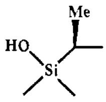
Table II. Oxidation of **5** or **9** To Give Alcohols **7** or **10**

R	product	yield,[a] %	$[\alpha]_D$ (c 1, $CDCl_3$), deg	lit. $[\alpha]_D$	% ee GC[e]
Me	**7a**	91	−39	−41.3[b]	98.5
nPr	**7c**	90	−45	−48.6[b]	>99.5
Et	**7b**	92	−44	−47.6[c]	99.0
$PhCH_2$	**7d**	82	−14	−56.1[d]	[f]
$I(CH_2)_5$	**10c**	84	−21		
$Cl(CH_2)_3$	**10a**	89	−33		
$Cl(CH_2)_4$	**10b**	87	−32		

[a] After flash chromatography. [b] Reported values for Aldrich. [c] See: Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657–1660. [d] See: Berti, G.; Bottari, F.; Ferrarini, P. L.; Macchia, B. *J. Org. Chem.* **1965**, *30*, 4091–4096. [e] The % ee was determined by GC according to ref 17. [f] The % ee of **7d** was determined by ^1H NMR using $Eu(tfc)_3$ to be better than 95%. We are unable at the present time to account for the discrepancy between the ^1H NMR determination and the literature $[\alpha]_D$ values.

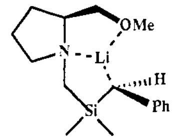
infra), compound **5a** was formed as a mixture of diastereomers (75:25, 50% de). *However, when the same reaction was carried out in ether as solvent, compound* ***5a*** *was obtained as a single diastereomer.* Since the ^1H NMR signals of the Si–Me of the two diastereomers are clearly separable (δ = 0.057 and −0.081 for the major diastereomer and δ = 0.002 and −0.034 for the minor one) at 200 MHz, the diastereomeric excess must be better than the detection limit of NMR. similar alkylation of the carbanion **4** in ether with several alkyl halides gave the corresponding alkylated products **5** in good yield (Table I), again in high diastereomeric excess according to ^1H NMR.

The usefulness of organosilicon compounds in synthesis is due in large part to the ease by which the silyl group can be replaced under electrophilic substitution conditions and can thus be considered as a latent functional group.[13] However, in the case of an alkylsilane where electrophilic substitution has to occur at a saturated carbon, the presence of one or more electronegative groups such as halogen or oxygen (or its equivalent) on the silyl moiety is often required to facilitate the reaction.[14,15] Recently we found, however, that (aminomethyl)silanes can be readily oxidized to the corresponding silanols.[16] Indeed, when **5a** was treated with H_2O_2, oxidative cleavage of the aminomethyl carbon–silicon bond occurred to give silanol **6** together with phenylethanol (**7a**). If the oxidation was carried out with H_2O_2 and $KHCO_3$ for a longer period (15 h), complete conversion of **5a** via **6** into (S)-(−)-phenylethanol (**7a**) took place. Similar oxidation of **5b,c** gave the corresponding arylcarbinols **7**, again in good yield. In all cases, the arylcarbinols have the S configuration. For compound **7c**, the enantiomeric excess was found to be better than 99.5%, the detection limit of the capillary gas chromatographic method.[17]

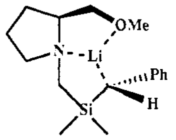


6

We attribute the stereochemical results in the following manner. The carbanion **4** is most likely to have the lithium ion coordinated to both the nitrogen and the oxygen atoms of the pyrrolidine ligand as in **8a** or **8b**. Similar internal chelation has been suggested for other silyl carbanions.[18] Of the two diastereomeric structures, **8a** is likely to be preferred because the more bulky phenyl group is placed exo to the bicyclic system. The electrophile RX reacts with **8a** presumably with retention of stereochemistry in a S_E-type reaction, to give **5** with the S configuration at the benzylic carbon. Since it is well established that oxidative cleavage of the carbon–silicon bond occurs with retention of stereochemistry,[14] S-arylcarbinol **7** is obtained as the final product.



8a



8b

Alkylation of the carbanion **4** with dihalides can be selectively controlled at the monoalkylation stage to give compounds **9**, again with the same high diastereoselectivity (Table I). Subsequent oxidation of **9** gave the halo alcohols **10** (Table II). Either **9** or **10** can be manipulated further by functional-group transformations. An example is the conversion of the halo alcohols **10a,b** under basic conditions to the optically active cyclic ethers **11a,b**.

The present results demonstrate that highly stereoselective reaction can be achieved with chiral organosilicon compounds. Since the chemistry of α-silyl carbanions[19] as well as the electrophile substitution reactions of organosilicon compounds[13] have been extensively utilized in organic synthesis, we expect that chiral organosilicon compound **1** and similar reagents will find application in enantioselective synthesis.

Acknowledgment. We thank NSERC of Canada and FCAR of Quebec for financial support of this research.

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Synthesis, Structure, and Reactivity of Substituted Niobocene Acyl Compounds

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The migratory insertion reaction of alkylcarbonyl metal compounds is one of the most fundamental reactions in organometallic chemistry.[2] An interesting comparison arises in the group V metals, since vanadocene systems readily form acyls via this route[3] while niobium and tantalum analogues[4] do not (eq 1 and 2).[5]

$$Cp_2VMe + 2CO \rightarrow Cp_2V(CO)(COMe) \qquad (1)$$

$$Cp_2NbMe + CO \rightarrow Cp_2Nb(CO)(Me) \qquad (2)$$

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(5) Abbreviations used: Cp = (η^5-C_5H_5), Cp′ = (η^5-$C_5H_4SiMe_3$), Cp* = (η^5-C_5Me_5).

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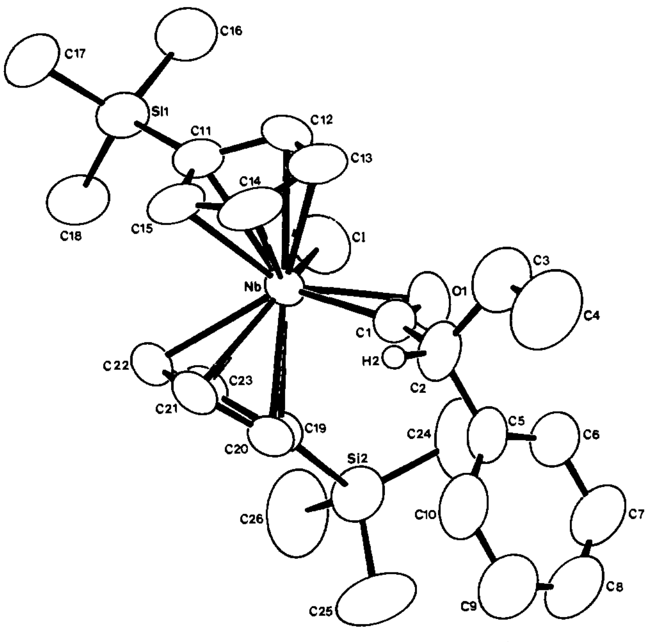
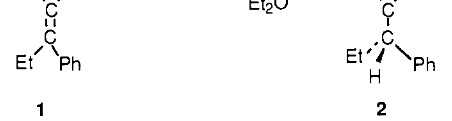


Figure 1. ORTEP drawing of the cation in **2** with most of the hydrogens omitted for clarity. Key bond lengths: Nb–Cℓ 2.446 (2); Nb–C1, 2.121 (5); Nb–O1, 2.233 (4); C1–O1, 1.242 (5); C1–C2, 1.506 (8) Å. Angles: Cℓ–Nb–O1, 80.9 (1), O1–Nb–C1, 32.4 (2); Nb–C1–O1, 78.8 (3); O1–C1–C2, 127.1 (5)°.

Brintzinger reported that $[Cp_2Nb(CO)_2][BF_4]$ reacts with MeLi to give $Cp_2Nb(Me)(CO)$ and suggested the intermediacy of $Cp_2Nb(COMe)(CO)$.[4c] Also, Schrock reported the reaction of Cp^*TaMe_4 with CO to give an acetone complex $Cp^*Ta(Me)_2(O{=}CMe_2)$;[6] an acyl intermediate is also likely in this process.[7] However, there are no isolable acylmetallocenes for these metals. We recently reported the preparation of the C=O bound ketene complexes *exo*-$Cp'_2Nb(Cl)(O{=}C{=}CR_2)$ (R_2 = Me_2, Ph_2, MePh, EtPh) and described the conversion of one derivative to the first hydride–ketene complex, *exo*-$Cp'_2Nb(H)(O{=}C{=}CMePh)$.[8] Since complexed heterocumulenes often exhibit enhanced nucleophilicity at the free terminus,[9] we sought the conversion of these compounds to niobocene acyls. Herein we describe the preparation, structure, and reactivity of two such compounds, one of which is a highly electron deficient acyl hydride compound which results from the preferential protonation of a ketene ligand.

The addition of 1.1 equiv of $HBF_4{\cdot}OEt_2$ to an ether suspension of yellow $Cp'_2Nb(Cl)(O{=}C{=}CEtPh)$ (**1**) causes the suspended solid to dissolve immediately with bleaching of the yellow color. After 30 s (25 °C), a colorless solid precipitates (70%) and is isolated by filtration; it may be recrystallized from CH_2Cl_2/Et_2O. The product is identified as the cationic acyl $[Cp'_2Nb(Cl)(\eta^2\text{-}COCHEtPh)][BF_4]$ (**2**) (eq 3). While the reaction proceeds

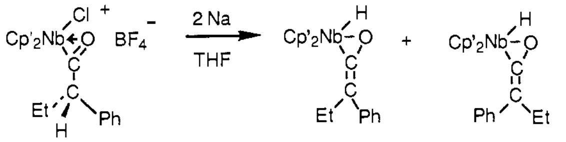


(3)

1 **2**

cleanly for other ketene complexes (as seen by' NMR), the products are isolated as pale yellow oils; as such, the chemistry to be discussed below was carried out with **2**. The ^1H NMR spectrum of **2** is consistent with the proposed formulation,[10] and the IR spectrum contains an acyl C=O stretch at 1615 cm^{-1}, indicative of an η^2-acyl.[11] The crystal structure determination[12] (Figure 1) confirms this. The cation and anion are well separated, and the closest non-hydrogen cation–anion contact (3.191 (9) Å) is between a BF_4^- fluoride and a Cp′ carbon (C13). The acyl ligand is in the O-inside configuration, as is seen in the thermodynamic isomer of the isoelectronic zirconium analogue $Cp_2Zr(Cl)(COMe)$.[13] Key distances and angles for **2** are given in the figure caption.

Since trivalent $(C_5R_5)_2Nb(COR)(L)$ is otherwise unavailable (eq 2), we sought the reduction of compound **2** (a Nb(V) compound) as a means of generating such a species and observing its degradation pathway(s). Reduction with 2 equiv of amalgamated sodium proceeds as shown in eq 4. The product is the ketene–

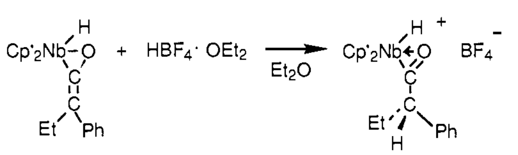


(4)

2 **E-3** **Z-3**

hydride compound *exo*-$Cp'_2Nb(H)(O{=}C{=}CEtPh)$ (**3**), isolated as a mixture of *E* and *Z* isomers; this class of compounds is known to undergo facile *E*–*Z* isomerization in THF solution.[8] To probe the mechanism by which **3** arises, the deuterium analogue **2**-d_1 was prepared from **1** and D_2SO_4. Treatment of this compound with sodium (as in eq 4) gave rise to $Cp'_2Nb(D)(O{=}C{=}CEtPh)$, as indicated by ^1H and ^2D NMR; the latter confirmed that the Nb–D site was the only deuterated position. As such, the acyl β-hydrogen is the source of the hydride ligand in **3**.[14]

We indicated earlier that the chemistry of the chloro ketene complexes $Cp'_2Nb(Cl)(O{=}C{=}CR_2)$ is dominated by the ketene ligand,[8] and the protonation chemistry (eq 3) also occurs there. However, in complex **3** the hydride is also potentially reactive toward electrophiles. As such, we treated **3** with $HBF_4{\cdot}Et_2O$ in order to probe the regiochemistry of addition. The reaction (eq 5) proceeded cleanly to the cationic acyl hydride **4**, with no sign



(5)

3 **4**

of hydride protonolysis. The formulation of **4** is confirmed by ^1H NMR, which shows ethyl and phenyl resonances, eight Cp′-H and two $SiMe_3$ resonances for the nonequivalent Cp′ groups, the acyl β-hydrogen (5.13 ppm, apparent triplet), and the Nb–H at 2.79 ppm;[10] this latter resonance is relatively far downfield for a metal hydride, but this is to be expected for a cationic Nb(V) hydride. Compound **4** is more conveniently prepared from chloro acyl **2** without isolation of the intermediate **3**, and the yield of this two-step sequence is 61% (based on **2**); **4** can be recrystallized from CH_2Cl_2/Et_2O to give well-formed transparent parallelepipeds. Like **2**, it is reasonably air-stable in the solid state for several hours, but gradually yellows; both are indefinitely stable under inert atmosphere. Compound **4** is a member of a relatively small

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class of monometallic acyl hydrides[15,16] and is unusual even among this group. Most other known examples have been prepared by oxidative addition of aldehydes to late-transition-metal centers, and none are as electron-deficient as this cationic Nb(V) derivative. In spite of this, **4** shows no tendency (at 25 °C) to eliminate aldehyde, presumably because this is precluded by the O-inside geometry. If **4** is treated with 2 equiv of sodium, it reverts to the ketene hydride complex **3**; mechanistic studies are in progress.

In summary, then, we have utilized metal-ketene precursors to prepare and characterize the first acylniobocene compounds. These highly substituted derivatives show a tendency to degrade via β-H elimination, giving ketene-hydride complexes. Studies of the chemistry of these and related compounds are ongoing.

Acknowledgment. Support was provided by Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of spectral and analytical data for **2** and **4**, synthetic procedures, and listings of unit cell data, bond lengths and angles, atomic coordinates, and thermal parameters for **2** (11 pages); listing of observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

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Correlating Temperature Dependence to Free Energy Dependence of Intramolecular Long-Range Electron Transfers[†]

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Recent experiments have demonstrated a simple relationship between the rates and energetics for electron-transfer (ET) reactions.[1-6] The dependence of long-range intramolecular ET rate constants on the free-energy change ($\Delta G°$) remarkably confirmed predictions of theory.[7] Those data together with a fit to theory could be used to predict the activation energies for the ET reactions with the knowledge of temperature dependence of $\Delta G°$ and the solvent reorganization energy. Therefore the measurement of temperature-dependence, reported in Figure 1, provides a critical test of the internal consistency of electron-transfer theory and its implementation in describing ET rate as a function of $\Delta G°$.

The reaction studied is the charge-shift ET from biphenylyl$^-$ (B$^-$) to naphthyl (N) group in the rigid molecule BSN shown in the inset to Figure 1. ET rates were measured in the temperature range −94 to 100 °C[8] by pulse radiolysis, which is used to add an electron to the bifunctional molecule. Time-dependent concentrations of the radical anions were followed by their optical absorption. Sample preparation and data analysis have been described elsewhere.[1] Solutions in 2-methyltetrahydrofuran (MTHF) in silica cells were held in an insulated metal block which was cooled by cold nitrogen gas and regulated to ±0.5 °C by a temperature controller (Love Control 585).

$\Delta G°$ and T Dependence. Earlier measurements[1] at room temperature of ET rates in the molecule shown in Figure 1 and seven others in which different acceptor groups replaced the naphthyl provided a range of $\Delta G°$ from −0.06 to −2.5 eV. Those data were well-described by nonadiabatic ET theory of eq 1, in which the ET reaction is considered coupled to reorganization of both low-frequency ($h\nu \leq kT$) motions of the solvent and high-frequency ($h\nu \gg kT$) skeletal vibrations of the donor and acceptor groups. The solvent reorganization energy ($\lambda_s = 0.75$ eV), the

$$k_{el} = (\pi/\hbar^2\lambda_s k_B T)^{1/2}|V_2|\sum_{w=0}^{\infty}(e^{-S}S^w/w!)\exp\{-[(\lambda_s + \Delta G° + wh\nu)^2/4\lambda_s k_B T]\} \qquad S = \lambda_v/h\nu \quad (1)$$

reorganization energy ($\lambda_v = 0.45$ eV) of high frequency modes, represented by a single average frequency ($h\nu = 1500$ cm^{-1}), and electronic coupling matrix element (V) were determined from dependence of k_{et} on $\Delta G°$. The ET rate predicted by eq 1 with use of these reorganization parameters is plotted along with the measured ET rates as a function of temperature in Figure 1. This comparison must consider the temperature dependence of $\Delta G°$ and λ_s.

Thermodynamics. The temperature dependence of $\Delta G°$ was determined from direct measurement of the reaction equilibrium constant, K_{eq} (B$^-$SN $\rightleftharpoons$ BSN$^-$).[9] Over the temperature range 100 to −94 °C $\Delta G°$ can be described as $\Delta H° - T\Delta S°$ with $\Delta H° = -1.5 \pm 0.1$ kcal/mol and $\Delta S° = -0.49 \pm 0.37$ cal/mol·K. This standard entropy change is very small: $T\Delta S° = -0.15 \pm 0.11$ kcal/mol at 25 °C, which is only one tenth of $\Delta H°$ or one fourth of kT. This observation is consistent with an early report.[10] It is also consistent with the expectation that little entropy change

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[‡] Argonne National Laboratory.

[§] University of Chicago.

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(9) To accurately determine K_{eq} at temperatures below −20 °C, mixtures of BC and NC, in which the spacer is cyclohexane were used. At room temperature and above K_{eq} measured with BC/NC or BS/NS mixtures agree with each other and those obtained with the bifunctional molecule BSN.

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