$(Me)]Cl_3$ (0.20 g, 0.49 mmol) was dissolved in cold (−30 °C) dichloromethane (8 mL). Pyridine (10 μL, 1.2 mmol) was added, and the reaction was warmed to room temperature. After 20 min the solvent was removed in vacuo and the lime green solid was washed with pentane, dried in vacuo, and recrystallized from dichloromethane by adding ether: ^1H NMR (CD_2Cl_2, −20 °C) δ 9.02 (d, 4, py, sym isomer), 8.62 and 8.52 (d, 2 each, py, asym isomer), 7.80, 7.67, 7.41 and 7.15 (all other py resonances combined), 4.11 (s, 6, CMe, asym isomer), 3.72 (s, 6, CMe, sym isomer), 1.16 (s, 9, $CCMe_3$, asym isomer), 0.99 (s, 9, $CCMe_3$, sym isomer); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 171.8, 144.6, 143.1 and 126.2 ($\mathit{C}CMe_3$ and $\mathit{C}Me$), 153.3, 152.6, 151.0, 140.1, 139.3, 138.3, 125.1, 124.3, and 123.4 (py), 398.2 ($\mathit{C}CMe_3$), 32.3 and 32.1 ($CC\mathit{Me}_3$), 30.1 ($C\mathit{C}Me$), 16.5 and 13.6 ($C\mathit{Me}$). Anal. Calcd for $WC_{19}H_{25}N_2Cl_3$: C, 39.92; H, 4.41; N, 4.90. Found: C, 40.23; H, 4.51; N, 5.19.

$W[C(CMe_3)C(Me)C(Me)](Me_2NCH_2CH_2CH_2NMe_2)Cl_3$. A procedure similar to that used to make $W[C(CMe_3)C(Me)C(Me)](py)_2Cl_3$ is employed in this reaction: ^1H NMR (CD_2Cl_2, 20 °C) δ 4.61 (s, 6, CMe), 2.86 and 2.69 (s with broad resonances underneath, 8 each, $\mathit{Me}_2N(C\mathit{H}_2)_2N\mathit{Me}_2$), 1.27 (s, 9, $CCMe_3$); ^1H NMR (CD_2Cl_2, −70 °C) δ 4.53 and 4.36 (br, s, 3 each, CMe), 2.76 and 2.61 (br s, 16 total, $\mathit{Me}_2N(C\mathit{H}_2)_2N\mathit{Me}_2$), 1.15 (s, 9, $CCMe_3$); ^{13}C NMR (CD_2Cl_2) δ 162.4 (s, $\mathit{C}CMe_3$), 127.6 (br s, $\mathit{C}Me$), 63.8 (t, J_{CH} = 141 Hz, $N\mathit{C}H_2$), 58.5 (t, J_{CH} = 137 Hz, $N\mathit{C}H_2$), 54.2 (q, J_{CH} = 139 Hz, $(\mathit{C}H_3)_2N$), 51.4 (q, J_{CH} = 138 Hz, $(\mathit{C}H_3)_2N$), 39.0 (s, $C\mathit{C}Me_3$), 32.9 (q, J_{CH} = 127 Hz, $CC\mathit{Me}_3$), 12.9 (q, J_{CH} = 130 Hz, $C\mathit{Me}$). Anal. Calcd for $WC_{15}H_{31}N_2Cl_3$: C, 34.01; H, 5.90; N, 5.29. Found: C, 34.50; H, 5.91; N, 5.27.

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE 80-23448 to M.R.C. and CHE 81-21282 to R.R.S.). We thank J. H. Freudenberger for miscellaneous analyses, Robert C. Murray for the preparation of $W(\eta^5\text{-}C_5Et_3Me_2)Me_4$, and Dr. John C. Dewan of the MIT X-ray facility for the structure of $W(\eta^5\text{-}C_5Et_3Me_2)Me_4$.

Registry No. $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$, 91230-63-6; $W[C(CMe_3)C(Me)C(Me)]Cl_3$, 83487-37-0; $W[C(CMe_3)C(Et)C(Et)]Cl_3$, 83487-36-9; $W[C(CMe_3)C(Me)C(Me)](OCMe_3)Cl_2$, 83487-38-1; $W[C(CMe_3)C(Et)C(Et)](OCMe_3)Cl_2$, 91230-60-3; $W[C(CMe_3)C(Me)C(Me)][O\text{–}2,6\text{–}C_6H_3(i\text{–}Pr)_2]Cl_2$, 91229-81-1; $W[C(CMe_3)C(Me)C(Me)](OCMe_2CMe_2O)Cl$, 91238-46-9; $W[C(CMe_3)C(Me)C(Me)][O\text{–}2,6\text{–}C_6H_3(i\text{–}Pr)_2]_2Ch$, 91229-82-2; $W[C(CMe_3)C(Me)C(Me)](OCMe_2CMe_2O)(OCMe_3)$, 83487-39-2; $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$, 83487-40-5; $W(C_3Et_3)[O\text{–}2,6\text{–}C_6H_3(i\text{–}Pr)_2]_3$, 91229-77-5; $W(C_3Pr_3)[O\text{–}2,6\text{–}C_6H_3(i\text{–}Pr)_2]_3$, 91229-78-6; $W(C_3Et_3)[OCH(CF_3)_2]_3$, 91202-82-3; $W[C(CMe_3)C(Et)C(Et)][OCH(CF_3)_2]_3$, 91202-81-2; $W(C_3Pr_3)[OCH(CF_3)_2]_3$, 91202-83-4; $W(C_3Me_3)[OCMe(CF_3)_2]_3$, 91202-84-5; $W(C_3Et_3)[OCMe(CF_3)_2]_3$, 91208-74-1; $W(CHCMe_3)(OCMe_2CMe_2O)(OCMe_3)_2$, 91230-61-4; $\{W[\eta^5\text{–}C_5Me_4(CMe_3)]Cl_4\}_2$, 83511-04-0; $W[\eta^5\text{–}C_5Me_4(CMe_3)](MeC{\equiv}CMe)Cl_2$, 83511-02-8; $W[\eta^5\text{–}C_5Et_4(CMe_3)](EtC{\equiv}CEt)Cl_2$, 83511-01-7; $\{W(\eta^5\text{–}C_5Et_4(CMe_3)]Cl_4\}_2$, 83511-03-9; $W[\eta^5\text{–}C_5Me_4(CMe_3)](OCMe_3)O_2$, 91230-64-7; $W(\eta^5\text{–}C_5Et_5)(OCMe_3)O_2$, 91230-65-8; $W(\eta^5\text{–}C_5Me_2Et_3)(OCMe_3)O_2$, 91230-66-9; $W[\eta^5\text{–}C_5Me_2Et_2(CMe_3)](OCMe_3)O_2$ (isomer A), 91230-67-0; $W[\eta^5\text{–}C_5Me_2Et_2(CMe_3)](OCMe_3)O_2$ (isomer C), 91230-68-1; $\{W[\eta^5\text{–}C_5Me_2Et_2(CMe_3)]Cl_4\}_2$ (isomer A), 91230-69-2; $\{W[\eta^5\text{–}C_5Me_2Et_2(CMe_3)]Cl_4\}_2$ (isomer C), 91230-76-1; $W[\eta^5\text{–}C_5Me_2Et_2(CMe_3)](CCMe_3)Cl_2$ (isomer A), 91230-70-5; $W[\eta^5\text{–}C_5Me_2Et_2(CMe_3)](CCMe_3)Cl_2$ (isomer C), 91230-71-6; $W[C(CMe_3)C(Me)C(Me)](py)_2Cl_3$ (sym isomer), 91230-72-7; $W[C(CMe_3)C(Me)C(Me)](py)_2Cl_3$ (asym isomer), 91279-92-4; $W(CHMe_3)(OCMe_3)_2Cl_2$, 91230-62-5; $W(\eta^5\text{–}C_5Et_3Me_2)(O)Cl_3$, 91230-73-8; $W(\eta^5\text{–}C5Et_3Me_2)Cl_4(PMe_3)$, 91230-74-9; $W(\eta^5\text{–}C_5Et_3Me_2)Me_4$, 91230-75-0; $W(CCMe_3)(dme)Cl_3$, 83416-70-0; $W(CEt)(OCMe_3)_3$, 82228-88-4; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; $Zn(CH_2CMe_3)_2$, 54773-23-8; $ZnMe_2$, 544-97-8; 2–butyne, 503-17-3; 3–hexyne, 928-49-4.

Supplementary Material Available: A table of anisotropic thermal parameters for $W[C_3Me_2(CMe_3)](Me_2N(CH_2)_2NMe_2)Cl_3$, a list of observed and calculated structure factor amplitudes for $W[C_3Me_2(CMe_3)][Me_2N(CH_2)_2NMe_2]Cl_3$, a detailed description of the preparation of $W(\eta^5\text{-}C_5Et_3Me_2)Me_4$ from $W(\eta^5\text{-}C_5Et_3Me_2)(OCMe_3)O_2$ and its crystal structure, including a figure, crystal data, final positional and thermal parameters, and final observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Communications

A New Procedure for the Synthesis of α-Silylated Esters and Lactones. Migration of Silicon from Oxygen to Carbon at High Pressure[1]

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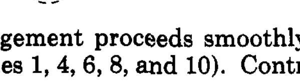
Received May 2, 1984

Summary: High pressure (10 kbar) induces migration of silicon of O-silylated ketene acetals from oxygen to α-carbon, giving α-silylated esters and lactones in high yields.

α-Silylated esters and lactones are becoming increasingly important as a new class of synthetic intermediates, and several synthetic methods have been developed as witness for example the recent elegant method of Larson.[2] We now wish to report an entirely new approach to this problem: high pressure (ca. 10 kbar) induces the migration of silicon in O-silylated ketene acetals from oxygen to α-carbon (eq 1). The results are summarized in Table I.



(1)

The rearrangement proceeds smoothly at room temperature (entries 1, 4, 6, 8, and 10). Control experiments reveal that such rearrangement does not occur at room temperature in CH_2Cl_2 at atmospheric pressure. The migration occurs even in a ketene acetal disubstituted at

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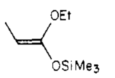
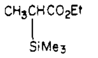
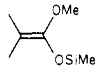
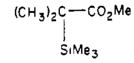
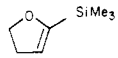
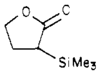
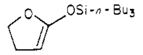
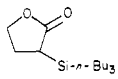
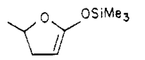
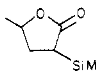
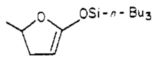
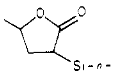
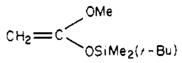
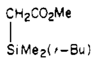
(1) Organometallic High Pressure Reaction. 5. Part 4: Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1984**, 548.

(2) Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418. All previous approaches are listed in this paper.

0276-7333/84/2303-1583$01.50/0

Table I. Rearrangement of O-Silylated Ketene Acetals to α-Silylated Esters at High Pressure

entry	O-silylated ketene acetal	reactn conditns	α-silylated ester or lactone	yield,[a] %
1		10 kbar, 25 °C, 1 day	 $CH_3CH(SiMe_3)CO_2Et$	80
2		10 kbar, 50 °C, 7 days		80
3		10 kbar, 70 °C, 7 days	 $(CH_3)_2C(SiMe_3)—CO_2Me$	82
4	 1	10 kbar, 25 °C, 1 day	 2	88
5		8 kbar, 50 °C, 7 days		85
6	 3	10 kbar, 25 °C, 1 day	 4	80
7		10 kbar, 60 °C, 3 days		80
8	 5	10 kbar, 25 °C, 1 day	 6[b]	90
9		9 kbar, 50 °C, 7 days		88
10	 7	10 kbar, 25 °C, 1 day	 8[c]	80
11		10 kbar, 60 °C, 3 days		81
12	 $CH_2{=}C(OMe)OSiMe_2(t\text{-}Bu)$	10 kbar, 60 °C, 7 days	 $CH_2(SiMe_2(t\text{-}Bu))CO_2Me$	15[d]

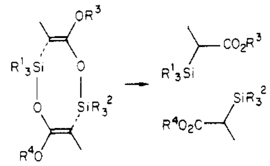
[a] Isolated yield by Kugelrohr distillation except entry 12. [b] Two stereoisomers are produced in a ratio of ca. 4:6. [c] Two stereoisomers may be produced, but the ratio is not determined. [d] By ^{1}H NMR analysis.

the migration terminus (entry 3). Although the tri-*n*-butylsilyl derivatives undergo a facile migration (entries 6, 7, 10, and 11), the rearrangement of the *tert*-butylsilyl derivative is quite sluggish (entry 12). We also applied the high pressure methodology[3] to silyl enol ethers such as isopropenoxytrimethylsilane and 1-phenyl-1-(trimethylsiloxy)-1-propene, but the starting materials were recovered without change after 7 days at 60 °C at 10 kbar.[4]

The O-silylated ketene acetal (2 mmol) and dry CH_2Cl_2 (ca. 1 mL) were placed in a Teflon capsule of 1.5-mL capacity. High-pressure experiments were carried out in a stainless-steel die at room temperature. The die was compressed via a piston, kept at an appropriate temperature for the indicated times, and then depressurized. The reaction mixture was concentrated and analyzed by ^{1}H NMR and GLPC. The rearrangement was complete except in the case of entry 12, in which a large portion of the starting O-silylated compound was recovered. Normally, α-silylated materials were produced along with small amounts (<5%) of the corresponding desilylated compounds.[5]

We examined the high-pressure reaction of an equimolar mixture of 1 and 7 in order to learn whether the novel migration reaction proceeds intramolecularly[6] or intermolecularly. The pressure (10 kbar) was released after 3 days at 60 °C. GLPC examination revealed that the migration goes to completion and the silyl groups are scrambled almost completely; the ratio of 2:4:6:8 was 1:0.8:1:1.1.[7] Similarly, an equimolar mixture of 3 and 5 produced 2, 4, 6 and 8 in a ratio of 1:1:1.1:1.1.[7] Although an equimolar mixture of 2 and 8 was compressed under similar conditions, the starting materials were recovered without change. It was also confirmed that the scrambling between 4 and 6 does not occur at high pressure. An equimolecular mixture of 1 and 7 was compressed at room temperature, and then the pressure was released immediately. ^{1}H NMR and GLPC analyses of the recovered ketene acetals revealed that the scrambling of the silyl groups does not occur in the substrate. Taken together, these results suggest that the migration proceeds intermolecularly. A possible transition state is depicted in Scheme I. In conclusion, the present findings provide not only a new method for the synthesis of α-silylated esters and lactones

Scheme I. Intermolecular Silicon Migration from Oxygen to Carbon



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(3) For a general review, see: Isaacs, N. S. "Liquid Phase High Pressure Chemistry"; Wiley: New York, 1981. le Noble, W. J.; Kelm, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 841. Dauben, W. G.; Krabbenhoft, H. O. *J. Org. Chem.* **1977**, *42*, 282. A description of the high-pressure equipment employed in this study will appear shortly: Matsumoto, K.; Sera, A.; Uchida, T. *Synthesis*, in press.

(4) For synthesis of α-silylated ketones, see: Sato, S.; Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1983**, 3855 and references cited therein.

(5) The reason for the formation of the desilylated compound is not clear. In the reaction of tri-*n*-butylsilyl derivatives, column chromatography with silica gel was employed prior to distillation to remove the tri-*n*-butylsilyl residue which was formed by the desilylation process.

(6) The effect of pressure on the degenerate migration of the Me_3Si group of 5-(trimethylsilyl)cyclopentadiene has been reported: Schulman, E. M.; Merbach, A. E.; Turin, M.; Wedinger, R.; le Noble, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3988.

(7) These ratios indicate that the total material balances with respect to the silyl groups and the lactone moieties are not in good agreement, presumably owing to the desilylation.

but also new insight into the silicon migration from oxygen to carbon, which has previously thought to proceed intramolecularly.[8]

Registry No. 1, 51425-66-2; 2, 57025-69-1; 3, 91390-63-5; 4, 91390-59-9; 5, 74477-44-4; *cis*-6, 91390-60-2; *trans*-6, 91390-65-7; 7, 91390-64-6; *cis*-8, 91390-61-3; *trans*-8, 91390-66-8; (*E*)-[(1-ethoxy-1-propenyl)oxy]trimethylsilane, 73967-97-2; [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane, 31469-15-5; ethyl 2-(trimethylsilyl)propanoate, 13950-55-5; methyl 2-methyl-2-(trimethylsilyl)propanoate, 55499-73-5; dimethyl[(1-methoxyethenyl)oxy]*tert*-butylsilane, 77086-38-5; methyl (dimethyl(*tert*-butyl)silyl)acetate, 91390-62-4.

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[8] Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. Lutsenko, I. F.; Baukov, Y. I.; Kostyuk, A. S.; Savelyeva, N. I.; Krysina, V. K. *J. Organomet. Chem.* **1969**, *17*, 241. Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1978**, *43*, 881. Casey, C. P.; Jones, C. R.; Tukada, H. *Ibid.* **1981**, *46*, 2089.

Carbonylation of $(\eta^5\text{-}C_5H_5)_2Zr(Cl)CH_2P(C_6H_5)_2$: Formation of a Dinuclear Zirconocene(IV) Phosphine Complex via Intermolecular Proton Transfer

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Received April 9, 1984

Summary: Carbonylation of $Cp_2Zr(Cl)CH_2PPh_2$ results in the formation of Ph_2PCH_3 and $(Cp_2ZrCl)_2(\mu\text{-}Ph_2PCH{=\!=}CO)$. The latter has been characterized by IR and NMR, and the structure has been determined by X-ray diffraction. A mechanism is proposed involving cleavage of an alkyl-Zr bond by a methylene proton of a simple acyl. Bridging by oxygen and phosphorus then leads to the observed product.

In a recent report Choukroun and Gervais describe the carbonylation of $Cp_2Zr(Cl)CH_2PPh_2$ (1) as leading to the normal acyl product $Cp_2Zr(Cl)COCH_2PPh_2$ (2).[1] In the course of our work in this area[2,3] we had attempted to carry out the same reaction but were puzzled by both the unexpected insolubility of the carbonylation product as well as by its anomalously low infrared CO stretching frequency (ν_{CO} = 1520 cm^{-1}). Typical values for $Cp_2Zr(Cl)COR$ are ν_{CO} > 1550 cm^{-1}.[4] Via a modified carbonylation technique we have recently succeeded in crystallizing a carbonylation product of 1. Herein we describe the structure of this material, an unusually bridged dinuclear complex the formation of which has significant implications on other recent studies of the carbonylation of group 4 metallocene derivatives.

We have carried out carbonylation reactions on 1 in several different ways. Bubbling dry CO through a THF or benzene solution 0.01–0.1 M in 1, or stirring, or shaking such a solution under 1 atm of CO gives rise first to a deep reddish solution showing numerous new NMR resonances in the Cp region. Over a period of hours, the color of the solution fades as the insoluble, white powdery carbonylation product appears. The material is sufficiently soluble in $CDCl_3$ to allow the collection of the following 360-MHz NMR data: δ 5.19 (d, *J* = 1.5 Hz, 1 H), 6.06 (s, 10 H), 6.12 (d, *J* = 0.8 Hz, 10 H), 7.45 (m, 6 H), 7.86 (m, 4 H), clearly inconsistent with structure 2. The elemental analysis, even given the usual problems associated with analyses of zirconocene alkyls, is also at odds with a simple acyl.[5] In an attempt to generate crystals of sufficient quality for X-ray analysis, the space above a concentrated THF solution of 1 in an NMR tube was gently flushed and filled with CO, and the system left undisturbed to permit slow diffusion of the gas into the solution. This experiment resulted in the formation of small but suitable crystals for X-ray examination.

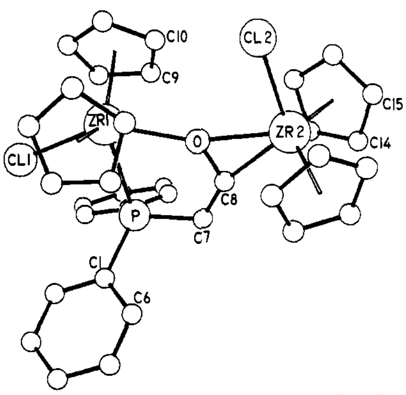

Figure 1. Computer drawn representation of 3. A mirror plane containing atoms Zr(1), Zr(2), Cl(1), Cl(2), P, O, C(7), and C(8) bisects the molecule; thus the two Cp rings on Zr(1) are identical, as are the two Cp rings on Zr(2) and the two phenyl groups on P. In this figure the top of the mirror plane is tilted toward the viewer.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 3

Bond Distances

Zr(1)-Cl(1)	2.564 (3)	Zr(2)-C(8)	2.231 (9)
Zr(1)-P	2.752 (3)	P-C(7)	1.776 (12)
Zr(1)-O	2.303 (8)	C(7)-C(8)	1.313 (14)
Zr(2)-Cl(2)	2.563 (3)	C(8)-O	1.330 (16)
Zr(2)-O	2.278 (7)		

Bond Angles

Cl(1)-Zr(1)-P	74.1 (1)	Zr(1)-P-C(7)	101.6 (4)
P-Zr(1)-O	69.7 (2)	Zr(1)-O-C(8)	127.1 (5)
Cl(2)-Zr(2)-O	83.2 (2)	Zr(2)-C(8)-C(7)	159.9 (11)
O-Zr(2)-C(8)	34.3 (4)	Zr(2)-C(8)-O	74.8 (5)
Zr(1)-O-Zr(2)	161.9 (4)	P-C(7)-C(8)	116.3 (10)

Crystals of this material are monoclinic of space group *C*2/*m* with *a* = 16.762 (4) Å, *b* = 16.366 (4) Å, *c* = 11.488 (3) Å, β = 112.65 (2)°, *V* = 2908 (1) Å^3 (*T* = 140 K), and *Z* = 4. The structure, determined from 1347 graphite-monochromatized Mo Kα reflections (λ = 0.71069 Å) measured at 140 K for which $I > 3\sigma(I)$, was solved by direct methods (program SHELXTL, version 3). Blocked cascade least-squares refinement of 193 parameters (non-hydrogen atoms anisotropic, hydrogen atoms in calculated positions with fixed geometry) gave final $R = R_w = 0.039$.

The compound is thus identified as an oxygen-bridged dinuclear species with two distinct Cp_2ZrCl fragments also linked by a PCC bridge (Figures 1 and 2 and structure 3). In the bridge, the PCC bond angle is 116°, the OCC bond

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[5] Anal. Calcd for $C_{24}H_{22}ClOPZr$ (simple acyl): C, 59.54; H, 4.58; Cl, 7.32; P, 6.40. Calcd for $C_{34}H_{31}Cl_2OPZr_2$ (actual product): C, 55.19; H, 4.22; Cl, 9.58; P, 4.19. Found: C, 53.07; H, 4.20; Cl, 8.83; P, 3.46. The actual purity of 3 as isolated has been determined by NMR of a fully dissolved sample (CD_2Cl_2, 500 MHz): 3, 97.6%; $(CpZrCl)_2O$, 2.4%; Cp_2ZrCl_2, undetectable (<0.3%). No other non-solvent-derived signals are present.

0276-7333/84/2303-1585$01.50/0