acquired by using five interferometer scans (consuming ca. 3 s). The seven spectra in Figure 2, selected from this sequence, refer to potentials (as indicated) where each of the seven redox states is almost exclusively present. Each spectrum displays an intense potential-dependent terminal carbonyl band ($\nu_{CO}{}^{1}$), at 2076 cm^{-1} for $n = 0$ and 1973 cm^{-1} for $n = -6$, and a weaker doubly bridging carbonyl band ($\nu_{CO}{}^{b}$) centered at 1836 cm^{-1} for $n = 0$ and 1766 cm^{-1} for $n = -6$. The relative intensities of these features are consistent with the 22 terminal and eight bridging carbonyls present in the solid-state structure of $[Pt_{24}(CO)_{30}]^{2-}$,[5] indicating that the overall cluster configuration is maintained for all seven redox forms.

Figure 2 shows that sequential one-electron reduction of the $[Pt_{24}(CO)_{30}]^{n}$ species results in near-uniform decreases in $\nu_{CO}{}^{1}$ and $\nu_{CO}{}^{b}$; the $\nu_{CO}{}^{1}$ downshift is 15 cm^{-1} for $[Pt_{24}(CO)_{30}]^{0/1-}$ increasing to 19 cm^{-1} for $[Pt_{24}(CO)_{30}]^{5-/6-}$. The $\nu_{CO}{}^{1}$ vs potential dependence is also included (circles, dashed trace) in Figure 1. Sharp reversible alterations in $\nu_{CO}{}^{1}$ occur within narrow (40–50 mV) potential regions that match consistently to the voltammetric E_f values. This confirms that the infrared spectral shifts correspond to the same redox transformations observed by cyclic voltammetry. Corresponding Raman spectroelectrochemical measurements were also undertaken in order to examine the redox-induced changes in the Pt–C stretch, ν_{PtC}, region. Although relatively concentrated ($\gtrsim$5 mM) $[Pt_{24}CO_{30}]^{2-}$ solutions were required to obtain reliable spectra (514.5-nm laser excitation), ν_{PtC} was observed to increase with increasingly negative n (e.g., ca. 450 cm^{-1} for $n = -2$, 480 cm^{-1} for $n = -6$).

These results provide an unprecedented opportunity to examine the sensitivity of the carbonyl bonding to the "surface charge density" of a high-nuclearity metal cluster. The almost linear decrease of $\nu_{CO}{}^{1}$ observed as n becomes more negative is not surprising in that the extent of $d\pi(Pt) \rightarrow \pi^*(CO)$ backbonding should be related directly to the overall negative charge of the Pt_{24} core (the "charge effect").[10] A plot of $\nu_{CO}{}^{1}$ versus the excess electronic charge per *surface* Pt atom has a slope of 405 cm^{-1}/e; interestingly, the observed $\nu_{CO}{}^{1}$ values for the hcp $[Pt_{26}(CO)_{32}]^{2-}$ and ccp $[Pt_{38}(CO)_{44}]^{2-}$ dianions (2042 and 2052 cm^{-1}, respectively[11]) fall on the same line.

Such charge-induced ν_{CO} frequency shifts are entirely analogous to the potential-induced ν_{CO} shifts for CO chemisorbed to metal electrodes.[12] Figure 1 also includes a plot (solid line) of $\nu_{CO}{}^{1}$ versus electrode potential, E, obtained for an irreversibly adsorbed CO monolayer on polycrystalline platinum in the same dichloromethane medium.[13] (These results were obtained by surface FTIR as described in ref 9.) Intriguingly, the Pt surface and cluster systems display similar $\nu_{CO}{}^{1}$ vs E behavior. Of course, the "discrete" $\nu_{CO}{}^{1}$ vs E dependence for the cluster reflects in part its microscopic dimensions. The spacings between adjacent E_f values alternate between small (ca. 0.25 V, $n = -1, -3, -5$) and larger values (ca. 0.5–0.8 V; $n = -2, -4$), suggesting that the added electrons enter successive LUMOs in a pairwise fashion.[14] The average $\nu_{CO}{}^{1}$ vs E slope for the cluster, ca. 30–40 cm^{-1} V^{-1}, is somewhat larger than for the electrode case, 20 cm^{-1} V^{-1}. This difference possibly reflects the influence of ionic solvation, which will shift the E_f values increasingly in the positive direction as the cluster charge increases. As expected on this basis, the $\nu_{CO}{}^{1}$ values in the surface and cluster environments are closest at potentials (>0.7 V) where the latter is uncharged. Quantitative comparison with $\nu_{CO}{}^{1}$ for an uncharged Pt electrode is hampered by a lack of reliable potential of zero charge values.[15] Nevertheless, $\nu_{CO}{}^{1}$ for a saturated CO layer on Pt(111) in ultrahigh vacuum at 300 K (2095 cm^{-1})[16] is significantly higher than for the neutral cluster $Pt_{24}(CO)_{30}$ (2076 cm^{-1}). This difference may reflect a greater degree of dipole–dipole coupling between CO molecules on the planar Pt(111) surface.[16]

Further studies of the carbonyl vibrational properties in cluster and surface electrochemical environments, including single crystals, are underway.

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[9] For further experimental details of the FTIR spectroelectrochemical procedures, see: (a) Corrigan, D. S.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 5300. (b) Corrigan, D. S.; Leung, L.-W. H.; Weaver, M. J. *Anal. Chem.* **1987**, *59*, 2252. (c) Leung, L.-W. H.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 4019.

[10] (a) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054. (b) Cirjak, L. M.; Ginsburg, R. E.; Dahl, L. F. *Inorg. Chem.* **1982**, *21*, 940. (c) Kubat-Martin, K. A.; Barr, M. E.; Spencer, B.; Dahl, L. P. *Organometallics* **1987**, *6*, 2570.

[11] Lewis, G. J.; Dahl, L. F., unpublished results.

[12] For example, see: (a) Lambert, D. K. *J. Chem. Phys.* **1988**, *89*, 3847 and references therein. (b) Mehandru, S. P.; Anderson, A. B. *J. Phys. Chem.* **1989**, *93*, 2044.

[13] Roth, J. D.; Weaver, M. J., unpublished results.

[14] The smaller potential ranges over which the odd-electron species ($n = -1, -3, -5$) are stable is consistent with the known tendency of Pt complexes to possess an even electron count with no unpaired electrons.

[15] Chang, S. C.; Leung, L.-W. H.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 5341.

[16] Olsen, C. W.; Masel, R. I. *Surf. Sci.* **1988**, *201*, 444.

Metal-Mediated Addition of Carbon Dioxide to the Activated Benzene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$

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The benzene ligand in $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) can be activated toward electrophiles by naphthalenide reduction to a dianionic species, formulated as the η^4-benzene complex $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ ($\mathbf{1}^{2-}$).[1] Electrophiles add to the arene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ under exceptionally mild conditions to give substituted cyclohexadienyl complexes,[1] and the established potential of such species as intermediates in the modification of simple arenes[2] has led us to explore the range of carbon-centered electrophiles that can add to $\mathbf{1}^{2-}$.

Although $PhCH_2Cl$ successfully adds to $\mathbf{1}^{2-}$, substrates such as CH_3I, $CH_3CH_2CH_2I$, and $(CH_3)_2CHBr$ oxidize $\mathbf{1}^{2-}$ to **1**. This is consistent with initial single-electron transfer (SET) to generate a halide anion and an organic radical, and it is only when SET leads to a relatively stable radical (such as benzyl) that recombination can allow carbon–carbon bond formation. This reasoning led us to search for acidic electrophiles with a tendency to react by two-electron pathways. Previous experience with the addition of CO_2 to dianionic transition-metal complexes[3] suggested that CO_2 would fit these reactivity requirements, and CO_2 does indeed add to the activated η^4-benzene in $\mathbf{1}^{2-}$ to give an intermediate cyclohexadienyl carboxylate complex, which can be oxidized and silylated to form $[Cr(\eta^6\text{-}C_6H_5CO_2SiMe_3)(CO)_3]$ (**5**). As shown in Scheme I, the unprecedented addition has a surprising endo stereochemistry, as established by ^{1}H NMR spectra of the silylated cyclohexadienyl complex $\mathbf{6}^-$.

Carbon dioxide (34.7 mL, 1.55 mmol) was added by syringe to a solution of $\mathbf{1}^{2-}$ that had been prepared as described previously[1] by potassium naphthalenide (0.24 M) reduction of **1** (0.302 g, 1.41 mmol) in tetrahydrofuran (THF, 30 mL) at −78 °C. This

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[1] Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644.

[2] (a) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36. (b) Jaouen, G. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 59. (c) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

[3] (a) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604. (b) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797. (c) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

0002-7863/90/1512-2832$02.50/0

Scheme I

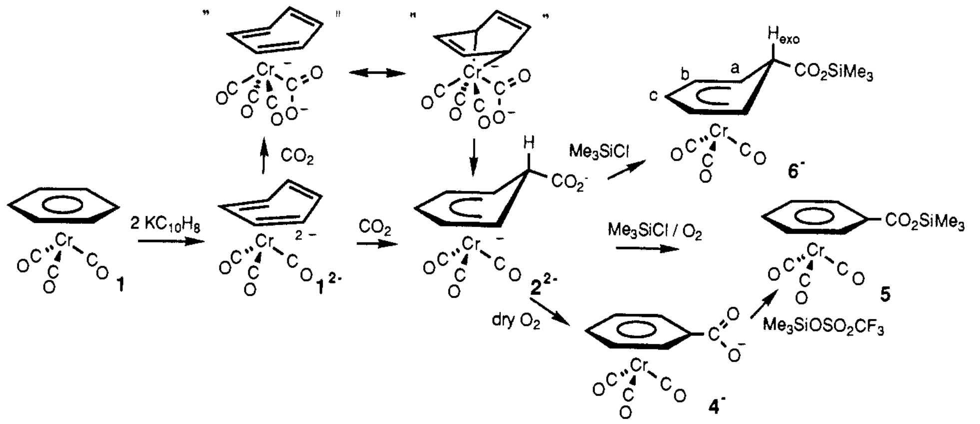

Table I. Carbonyl and Carboxylate IR Stretching Absorptions (cm^{-1}) of the Principal Complexes in Scheme I, Some ^{13}CO$_2$-Derived Isotopomers, and Related Complexes[a]

complex	$\nu_{C\equiv O}$	$\nu_{^{12}C=O}$	$\nu_{^{13}C=O}$
$[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**)	1969 (s), 1890 (s)		
$[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ (**1**$^{2-}$)	1803 (m), 1660 (s, br)		
$[Cr(\eta^5\text{-}C_6H_6CO_2)(CO)_3]^{2-}$ (**2**$^{2-}$)	1893 (s), 1784 (s), 1749 (s)	1585 (m, br)	1530 (m)
$[Cr(\eta^5\text{-}C_6H_7)(CO)_3]^-$ (**3**$^-$)	1897 (s), 1809 (s), 1742 (s)		
$[Cr(\eta^6\text{-}C_6H_5CO_2)(CO)_3]^-$ (**4**$^-$)	1967 (s), 1890 (s)	1598 (s)	
$[Cr(\eta^6\text{-}C_6H_5CO_2SiMe_3)(CO)_3]$ (**5**)	1976 (s), 1905 (s)	1709 (m)	
$[Cr(\eta^5\text{-}C_6H_6CO_2SiMe_3)(CO)_3]^-$ (**6**$^-$)	1899 (s), 1800 (s), 1781 (sh), 1750 (sh)	1710 (sh)	1660 (m)

[a] All spectra were recorded in THF. All anions have K$^+$ counterions.

resulted in a color change from dark green to deep red. The IR spectrum of the clear solution (carbonyl and carboxylate stretching absorptions of the principal complexes in Scheme I are summarized in Table I) showed that the CO absorptions of **1**$^{2-}$ had been replaced by the absorptions shown in Figure 1a. The three strong bands at 1893 (s), 1784 (s), and 1749 (s) cm^{-1} are very similar in position, intensity, and appearance to the CO stretching absorptions of the cyclohexadienyl complex $[Cr(\eta^5\text{-}C_6H_7)(CO)_3]^-$ (**3**$^-$),[1] strongly suggesting that CO$_2$ has added to the η^4-benzene ligand to make the η^5-cyclohexadienyl carboxylate **2**$^{2-}$ shown in Scheme I. This would suggest assignment of the broad, medium-intensity band at 1585 cm^{-1} to a carboxylate functionality derived from the added CO$_2$, and this has been confirmed by a labeling study in which ^{13}CO$_2$ was used to establish an isotope shift of ca. 55 cm^{-1} for this absorption (Figure 1a).

Attempts to isolate the proposed cyclohexadienyl carboxylate complex by counterion metathesis using NEt$_4$Br or PPNCl, or by crown ether complexation of the alkali-metal cation, have been unsuccessful and we therefore attempted derivatization of the material. The cyclohexadienyl complex was oxidized by addition of excess dry O$_2$ to a solution prepared as described above to give a species whose infrared spectrum (Figure 1b) contains two strong absorptions at 1967 and 1890 cm^{-1} [characteristic of carbonyl absorptions in neutral (arene)chromium tricarbonyl complexes; cf **1** in Table I] together with a broad strong band at 1598 cm^{-1} assigned to a carboxylate stretch. Identification as the benzoate complex **4**$^-$ (Scheme I) was confirmed by silylation using Me$_3$SiOSO$_2$CF$_3$ (1.1 equiv based on **1**) to give the neutral silyl ester $[Cr(\eta^6\text{-}C_6H_5CO_2SiMe_3)(CO)_3]$ (**5**). Complex **5** was isolated by removal of the solvent under reduced pressure followed by trituration into heptane and recrystallization at −78 °C and has been fully characterized[4] (see Figure 1c for solution IR). The complex can be prepared from **1** in one pot by initial CO$_2$ addition followed by the addition of oxygenated trimethylsilyl chloride to give **5** directly in 45% overall recrystallized yield.

The characterization of **5** strongly supports the proposed formulation of **2**$^{2-}$, but leaves open an intriguing question: is **2**$^{2-}$ formed by direct exo addition to **1**$^{2-}$ (as in the addition of PhCH$_2$Cl to **1**$^{2-}$),[1] or is it formed by a metal-mediated addition leading to **2**$^{2-}$ as the endo isomer (as in the protonation of **1**$^{2-}$)?[1,5] This question has been addressed (Scheme I) by silylation of unoxidized **2**$^{2-}$ using Me$_3$SiCl (1 equiv based on **1**) to give the cyclohexadienyl silyl ester **6**$^-$.[6] Attempts to isolate **6**$^-$ as NEt$_4^+$, PPN$^+$, K(18-crown-6)$^+$, or K(DME)$^+$ salts were unsuccessful and led to decomposition, but K-**6** has been characterized in solution by IR (Figure 1d)[7] and ^{1}H NMR[8,9] studies. The chemical shifts and coupling patterns of the cyclohexadienyl protons (particularly the absence of the characteristic H$_{endo}$–H$_{vicinal}$ coupling[10]) unambiguously establish that **6**$^-$ is formed exclusively (>97%) as the endo isomer, implying that **2**$^{2-}$ is also endo and is therefore formed by a metal-mediated addition (Scheme I).[5] There is no precedent for the carboxylation of an η^4-arene ligand, but the reaction has a close mechanistic precedent in Brookhart's report of the carboxylation of the diene in an isoelectronic $[Mn(diene)(CO)_3]^-$ complex[11] and is also related to the carboxylations of electron-rich diene and alkene complexes reported by Walther, Hoberg, and others.[12]

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(4) ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 5.67 (d, J = 6.5 Hz, 2 H, *o*-H); 4.43 (t, J = 6.2 Hz, 1 H, *p*-H); 4.19 (t, J = 6.2 Hz, 2 H, *m*-H); 0.27 [s, 9 H, (CH$_3$)$_3$]. Anal. Calcd for C$_{13}$H$_{14}$CrO$_5$Si: C, 47.27; H, 4.27. Found (Multichem, Lowell, MA): C, 47.41; H, 4.27.

(5) Direct endo carboxylation is also conceivable, but seems sterically unlikely.

(6) Attempts to oxidize **6**$^-$ to **5** using Ph$_3$C$^+$, O$_2$, or I$_2$ led to complex mixtures, suggesting that the one-pot conversion of **2**$^{2-}$ to **5** using oxygenated Me$_3$SiCl involved an oxidation/silylation sequence, rather than a silylation/oxidation sequence.

(7) Samples of **6**$^-$ prepared from ^{13}CO$_2$ exhibited an IR absorption at 1666 (m) cm^{-1}, establishing that the shoulder at 1710 corresponds to the ester carbonyl stretch of unlabeled **6**$^-$.

(8) ^{1}H NMR (300 MHz, acetone-d_6; see Scheme I for nomenclature): δ 5.09 (t, J_{Hc-Hb} = 5.0 Hz, 1 H, H$_c$), 4.44 (d of d, J_{Hb-Hc} = 5.0 Hz, J_{Hb-Ha} = 7.1 Hz, 2 H, H$_b$), 3.33 (s, 1 H, H$_{exo}$), 2.36 (d, J_{Ha-Hb} = 7.1 Hz, 2 H, H$_a$), 0.29 [s, 9 H, (CH$_3$)$_3$]. ^{1}H NMR assignments have been fully confirmed by narrow-band decoupling.

(9) The use of other silylating agents, including *t*-BuMe$_2$SiCl and Ph$_3$SiCl, was also successful and led to spectroscopically similar (IR and ^{1}H NMR) silyl ester cyclohexadienyl complexes, but these were not more tractable than **6**$^-$.

(10) (a) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (b) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6314. (c) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. (d) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479. (e) White, C.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3322–3326.

(11) Brookhart, M.; Noh, S. K.; Timmers, F. J. *Organometallics* **1987**, *6*, 1829.

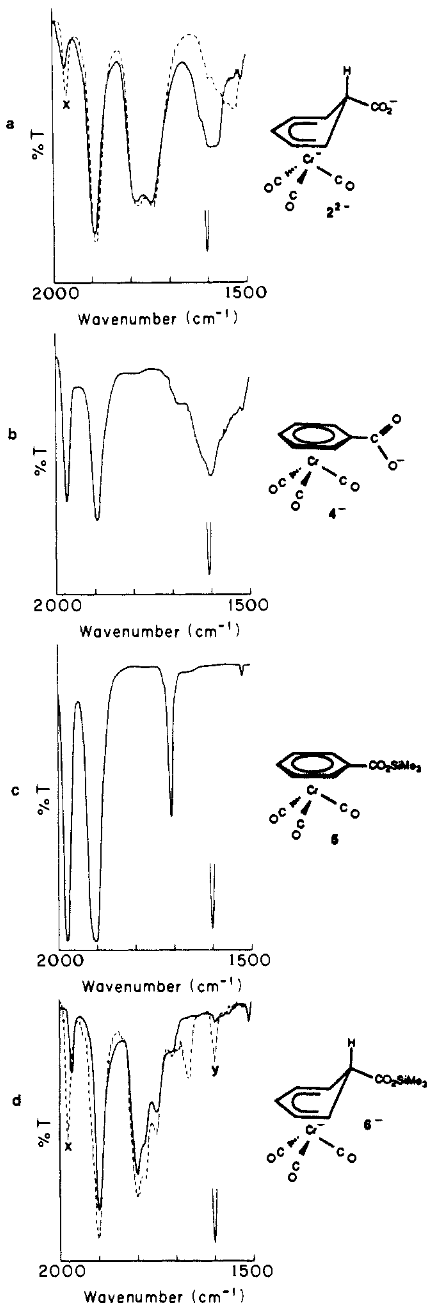

Figure 1. Solution IR spectra (%T) in C≡O and C=O stretching region of the principal CO_2 adducts and derivatives in Scheme I. Peaks marked x correspond to **1** impurities. Spectra of samples prepared from $^{12}CO_2$ are indicated by solid lines, and those of $^{13}CO_2$-derived samples are indicated by dashed lines. Control experiments using $^{12}CO_2$ have established that the peak marked y arises from the presence of excess carbon dioxide in the labeled run.

Direct carboxylation of an arene under mild conditions, without initial deprotonation by a strong base such as an alkyllithium, would appear to be unprecedented except for the mechanistically complex[13] and commercially important[14] Kolbe–Schmitt carboxylation of phenolates. Our results suggest that the carboxylation of reductively activated ligands, including arenes, may provide an attractive general strategy for the incorporation of CO_2 into useful organic molecules, and further experiments along these lines are being pursued in our laboratory.

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Registry No. $\mathbf{1}^{2-}2K^+$, 113303-46-1; $\mathbf{2}^{2-}2K^+$, 125666-44-6; $\mathbf{2}^{2-}2K^+$ ($^{13}CO_2$ labeled), 125666-48-0; $\mathbf{3}^-K^+$, 113303-48-3; $\mathbf{4}^-K^+$, 125666-45-7; **5**, 125666-46-8; $\mathbf{6}^-K^+$, 125666-47-9; $\mathbf{6}^-K^+$ ($^{13}CO_2$ labeled), 125666-49-1; $[Cr(\eta^5\text{-}C_6H_6CO_2SiMe_2Bu\text{-}t)(CO)_3]K$, 125666-50-4; $[Cr(\eta^5\text{-}C_6H_6CO_2SiPh_3)(CO)_3]K$, 125666-51-5; CO_2, 124-38-9.

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(12) As summarized in recent reviews: (a) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (b) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.

(13) (a) Kolbe, H. *Justus Liebigs Ann. Chem.* **1860**, *113*, 125. (b) Schmitt, R. *J. Prakt. Chem.* **1885**, *31*, 397. (c) Lindsey, A. S.; Jeskey, H. *Chem. Rev.* **1957**, *57*, 583. (d) Ayres, D. C. *Carbanion Synthesis*; Oldbourne: London, 1966; pp 168–173. (e) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Interscience: New York, 1985; p 491.

(14) Erickson, S. H. In *Kirk-Othmer Concise Encylopedia of Chemical Technology*; Eckroth, D., Ed.; Wiley-Interscience: New York, 1985; p 1039.

Solvolytic Acceleration Accompanying (Trimethylsilyl)methyl Migration

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It has been reported that a γ-silyl substituent enhances the solvolytic reactivity of secondary alkyl sulfonate esters by factors of 10–10^2.[1] The carbocation involved is stabilized by interaction with the back lobe of the silicon–carbon bond in either a "W" or an "endo-Sickle" conformation.[2] Products of unrearranged substitution and minor yields of cyclopropanes from 1,3-deoxysilylation were found in each instance in which one of these conformations is possible.

As shown in Table I, the solvolysis rates for **1** and **2** are larger than those for the analogous neopentyl and pinacolyl esters by factors of 400–21 800. These accelerations are the largest ever attributed to a single γ-silyl group.[3]

As outlined in Scheme I, the products from the solvolysis in 80E of both esters derive exclusively (for **1**) or predominately (for **2**) from the intermediate tertiary ion **4**, which is formed by migration of the (trimethylsilyl)methyl group. Products were isolated from both the deuterated and undeuterated sulfonate esters in order to distinguish between methyl and (trimethylsilyl)methyl migration. The alkenes formed with loss of Me_3Si^+ were isolated by vacuum transferring the volatiles into NMR tubes containing $CDCl_3$. The alkenes that retained the TMS group were identified as the alcohols resulting from the hydroboration/oxidation of a pentane-extracted reaction mixture.

Interestingly, *none of the products are derived from methyl migration* even though the carbocation so formed would be not only tertiary but also β-silyl stabilized. The ability of γ-silicon to direct carbon and hydrogen rearrangements to yield β-silyl carbocation intermediates is well documented.[4] In the present examples, it is clear that the stability of that potential intermediate does not control the rearrangement; our results show that $(CH_3)_3SiCH_2$ has a far greater migratory aptitude than CH_3. Preferences for (trimethylsilyl)methyl migration over methyl migration[5a] and over ring expansion[5b,c] have been reported.

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(1) (a) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842–844. (b) Shiner, V. J., Jr.; Ensinger, M. W.; Rutkowske, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 804–809. (c) Shiner, V. J., Jr.; Ensinger, M. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 7199–7205.

(2) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914–3915.

(3) Kirmse and Sollenbohmer found a solvolytic acceleration factor of 10^4 to be associated with substitution of two trimethylsilyl groups at the γ-position (C_6) of *exo*-2-norbornyl *p*-nitrobenzoate, indicating that the characteristic Wagner–Meerwein rearrangement of this compound may be assisted either by a percaudal interaction or by enhanced migratory aptitude of the alkyl group bearing two α-silyl substituents. Kirmse, W.; Sollenbohmer, F. *J. Am. Chem. Soc.* **1989**, *111*, 4127–4129.

(4) (a) Fleming, I.; Patel, S. K. *Tetrahedron Lett.* **1981**, *22*, 2321–2324. (b) Fleming, I.; Michael, J. P. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1549–1556. (c) Fleming, I.; Loreto, M. A.; Wallace, I. H. M.; Michael, J. P. *J. Chem. Soc., Perkin Trans. 1* **1986**, 349–359. (d) Asaoka, M.; Takei, H. *Tetrahedron Lett.* **1987**, *28*, 6343–6346. (e) Ishibashi, H.; Nakatani, H.; Sakashita, H.; Ikeda, M. *J. Chem. Soc., Chem. Commun.* **1987**, 338–340. (f) Tanino, K.; Katoh, T.; Kuwajima, I. *Tetrahedron Lett.* **1988**, *29*, 1815–1818.