Synthesis, reactivity, and molecular structure of silatrane manganese complex [(phenylsilatrane)Mn(CO)2P(OMe)3]ClO4

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A significant shortening of both methine carbon–phosphorus bond distances for 2 compared to the methylene–phosphorus bonds of 1 are consistent with the delocalized partial multiple P–C bond character expected upon deprotonation of 1. The ylide carbon–phorphorus bond distance of 1, *d*(P4–C5) = 1.73 (1) Å, indicates significant double-bond character.[4] The corresponding carbon–phosphorus bond distance of 2 is slightly longer, 1.772 (7) Å, again consistent with delocalized vs localized carbon–phosphorus ylide double bonds in 2 vs 1, respectively. This delocalization has no apparent effect on the ylide carbon–nickel bond distances but does increase the phosphorus–nickel bond distance of 2 compared to 1.

A survey of the chemistry of 1 with CO, CO$_2$, and ethylene indicates no significant reactivity at 1 atm. Our ongoing efforts are based on employing the new phosphorus ylide, (methylenediphenylphosphino)(diphenylphosphino)methane (A), as a ligand in monochelate complexes related to existing nickel olefin homologation and polymerization catalysts.[1-7]

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Supplementary Material Available: Textual presentation of experimental procedures, tables of experimental details and results, torsional angles, positional and isotropic thermal parameters, general temperature factor expressions, and bond distances and angles, and a figure showing observed and calculated ^{31}P{^{1}H} NMR spectra at 81 MHz for 1 (18 pages); a listing of observed and calculated structure factors for 1 (12 pages). Ordering information is given on any current masthead page.

Synthesis, Reactivity, and Molecular Structure of [(phenylsilatrane)Mn(CO)$_2$P(OMe)$_3$]ClO$_4$

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Summary: [(phenylsilatrane)Mn(CO)$_2$P(OMe)$_3$]ClO$_4$ (2) has been prepared by reaction of [(phenylsilatrane)Mn(CO)$_3$]ClO$_4$ (1) with P(OMe)$_3$. Compound 2 undergoes regioselective reactions with MeLi, PhLi, and PhMgBr in CH$_2$Cl$_2$. However, 2 does not react regioselectively with carbanions in THF. Complex 2 crystallizes in the monoclinic space group $P2_1/n$ with a = 16.354 (4) Å, b = 6.585 (1) Å, c = 22.165 (5) Å, β = 97.52 (1)°, V = 2366.7 Å^3, and Z = 4. The structure was refined to R = 0.051 and R_w = 0.051 for all 4741 reflections.

In recent studies we and others have established the utility of (arene)Mn(CO)$_3$$^+$ cations in difunctionalizing cyclohexadienes by nucleophilic addition to coordinated arenes.[2] The factors influencing the observed regiochemistry of nucleophilic attack are very important and need clarification. The regioselectivity for the addition of nucleophiles to (C$_6$H$_5$X)Cr(CO)$_3$ can generally be controlled not only by the substituent on the arene but also by the conformation.[3] With alkyl substituents, while the expected meta attack predominates for small X (Me and Et), reaction at the para position increases with increasing steric bulk of X until it becomes the only site of attack for X = CH^{t}Bu$_2$.[4] This unusual observation has been rationalized in terms of the conformational preferences of the Cr(CO)$_3$ group.[3] We expect that the regiochemistry of (arene)Mn(CO)$_3$$^+$ would be very similar to that of (arene)Cr(CO)$_3$.[5]

Recently we reported the use of phenylsilatrane as a π-coordinating ligand for transition metals.[6] The chemistry of the Cr(CO)$_3$ and Mn(CO)$_3$$^+$ derivatives of phenylsilatrane has been studied.[6a,b] The Mn(CO)$_3$$^+$ derivative 1 undergoes regioselective reaction with RMgBr (R = Ph, Et, Et) in CH$_2$Cl$_2$ to give [η^5-1-(N(CH$_2$CH$_2$O)$_3$Si)-6-(R)-C$_6$H$_5$]Mn(CO)$_3$ and RMgBr (R = Ph, Me, Et) and LiR (R = CH$_2$CO$_2$CMe$_3$, CH$_2$CN, $\overline{\text{CHC(CH}_2)_3\text{S}}$) in THF to yield [$\eta^5$-3-(N(CH$_2CH_2$O)$_3$Si)-6-(R)-C$_6H_5$]Mn(CO)$_3$. The selectivity of the nucleophile addition to 1 is strongly dependent on the nucleophile and reaction medium. This special regioselectivity of compound 1 would partially come from the staggered conformation of metal carbonyls.[6c]

To elucidate the possible effects of various factors that may influence the regioselectivity of the carbanion addition, we have prepared [(N(CH$_2$CH$_2$O)$_3$SiC$_6$H$_5$)Mn(CO)$_2$P(OMe)$_3$]ClO$_4$ (2) from 1 and studied the reactivity of compound 2. In this note we report the synthesis of

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Table I. Crystal Data and Experimental Details for $[(N(CH_2CH_2O)_3SiC_6H_5)Mn(CO)_2P(OMe)_3]ClO_4$

formula	$C_{17}H_{26}ClMnNO_{12}PSi$
fw	585.85
cryst syst	$P2_1/n$
a, b, c, Å	16.354 (4), 6.585 (1), 22.165 (5)
β, deg	97.52 (1)
Z	4
d_{calcd}, g cm^{-3}	1.64
μ, cm^{-1}	8.2
cryst size, mm	0.50 × 0.30 × 0.05
radiation	Mo Kα (λ = 0.71073 Å)
scan method	ω–2θ
2θ range, deg	$2 < 2\theta < 52$
no. of rflns measd	5167
no. of rflns obsd, $F_o > \sigma(F_o)$	4398
no. of params refined	407
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.051
$R_w = (\sum(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2)^{1/2}$	0.051

compound 2 and its reaction with several nucleophiles. We also report the molecular structure of compound 2.

Experimental Section

General Considerations. All solvents were purified by standard methods, and reagent grade chemicals were used without further purification.

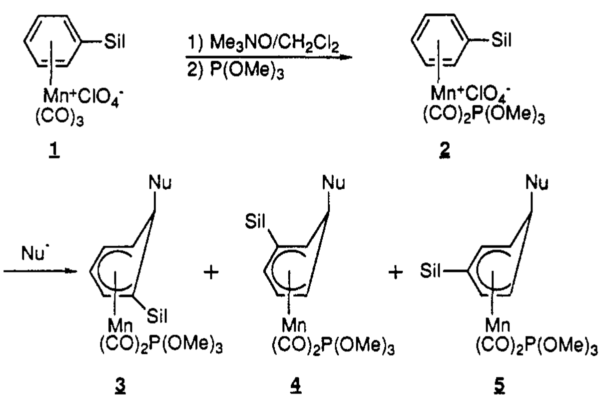
Elemental analyses were performed at the Chemical Center of the College of Engineering, Seoul National University, or at the Korea Basic Science Center. Instruments used in this work were a Varian XL-200 NMR spectrometer and a Perkin-Elmer 782 infrared spectrophotometer (spectra measured as films on NaCl by evaporation of solvent).

Compound 1 was synthesized as previously described.[6b] By published procedures,[6b,c] nucleophilic addition of $NaBH_4$, MeLi, PhLi, *t*-BuLi, $LiCMe_2CN$, MeMgBr, PhMgBr, and $LiCH_2CO_2CMe_3$ to 2 gave the corresponding cyclohexadienyl complexes 3–5. Experimental details and spectral and analytical data for compounds 3–5 are given in the supplementary material.

Synthesis of Compound 2. $[(N(CH_2CH_2O)_3SiC_6H_5)Mn(CO)_3]ClO_4$ (1.2 mmol, 0.588 g) and $P(OMe)_3$ (3.6 mmol, 0.42 mL) were stirred in dry dichloromethane (120 mL) under N_2 at room temperature while Me_3NO (1.34 mmol, 0.101 g) was added. After 30 min, the reaction mixture was washed with water (50 mL × 5) to remove excess Me_3NO. The dichloromethane solution was dried and concentrated. Recrystallization with CH_2Cl_2/diethyl ether gave yellow crystalline solids (yield 0.503 g, 75%): mp 158.9 °C dec; ^1H NMR ($CDCl_3$) δ 6.4–6.2 (m, 5 H, Ph), 3.92 (t, J = 5.9 Hz, OCH_2), 3.81 (d, J = 11.6 Hz, 9 H, $P(OCH_3)_3$), 3.19 (t, J = 5.9 Hz, 6 H, NCH_2) ppm; IR (NaCl) ν_{CO} 2000, 1950 cm^{-1}. Anal. Calcd for $C_{17}H_{26}ClMnNO_{12}PSi$: C, 34.85; H, 4.47; N, 2.39. Found: C, 35.07; H, 4.49; N, 2.35.

Collection and Refinement of X-ray Data for 2. Crystals of 2 were obtained by slow evaporation of a solution of compound 2 in CH_2Cl_2/acetone (1:1) at 10 °C. A yellow platelike crystal of dimensions 0.50 × 0.30 × 0.05 mm was mounted on a glass fiber in a random orientation. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.71073 Å) at ambient temperature (20 ± 1 °C). A preliminary diffractometric investigation indicated that 2 belongs to the space group $P2_1/n$. The lattice constants were determined by the last-squares refinement of the diffraction geometry for 25 intense reflections having $10 < \theta < 19°$. Crystal parameters for the complex and information on the procedure used for data collection and refinement are given in Table I. Intensity data were collected by the 2θ–ω scan technique; data were collected to a maximum 2θ value of 52°, and the ratio of peak-counting time to background-counting time was 2:1. A total of 5167 unique reflections were collected, of which 4741 were not systematically absent. Lorentz and polarization corrections were applied to the data, and an empirical absorption correction based on a series of ψ scans was applied (μ = 8.2 cm^{-1}, minimum relative transmission value of 0.853). The structure was solved by direct methods. Using 35 reflections (minimum E value of 1.20) and 5535 relationships, a total of 32 phase sets were produced. Only three heavy atoms (Mn, Si, and P) were located from an E-map prepared from the phase set. The remaining non-hydrogen atoms were located in succeeding DIRDIF-weighted Fourier syntheses. The O atoms of ClO_4 were disordered, and their occupancy factors and isotropic parameters were refined in alternating cycles. In the last stage, only the latter were refined. Hydrogen atoms were included at their calculated positions, and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as 1.0 for 4398 observed reflections ($I > \sigma_I$). The final difference Fourier map showed no significant residual electron density except for a few of maximum height 1.0 e/Å^3 around Cl(3). The distances of these peaks from Cl(3) were in the range of 1.3–1.5 Å, implying an even higher degree of disorder of the ClO_4 anion. These were refined as oxygens to occupancy factors around 0.1 and thermal parameters $B \approx 9$ Å^2. As their refinement was ill-tempered and was resistant to convergence, they were omitted from the model. Plots of $w(|F_o| - |F_c|)^2$ versus F_o, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using the Molen (Enraf-Nonius) program.[7]

Scheme I



a, Nu = Me ; b, Nu = Ph ; c, Nu = ^{t}Bu
d, Nu = H ; e, Nu = CMe_2CN ; f, Nu = $CH_2CO_2{}^tBu$

Sil = $Si(OCH_2CH_2)_3N$

Results and Discussion

The phosphite-substituted manganese complex 2 was synthesized by the reaction between 1 and $P(OMe)_3$. The yield was rather lower than those of other (arene)manganese complexes.[8] Complex 2 was stable in air but rather unstable in polar organic solvents such as acetone and acetonitrile. Nucleophilic addition reactions to complex 2 were studied in THF or CH_2Cl_2 in order to compare the reaction medium effect on the regioselectivity with that found in the reaction between compound 1 and carbanions.

There might be several kinds of medium effects on the reaction between 2 and carbanions. One of them would be the aggregation of organometallic compounds, such as RLi and RMgX, in the reaction medium.[9] However, the degree of aggregation of RLi or RMgX in CH_2Cl_2 has not been studied thoroughly. Thus, it is often not easy to interpret the product distribution according to the steric effect of carbanion in the solution. There would be some

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Table II. Reaction of Complexes 1 and 2 with Nucleophiles

			complex 2				complex 1			
			product distribn			combined	product distribn[a]			combined
nucleophile	medium	temp, °C	3	4	5	yield, %	3′	4′	5′	yield, %
MeLi	THF	0	64	16	20	91.0	0	9	91	42.0
MeLi	CH_2Cl_2	0	100	0	0	97.6	100	0	0	42.0
MeMgBr	THF	0	22	37	41	52.6	0	0	100	72.5
PhLi	THF	0	80	13	7	78.0				N.R.
PhLi	CH_2Cl_2	0	100	0	0	51.4				N.R.
PhMgBr	THF	0	0	42	58	71.1	0	25	75	57.2
PhMgBr	CH_2Cl_2	0	100	0	0	66.8	100	0	0	56.7
$NaBH_4$	THF	−3	0	35.5	64.5	79.5	0	6	94	76.6
$NaBH_4$	CH_2Cl_2	−3	0	45.5	54.5	35.6	0	6	94	74.0
t-BuLi	THF	0	49	19	32	84.6	5	41	54	43.3
t-BuLi	CH_2Cl_2	0	82	0	18	88.0				
$LiCMe_2CN$	THF	−78	0	60	40	84.0	0	46	54	52.0
$LiCMe_2CN$	CH_2Cl_2	0	0	51	49	83.2				
$LiCH_2CO_2CMe_3$	THF	−78	22	32	46	84.6	0	0	100	62.0
$LiCH_2CO_2CMe_3$	THF	0	12	40	48	89.0				
$LiCH_2CO_2CMe_3$	CH_2Cl_2	0	23	50	27	57.4				

[a] These data are reproduced from ref 6c for comparison: 3′ = ortho adduct; 4′ = meta adduct; 5′ = para adduct.

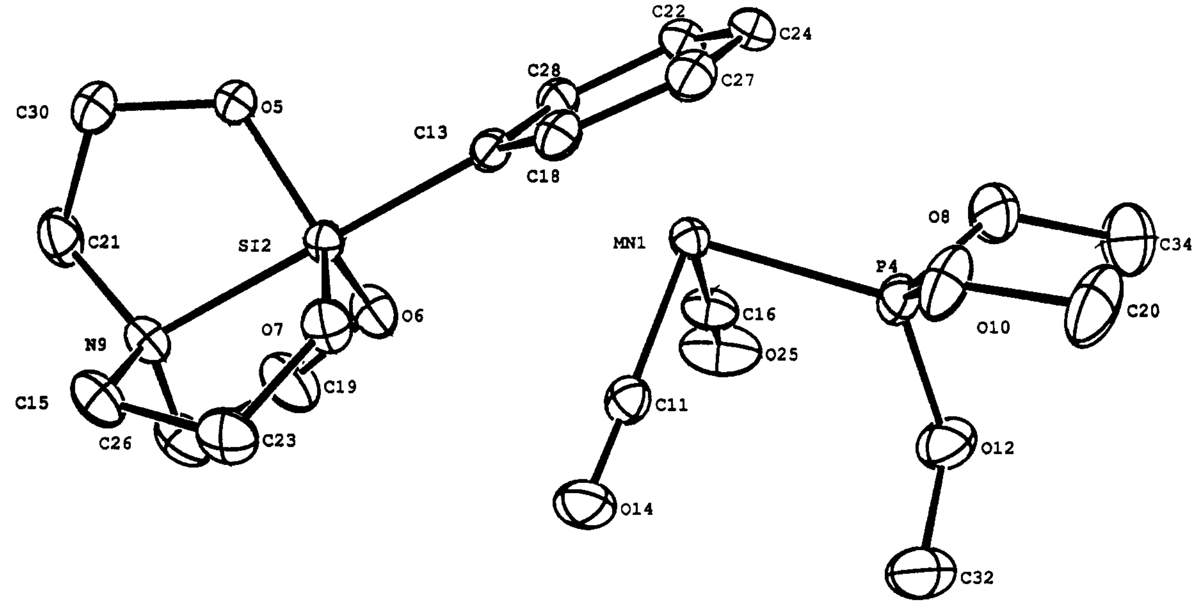

Figure 1. ORTEP drawing of the cation $[(N(CH_2CH_2O)_3SiC_6H_5)Mn(CO)_2P(OMe)_3]^+$, showing the labeling scheme with 30% thermal ellipsoids. The counteranion is omitted for simplicity.

interactions between oxygens on the silatrane moiety of compound 2 and metal cations, such as Na^+ and Li^+, in methylene chloride. However, there might be no such interactions in THF. This could be one of the differences in the reaction medium effects. In CH_2Cl_2, ortho adducts were obtained as a major product for the addition of MeLi, PhLi, ^{t}BuLi, and PhMgBr. However, in THF, other adducts were obtained as a major product. Table II and Scheme I show the results of the reaction between 2 and several kinds of carbanions.

For the reaction between 2 and MeLi, MeMgBr, PhLi, and ^{t}BuLi in THF, three kinds of isomers were obtained. When we compare the isomer ratios for RLi additions, the relative ortho adduct decreased in the following order: PhLi > MeLi > ^{t}BuLi. In contrast, the para adduct decreased in the following order: ^{t}BuLi > MeLi > PhLi. In THF, changing the nucleophile from MeMgBr to PhMgBr increased the relative para adduct at the expense of ortho adduct. For the addition of $LiCMe_2CN$ in THF, changing the reaction temperature does not result in any noticeable changes in the yield and isomer ratio.

For the addition reaction of MeLi, PhLi, and PhMgBr in CH_2Cl_2, the ortho adduct was found as the sole product. For the addition of ^{t}BuLi in CH_2Cl_2, the steric bulkiness might be the reason for the formation of some para adduct.

For the addition of $NaBH_4$, only meta and para adducts were obtained in the ratios of 1:1.8 and 1:1.2 in THF and CH_2Cl_2, respectively. The reason for the relatively low medium effect would be the insolubility of $NaBH_4$ in both solvents. The addition of $LiCH_2CO_2CMe_3$ was not regioselective in both solvents.

Compound 2 did not react with the carbanions of ethyl acetoacetate and ethyl cyanoacetate, or with sodium cyanide. The inertness of compounds 2 to the above nucleophiles might come from the large electron density buildup at the metal center. The replacement of CO by phosphite increases the electron density on the metal, and the electrophilicity of compound 2 would be much lower than that of 1.[10] As a result, strong carbanions are needed. Treatment of PhLi with 1 did not produce any organometallic compound. However, PhLi reacts with compound

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Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[(N(CH_2CH_2O)_3SiC_6H_5)Mn(CO)_2P(OMe)_3]ClO_4$

	Distances (Å)		
Mn1–P4	2.198 (1)	O6–C30	1.431 (5)
Mn1–C11	1.801 (4)	O7–C23	1.423 (5)
Mn1–C13	2.198 (3)	O8–C34	1.431 (6)
Mn1–C16	1.796 (4)	O10–C20	1.452 (6)
Mn1–C18	2.186 (3)	O12–C32	1.451 (7)
Mn1–C22	2.193 (4)	O14–C11	1.141 (5)
Mn1–C24	2.187 (3)	O25–C16	1.140 (5)
Mn1–C27	2.187 (3)	N9–C15	1.486 (5)
Mn1–C28	2.167 (4)	N9–C21	1.483 (5)
P4–O8	1.590 (4)	N9–C26	1.472 (5)
P4–O10	1.582 (3)	C13–C18	1.428 (5)
P4–O12	1.576 (3)	C13–C28	1.404 (5)
Si2–O5	1.658 (3)	C18–C27	1.399 (5)
Si2–O6	1.654 (3)	C19–C26	1.510 (7)
Si2–O7	1.660 (3)	C21–C30	1.504 (6)
Si2–N9	2.064 (3)	C22–C24	1.383 (6)
Si2–C13	1.921 (4)	C22–C28	1.423 (6)
O5–C30	1.422 (5)	C24–C27	1.413 (6)
	Bond Angles (deg)		
P4–Mn1–C11	90.9 (1)	O5–Si2–O16	119.4 (1)
P4–Mn1–C16	87.5 (1)	O5–Si2–O7	117.9 (1)
C13–C18–C27	122.4 (4)	O5–Si2–N9	85.9 (1)
C13–C28–C22	122.4 (3)	O5–Si2–C13	94.5 (1)
C18–C27–C24	119.7 (4)	O6–Si2–O7	121.2 (1)
C27–C24–C22	119.7 (4)	O6–Si2–N9	85.7 (1)
C24–C22–C28	119.9 (4)	O6–Si2–C13	93.6 (1)
C28–C13–C18	115.8 (3)	O7–Si2–N9	86.0 (1)
Si2–O5–C30	120.5 (2)	O7–Si2–C13	94.4 (2)
Si2–O6–C19	120.9 (3)	Si2–N9–C15	104.8 (2)
Si2–O7–C23	119.9 (3)	Si2–N9–C21	105.0 (2)
O5–C30–C21	109.0 (3)	Si2–N9–C26	105.4 (3)
O6–C19–C26	108.3 (4)	C15–N9–C21	113.3 (3)
O7–C23–C15	108.5 (3)	C15–N9–C26	113.4 (3)
C30–C21–N9	106.4 (3)	C21–N9–C26	113.8 (3)
C19–C26–N9	106.5 (3)	Mn1–C11–O14	178.5 (4)
C23–C15–N9	106.0 (3)	Mn1–C16–O25	178.9 (4)
N9–Si2–C13	179.2 (1)		

2 to give a high yield of phenyl adducts. When we compare the regioselectivity and the yield of compound 2 with the nucleophiles with those of compound 1, the regioselectivities decrease and the yields are improved slightly. However, the overall trends of nucleophilic addition to compound 2 are similar to those of compound 1.

Molecular Structure of 2. Final fractional atomic coordinates with equivalent isotropic parameters are given in Table III. The geometry of the cation unit showing the atomic numbering scheme used is depicted in Figure 1, and selected bond distances and angles are given in Table IV. The cation displays the well-known piano-stool conformation found[11] in half-sandwich complexes with the two carbonyl ligands and $P(OMe)_3$ in a nearly staggered orientation relative to the C atoms of the phenyl ring. When the tripod of $Mn(CO)_2P(OMe)_3$ is projected onto the plane of the arene ring, the torsion angles C22–G–Mn–C16, C13–G–Mn–C11, and C27–G–Mn–P are respectively 41.1 (7), 35.2 (2), and 39.2 (9)° (when the Mn atom is projected on the plane containing C(13), C(18), and C(28) atoms, G is the corresponding point). The staggered conformation of compound 2 appears to arise because of the steric bulk of the silatranyl group. $[(C_6H_5Si(OCH_2CH_2)_3N)Cr(CO)_3]$[6a] has been observed to have a similar conformation, in which the carbonyl groups are rotated by 32.5° from the syn-eclipsed form. The least-squares plane of the phenylsilatrane group is perpendicular to the pseudo-C_3 axis which passes through the center of the ring and the Mn atom. However, the planarity of the phenyl ring is almost broken. The ring C–C bond distances vary between 1.383 (6) and 1.428 (5) Å, and the alternating longer C–C bonds (1.413 (6), 1.423 (6), and 1.428 (5) Å) are those that project on the Mn–$P(OMe)_3$ and Mn–CO bonds.[12] The carbon–carbon bond distance projecting on the $P(OMe)_3$ ligand is 1.413 (6) Å.

Table IV. Non-Hydrogen Atom Positional and Equivalent Thermal Parameters for $[(N(CH_2CH_2O)_3SiC_6H_5)Mn(CO)_2P(OMe)_3]ClO_4$[a]

atom	*x*	*y*	*z*	*B*, Å²	occ
Mn1	0.92706 (3)	0.04624 (8)	0.34753 (2)	2.110 (9)	
P4	1.05080 (6)	0.1491 (2)	0.33283 (5)	2.98 (2)	
Si2	0.71561 (6)	0.0734 (1)	0.38816 (4)	2.08 (2)	
O5	0.6372 (1)	−0.0493 (4)	0.3493 (1)	2.79 (5)	
O6	0.7698 (2)	−0.0387 (4)	0.4471 (1)	3.28 (5)	
O7	0.7232 (2)	0.3214 (4)	0.3766 (1)	3.04 (5)	
O8	1.1036 (2)	−0.0364 (5)	0.3131 (2)	5.03 (8)	
O10	1.0464 (2)	0.3196 (5)	0.2822 (1)	4.39 (7)	
O12	1.1130 (2)	0.2280 (5)	0.3882 (1)	4.26 (7)	
O14	0.9060 (2)	0.3990 (5)	0.4255 (1)	4.42 (7)	
O25	1.0049 (3)	−0.1732 (5)	0.4554 (1)	5.61 (8)	
N9	0.6338 (2)	0.1489 (5)	0.4480 (1)	2.77 (6)	
C11	0.9150 (2)	0.2635 (6)	0.3949 (2)	2.77 (7)	
C13	0.7927 (2)	0.0017 (6)	0.3333 (2)	2.29 (6)	
C15	0.6114 (3)	0.3638 (6)	0.4337 (2)	3.71 (9)	
C16	0.9753 (3)	−0.0867 (6)	0.4135 (2)	3.27 (8)	
C18	0.8155 (2)	0.1403 (6)	0.2889 (2)	2.63 (7)	
C19	0.7386 (3)	−0.0534 (8)	0.5043 (2)	4.6 (1)	
C20	1.1174 (3)	0.4068 (9)	0.2587 (2)	5.7 (1)	
C21	0.5638 (3)	0.0064 (7)	0.4338 (2)	3.81 (9)	
C22	0.8937 (2)	−0.2372 (6)	0.2984 (2)	3.11 (8)	
C23	0.6867 (3)	0.4606 (6)	0.4143 (2)	3.83 (9)	
C24	0.9164 (2)	−0.0956 (7)	0.2576 (2)	3.26 (8)	
C26	0.6799 (3)	0.1211 (8)	0.5091 (2)	4.2 (1)	
C27	0.8767 (2)	0.0954 (7)	0.2523 (2)	3.20 (8)	
C28	0.8329 (2)	−0.1872 (6)	0.3363 (2)	2.59 (7)	
C30	0.5567 (2)	−0.0351 (7)	0.3666 (2)	3.64 (9)	
C32	1.1100 (4)	0.4259 (9)	0.4165 (3)	6.5 (1)	
C34	1.1909 (3)	−0.042 (1)	0.3120 (3)	6.5 (1)	
Cl3	1.37599 (6)	0.4305 (2)	0.34753 (5)	4.02 (2)	
O27	1.2995 (4)	0.5160 (9)	0.3607 (3)	9.4 (1)*	0.943
O29	1.4066 (5)	0.407 (1)	0.4371 (3)	7.9 (2)*	0.603
O33	1.3586 (7)	0.212 (2)	0.3590 (5)	9.9 (3)*	0.487
O41	0.4249 (7)	0.611 (2)	0.4025 (5)	9.1 (3)*	0.453
O42	0.4342 (4)	0.450 (1)	0.3333 (3)	7.8 (2)*	0.693
O44	0.3818 (8)	0.298 (2)	0.4234 (6)	8.7 (3)*	0.391
O51	0.9063 (8)	0.176 (2)	0.8283 (6)	5.9 (3)*	0.283
O52	0.069 (1)	0.087 (4)	0.141 (1)	5.2 (5)*	0.158

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labeling scheme. Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Complex 2 possesses the usual skeleton containing a five-coordinate silicon atom.[13] The N–Si–C13 angle is 179.2 (1)°. The Si atom is displaced by 0.13 Å from the center of the plane defined by O5, O6, and O7, toward C13. The stereochemistry of the Si atom is distorted trigonal bipyramidal. Introduction of $Mn(CO)_2(P(OMe)_3)^+$ into the phenylsilatrane does not affect the silatrane geometry very much. When we compare the N–Si bonds of 2 and $(\text{phenylsilatrane})Cr(CO)_3$[6a] with that of phenylsilatrane,[14] the N–Si bond of 2 is shortened in this case by 0.13 Å, to 2.064 (3) Å, while the N–Si bond in $(\text{phenylsilatrane})Cr(CO)_3$ is shortened by 0.08 Å, to 2.108 (5) Å. The positive charge on the manganese atom results in a contraction in the Si–N distances. When we compare the Si–C(phenyl)bonds of 2 and $(\text{phenylsilatrane})Cr(CO)_3$ with that of phenyl-

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silatrane,[13] the Si–C(phenyl) bond of **2** is lengthened in this case by 0.04 Å, to 1.921 (4) Å, and the Si–C(phenyl) bond in (phenylsilatrane)Cr$(CO)_3$[6a] is lengthened by 0.03 Å, to 1.907 (6) Å. The equatorial O–Si bond lengths in **2** (1.654 (3)–1.660 (3) Å, average 1.657 Å) are very close to the values (average 1.656 Å) in (phenylsilatrane)Cr$(CO)_3$.[6a] The C18–C13–C28 bond angle at the ipso carbon of the phenyl ring in **2** is 115.8 (3)°, which is very close to the value for (phenylsilatrane)Cr$(CO)_3$ (116.1 (6)°).[6a] Other numerical parameters for **2** are similar to those for (phenylsilatrane)Cr$(CO)_3$.[6a]

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Registry No. **1**, 129619-20-1; **2**, 138898-80-3; **3a**, 138856-08-3; **3b**, 138856-09-4; **3c**, 138856-10-7; **3f**, 138856-11-8; **4a**, 138856-12-9; **4b**, 138856-13-0; **4c**, 138856-14-1; **4d**, 138856-15-2; **4e**, 138856-16-3; **4f**, 138856-17-4; **5a**, 138856-18-5; **5b**, 138856-19-6; **5c**, 138856-20-9; **5d**, 138856-21-0; **5e**, 138856-22-1; **5f**, 138856-23-2; THF, 109-99-9; MeLi, 917-54-4; MeMgBr, 75-16-1; PhLi, 591-51-5; PhMgBr, 100-58-3; $NaBH_4$, 16940-66-2; *t*-BuLi, 594-19-4; $LiCMe_2CN$, 55440-70-5; $LiCH_2CO_2CMe_3$, 53503-61-0; CH_2Cl_2, 75-09-2.

Supplementary Material Available: Listings of complete interatomic distances and angles, anisotropic thermal parameters, positional and thermal parameters for hydrogen atoms, and torsion angles for non-hydrogen atoms for **2** and text giving experimental details and spectral and analytical data for compounds **3–5** (21 pages); a listing of observed and calculated structure factors for **2** (22 pages). Ordering information is given on any current masthead page.

Stable Bis(η^5-cyclopentadienyl)zirconacyclopentadiene Complexes

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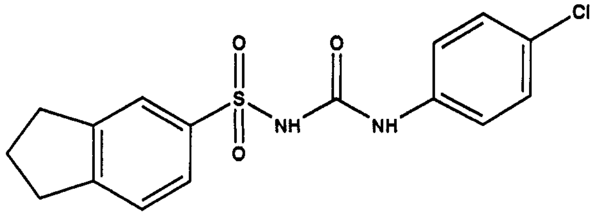
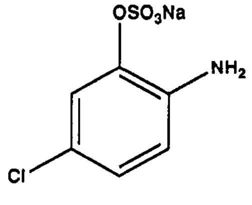
Summary: Attempts to synthesize fused bicyclic thiophenes by zirconocene-mediated cyclization of bis(trimethylsilyl) α,ω-diynes led to the isolation of air-stable bis(η^5-cyclopentadienyl)zirconacyclopentadiene complexes when there is a heteroatom (i.e. oxygen or substituted nitrogen) tethered between the acetylenes.

The excellent preclinical antineoplastic properties of a class of diarylsulfonylureas has culminated in clinical development of sulofenur (LY186641).[1] An effort to improve the pharmacological properties of this novel class of oncolytics has resulted in a search for more potent diarylsulfonylureas with decreased levels of circulating sodium 4-chloroaniline *O*-2-sulfate (PCAM1, the metabolite monitored as an indicator of methemoglobinemia).[2] The replacement of the benzenesulfonamide of the diarylsulfonylureas with substituted thiophene-2-sulfonamide has led to the discovery of compounds with increased potency. This paper will summarize the synthesis of fused bicyclic thiophenesulfonylureas with an emphasis on group IV transition-metal-mediated functionalization of bis(trimethylsilyl) α,ω-diynes.[3]

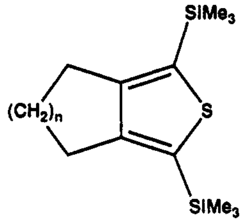


LY186641



PCAM1

The 5,6-dihydro-4*H*-cyclopenta[*b*]thiophene and 4,5,6,7-tetrahydrobenzo[*b*]thiophene were prepared by previously described procedures.[4] The 5,6-dihydro-4*H*-cyclopenta[*c*]thiophene and 4,5,6,7-tetrahydrobenzo[*c*]thiophene were synthesized by the alkylation of the corresponding bis(η^5-cyclopentadienyl)zirconacyclopentadienes with sulfur monochloride[5] followed by tetrabutylammonium fluoride desilylation of **1** and **2**, respectively. Methods for the synthesis of the corresponding *N*-(*p*-chlorophenyl)-*N'*-[(thiaindanyl)sulfonyl]ureas and



1 n = 1
2 n = 2

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