provides a new method for homologation of 1,2-, 1,3-, and 1,4-diols.



(1)

The results of the reaction of five-membered cyclic ortho esters are summarized in Table I.[6] A typical experimental procedure is illustrated for the reaction of **1c**. In a 10-mL reaction flask with an efficient condenser (dry ice–MeOH) was placed $Co_2(CO)_8$ (0.1 mmol, 34 mg). After the flask was flushed with CO (1 atm), $HSiMe_3$ (25 mmol, 3.0 mL)

(2) The reaction of ethylene carbonate with $HSiEt_2Me$ and CO (1 atm) in the presence of $Co_2(CO)_8$ in benzene at 25 °C gave 1,3-propanediol bis(trimethylsilyl) ether in 39% yield. Efforts to improve the yield of the product were in vain.

(3) 1,2-Diol cyclic sulfates have been demonstrated to behave like epoxides and to be much more reactive than epoxides: Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538.

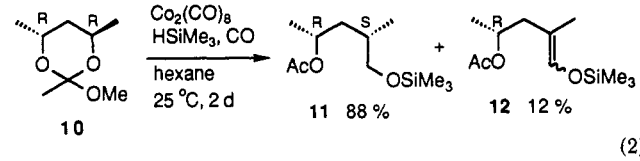
(4) For recent papers in this series, see: Chatani, N.; Sano, T.; Sonoda, N.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Org. Chem.*, in press. Chatani, N.; Ikeda, T.; Sano, T.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Org. Chem.* **1988**, *53*, 3387.

(5) All of the cyclic ortho esters used here were prepared by the treatment of diols with trimethyl orthoacetate in the presence of H_2SO_4 or chloroacetic acid. Trityl chloride is also an effective catalyst for the preparation of cyclic ortho esters: Newman, M. S.; Chen, C. H. *J. Am. Chem. Soc.* **1973**, *95*, 278.

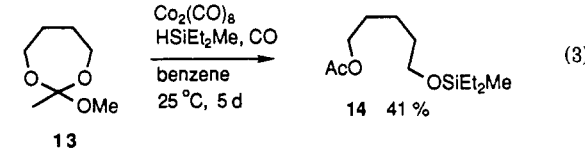
(6) All new products obtained here gave satisfactory spectral and analytical (C, H) data.

was added with use of a pressure syringe.[7] After 5 min, C_6H_6 (5 mL) and **1c** (2.5 mmol, 435 mg) were added and the mixture was stirred at 25 °C for 3 days under CO (1 atm). Analysis of the reaction mixture by GC showed it to contain a 94:6 mixture of **2c**[8] and **3c** in 72% yield. An analytical sample was obtained by Kugelrohr distillation followed by preparative GC (silicone OV-1). As mentioned above, the reaction of **1a** with $HSiEt_2Me$ and CO gave 1,3-propanediol derivative **2a** in high yield. A plausible reaction mechanism is shown in Scheme I.[9] Silylcobalt complex **4**[10] would be a key catalyst. Interaction of **4** with **1a** would give the alkylcobalt complex **6**, which is essential for CO insertion, via the silyloxonium ion **5**. The oxidative addition of $HSiR_3$, reductive elimination, and successive hydrosilylation give product **2a**. It is worthy of note that an orthoformate, an analogue of orthoacetate **1** but without the 2-methyl group, did not react at all. This suggests the importance of stabilizing the partial positive charge developing in **5**. In the case of substituted cyclic ortho esters such as **1b–e**, highly regioselective ring opening at the primary carbon center leading to **2** was observed. Reversed selectivity was obtained for the reaction of 2-methyl-2-methoxy-4-phenyl-1,3-dioxolane (**1f**).

Six-membered cyclic ortho esters **7** also reacted with a hydrosilane and carbon monoxide to afford the corresponding 1,4-diol derivatives **8** and **9** with high regioselectivities in fair to high yields, as shown in Table II.[6] The stereochemistry of the siloxymethylation process was examined by the use of (4*R*,6*R*)-2-methoxy-2,4,6-trimethyl-1,3-dioxolane (**10**), which was prepared from optically active (2*R*,4*R*)-2,4-pentanediol. The step of nucleophilic attack of $Co(CO)_4^-$ at **5** must be a stereodetermining step because CO insertion and subsequent processes occur with retention of configuration (see Scheme I). When **10** was subjected to the $Co_2(CO)_8$-catalyzed reaction with $HSiMe_3$ and CO, **11**[11] was obtained in 88% yield along with **12** in 12% yield (eq 2). It can be concluded that siloxymethylation occurred with inversion of configuration.[12]



(2)



(3)

The present reaction is also applicable to the seven-membered ortho ester **13**, providing 1,5-diol derivative **14** in 41% yield (eq 3).

In summary, the overall transformation is a novel siloxymethylative ring opening of cyclic ortho esters and provides a new method for homologation of 1,2-, 1,3-, and 1,4-diols to diols one carbon higher that are protected differently.

Acknowledgment. Partial support by grants from the Ministry of Education, Science, and Culture of Japan and encouragement by Professor Noboru Sonoda are greatly acknowledged.

(7) We have designed a special apparatus for the handling of $HSiMe_3$, which has a low boiling point.[1b]

(8) **2c**: ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, $SiCH_3$), 0.88 (t, J = 6.8 Hz, 3 H, CH_3), 1.22–1.37 (m, 4 H, CH_2), 1.51–1.56 (m, 2 H, CH_2), 1.77 (q, J = 6.8 Hz, CH_2), 2.02 (s, 3 H, CH_3CO), 3.60 (t, J = 6.8 Hz, 2 H, CH_2O), 4.97 (quint, J = 6.8 Hz, CHO); ^{13}C NMR ($CDCl_3$) δ -0.64, 13.93, 21.18, 22.54, 27.30, 34.05, 37.01, 59.02, 71.76, 170.67; IR (neat) 1743 cm^{-1} (C=O); MS m/e 246 (M^+, 0), 171 (8), 129 (14), 117 (100), 75 (48), 73 (47). Anal. Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.64. Found: C, 58.06; H, 10.66.

(9) For a detailed discussion on the mechanism of the $Co_2(CO)_8$-catalyzed reaction of epoxides with a hydrosilane and CO, see ref 1b.

(10) The reaction of $Co_2(CO)_8$ with $HSiR_3$ has been known to give $R_3SiCo(CO)_4$: Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. Baay, Y. L.; MacDiarmid, A. *Inorg. Chem.* **1969**, *8*, 986. Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 1019.

(11) The reaction of racemic **10** with $HSiMe_3$ and CO gave a 1:1 mixture of diastereoisomers, *R*S** and *R*R** isomers; these are easily separable by GLC. On the other hand, the chiral ortho ester **10** gave a single isomer that has the same retention time in GLC as the *R*S** isomer does. Furthermore, a carbon at which an acetoxy group attached in **11** is not a stereogenic center; therefore, **11** is the *RS* isomer. **11**: $[\alpha]_D^{19}$ = 11.7° (c = 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, $SiCH_3$), 0.88 (d, J = 6.8 Hz, 3 H, CH_3), 1.21 (d, J = 6.1 Hz, 3 H, CH_3), 1.58–1.72 (m, 3 H, CH_2, CH), 2.01 (s, 3 H, CH_3CO), 3.30–3.43 (m, 2 H, CH_2O), 4.99–5.06 (m, 1 H, CHO); IR (neat) 1742 cm^{-1} (C=O); MS m/e 232 (M^+, 0), 130 (43), 117 (89), 103 (47), 83 (66), 73 (100). Anal. Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found: C, 56.80; H, 10.45.

(12) For **1f**, the reversed regiochemistry (Table I) suggests that a different mechanism (S_N1 type) is operating.

Synthesis and Structure of a Monomeric Diarylstannylene

Hansjörg Grützmacher,*,† Hans Pritzkow,† and Frank T. Edelmann‡

Anorganisch Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg, FRG, and Anorganisch Chemisches Institut der Universität, Tammannstrasse 4, D-3400 Göttingen, FRG

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Summary: The novel diarylstannylene bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene **1** is synthesized conventionally from [2,4,6-(trifluoromethyl)phenyl]lithium and tin(II) chloride. It is a monomer in the solid state, as shown by an X-ray analysis, and is stabilized by intramolecular fluorine–tin contacts, which NMR data indicate also exist in solution. Compound **1** ($C_{18}H_4F_{18}Sn$) crystallizes in the monoclinic space group $P2_1/a$ (Z = 4) with a = 11.915 (6) Å, b = 13.801 (7) Å c = 12.961 (7) Å, β = 93.56 (4)°, and V = 2172.2 Å^3.

The existence of monomeric diarylstannylenes has been debated for a long time.[1] However, in the solid state these are polymeric with one exception. In 1981, Zuckerman et al. reported the synthesis of bis[2,6-bis(trifluoromethyl)-phenyl]stannylene and postulated it to be monomeric on the basis of Mössbauer spectroscopy.[2] To date, no stannylene that is monomeric in the solid state and forms only σ bonds between the dicoordinated tin atom and carbon

†Universität Heidelberg.
‡Universität Göttingen.

(1) Reviews: (a) Neumann, W. P. *Nachr. Chem., Tech. Lab.* **1982**, *30*, 190. (b) Connolly, J. W.; Hoff, C. *Adv. Organomet. Chem.* **1981**, *19*, 123. (c) Veith, M.; Recktenwald, O. *Top. Curr. Chem.* **1982**, *104*, 1.

(2) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.

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