Molecular and Electronic Structure of Electron-Transfer Active Main-Group Organometallics

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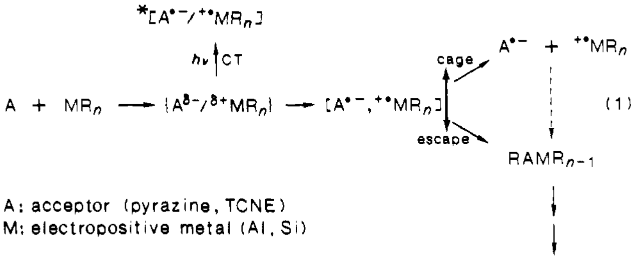
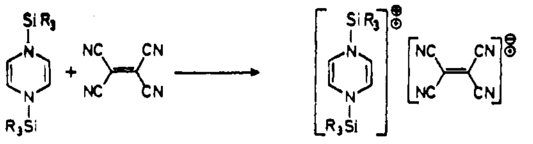
Abstract: The molecular structure of the single-electron-transfer (SET) reagent 1,4-bis(triisopropylsilyl)-1,4-dihydropyrazine (**1**) shows a virtually planar ring system with eight conjugating π electrons, effectively shielded N–Si bonds, and nonbonded contacts between ring and isopropyl hydrogen atoms. The compound undergoes an electrochemically reversible one-electron oxidation at a very low potential; electronic *and* steric stabilization as well as an apparently small geometry change on oxidation make this extremely electron-rich main-group organometallic molecule highly suitable for the study of outer-sphere SET processes. The color of yellow **1** and of related compounds is attributed to weak $\pi \rightarrow \sigma^*$(Si–C) transitions whereas the reverse assignment σ(M–C) $\rightarrow \pi^*$ and opposite direction of inter- and intramolecular electron transfer is noted for the intensely red isosteric bis(triisopropylaluminum) complex of pyrazine. The structural and electronic requirements and the various manifestations of electron transfer from main-group organometallics are discussed.

The concept of single electron transfer (SET)[1] has become very useful for an understanding of reactions involving organometallic compounds[2,3] because the generally polar bonds between metals and organic ligands are likely to participate in redox processes. In particular, the vast and important field of reduction of organic substrates by main-group organometallics ("carbanions", "nitranions"[4]) and hydrides has now frequently been shown to involve SET reactivity, as indicated by mechanistic studies including ESR observation of radical products and intermediates.[3,4] Unlike many first-row transition-metal systems such as $[\mathrm{Fe(phen)_3}]^{2+}$,[5] the main-group organometallic radical cations formed as primary products of process 1 are very reactive and cannot be observed under ordinary conditions,[2–4,6,7] even if the substrate radical anion may be perfectly stable.



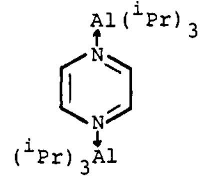
One notable exception to this rule has been found[8] in the form of the extremely electron-rich[9,10] 1,4-bis(trialkylsilyl)-1,4-dihydropyrazines. The isopropyl derivative **1** was observed to form stable, solvent-separated radical-ion pairs (2) in what appear to be outer-sphere electron-transfer reactions with the strong acceptors tetracyanoethylene (TCNE) and tetracyano-*p*-quinodimethane (TCNQ).[8] The stability of these primary SET products may be attributed to the low oxidation potential and ionization energy and/or to the steric shielding of the N–Si bonds of the donor. We have now studied the molecular and electronic structure of compound **1** in order to establish the influence of molecular and electronic structure on electron-transfer reactivity within this class of compounds.



(2)

1 R = $^{i}\mathrm{C_3H_7}$

The remarkable persistance of **1** toward oxidation by air (the methyl analogue is pyrophoric!)[9–11] has allowed detailed studies of its electrochemical behavior and of the absorption spectrum; corresponding data for the isosteric bis(triisopropylaluminum) complex **2** of pyrazine are used to assess the energies of the frontier orbitals that are involved in electron transfer from organometallics.



(3)

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Results and Discussion

Crystal Structure. Compound **1** crystallizes in a very simple form, with one molecule per unit cell (Figure 1). The molecule shows crystallographically imposed inversion symmetry (space group $P\bar{1}$); the six-membered ring is virtually planar (Figure 2) with a very slight distortion toward a chair conformation. It was noted before that organometallic stabilized 1,4-dihydropyrazines without further substituents at the ring carbon centers adopt an almost planar ring conformation,[12] in spite of the fact that these species then contain eight cyclically conjugating π electrons and thus represent heteroatom-modified antiaromatics.[10,13,14] Apparently, the preference[15] of the silyl-substituted nitrogen atom for a planar arrangement is so strong that the obvious destabilization of the HOMO in a planar 8π-electron system[16] (cf. electrochemistry) is tolerated.

Most geometrical parameters (Table II) concerning the π-electron-bearing ring system are quite similar to the values reported for the trimethylsilyl derivative;[12] however, the shortness of the

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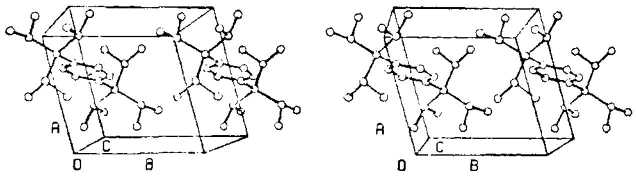

Figure 1. Stereoscopic view of the unit cell in crystals of **1**.

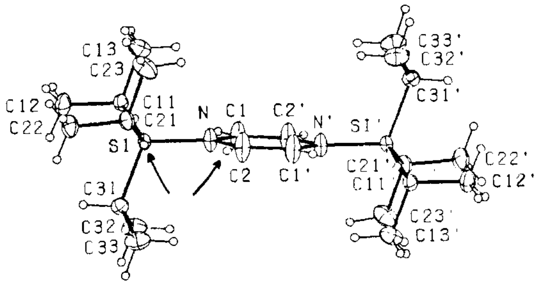

Figure 2. Molecular structure and numbering scheme of **1**. Arrows designate one of four close hydrogen contacts, here between H21 and H2 (numbers of H refer to bound carbon centers).

Table I. Distances (pm) and Angles (deg) of **1** in the Crystal

Si-C11	189 (2)
Si-C21	189 (2)
Si-C31	189 (2)
Si-N	174 (2)
N-C1	141.6 (5)
N-C2	141.4 (7)
C1-C2'	133 (1)
C2-C1'	133 (1)
C11-C12	153 (1)
C11-C13	153 (2)
C21-C22	153 (2)
C21-C23	153 (2)
C31-C32	153 (1)
C31-C33	153 (2)
C11-Si-C21	116.4 (<1)
C11-Si-C31	108.3 (<1)
C21-Si-C31	108.0 (<1)
C11-Si-N	106.3 (<1)
C21-Si-N	106.9 (<1)
C31-Si-N	110.7 (<1)
Si-N-C1	124.0 (<1)
Si-N-C2	124.0 (1)
C1-N-C2	111.6 (1)
N-C1-C2'	124.0 (1)
N-C2-C1'	124.2 (1)
C12-C11-C13	110.6 (1)
C22-C21-C23	110.4 (1)
C32-C31-C33	110.0 (1)
H-C bond lengths	H-C[methyl] 97.5 (94.2-101.1) ppm H-C[isopropyl] 98.0 (97.2-99.6) ppm H-C[ring] 95.1 (96.0-94.1) ppm
H-C-H bond angles	107.1 (106.0-108.8)
H-C-Si bond angles	104.6 (103.4-106.3)
C-C-H bond angles	C-C-H[ring] 119.4 (118.7-120.0) C-C-H[isopropyl] 107.0 (105.8-108.6) C-C-H[methyl] 111.7 (110.1-113.0)
N-C-H bond angles	116.5 (115.9-117.1)

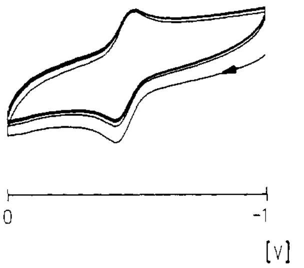

Figure 3. Cyclic voltammogram for **1** between +0.0 and -1.0 V vs SCE in acetonitrile.

Table II. Dihedral Angles between Defined Planes

planes	dihedral angles (deg) between planes
(A) N, C1, C2	A,B:0.0
(B) N', C1', C2'	A,C:1.1
(C) C1, C2', C1', C2	B,C:1.1
(D) N, C1, C2', N'	A,D:0.6
	B,D:0.6
(E) N, C2, C1', N'	D,E:0.0
(F)[a] N (-0.45), C1 (0.49), C2' (0.49),	D,F:0.0
N' (-0.49), C1' (-0.49), C2 (0.45)	E,F:0.0

[a] Deviations (in pm) from the best plane in parentheses.

Table III. Oxidation Potentials (in V vs SCE) of Compounds **1** and **3** in Acetonitrile

compd	$E^{0/\bullet+}$	$E^{\bullet+/2+}$	K_c[a]
1	-0.42	+0.45[c]	~10^{14}[c]
3[b]	-0.75	-0.61	236

[a] Stability constant $K_c = 10[\exp(\Delta E)/0.059\ \mathrm{V}]$. [b] From ref 26. [c] Irreversible oxidation, anodic peak potential at 100 mV/s scan rate given.

Si-N bond due to N→Si "multiple bonding"[15] (see discussion of the absorption spectrum) as well as the size and virtually antiperiplanar conformation of the triisopropylsilyl substituents lead to notable steric interference (Figure 2). The X-ray crystallographically found hydrogen atoms H(11,21,11',21') of the ^{i}Pr$_3$Si groups on one hand and the four ring protons H(1,2,1',2') on the other hand have distances of about 225.8 and 224.9 pm from one another, which is less than the sum of the van der Waals radii (≈240 pm).[17] Since X-ray crystal structure determinations generally *under*estimate internuclear distances involving hydrogen atoms, this result is clearly significant; it explains why compound **1** exhibits a low-field ^{1}H NMR shift for the ring protons (δ = 4.78 ppm)[8] relative to the values found for Me$_3$Si-,[10,11] Me$_3$Ge-,[9] Et$_3$Si-,[8] and ^{t}BuMe$_2$Si-substituted derivatives (δ = 4.64 ppm, all values for CDCl$_3$ solutions).[8] Attempts to introduce even larger silyl groups such as (Me$_3$Si)$_3$Si have thus been unsuccessful[18] because nonbonded interactions as described here must prevent the formation of the short Si-N bonds needed for stabilization of the 8π-electron system.

An advantage of the large ^{i}Pr$_3$Si groups is clear, however, from the view (Figure 2) of the molecular structure. The reactive Si-N bonds are quite effectively shielded from direct attacks by oxidants (TCNE, O$_2$) or hydrolyzing agents such as water while electron transfer may still occur, most likely in an outer-sphere fashion[1] from the unprotected center of the extremely electron-rich six-membered ring. It seems, therefore, that **1** is ideally suited for studying SET reactivity of main-group organometallics because the ^{i}Pr$_3$Si group is large enough to effectively protect the most vulnerable Si-N bonds but small enough to ensure stabilization of the 8π-electron system and to retain its character by not causing significant geometrical distortion.[19]

Electrochemistry. The most important feature of an outer-sphere electron-transfer reagent is its redox potential.[1] Although there are many electron-rich organosilicon compounds such as polysilanes, β-silyl-substituted π systems, or silylamines (cf. Scheme I) that can form persistent cation radicals,[7,20-22] none of these have exhibited electrochemically reversible oxidation behavior,[23-25] possibly due to electrode adsorption processes. Com-

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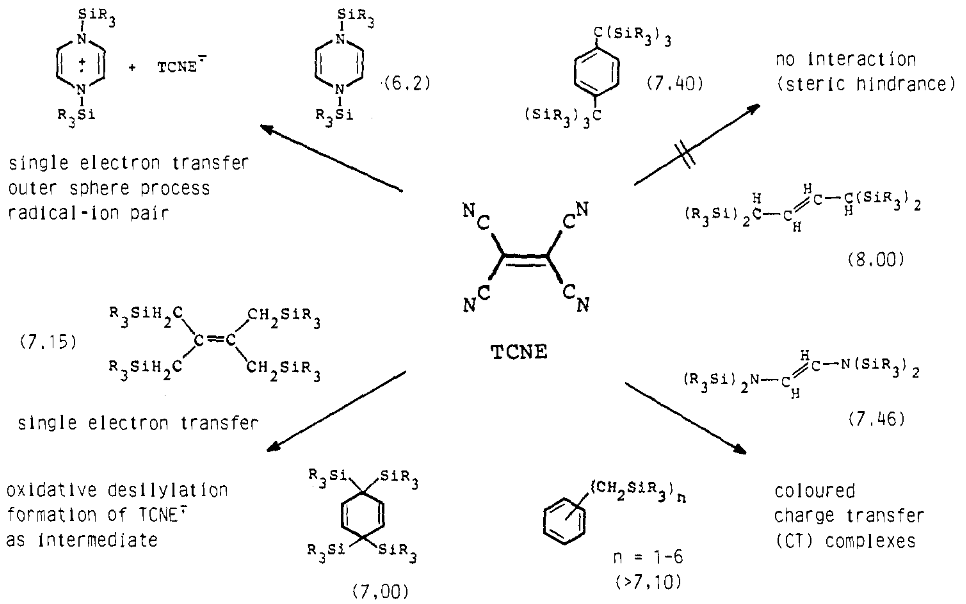
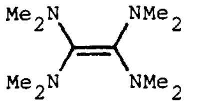
Scheme I. Four Different Stages in the Reaction between Organosilicon Donors and the Acceptor Tetracyanoethane (TCNE) As Exemplified by Reported Cases (See Text). Photoelectron Spectroscopically Determined Ionization Potentials of the Donor Molecules Indicated in Parentheses



pound **1** is different from all these systems, it exhibits a reversible one-electron oxidation wave in the cyclic voltammetry experiment (Figure 3; Table III) as befits an outer-sphere electron-transfer substrate. According to its π-electron excess, compound **1** is oxidized at a *negative* potential vs saturated calomel reference electrode and is thus able to reduce a number of substrates via outer-sphere SET; among main-group element compounds, only tetrakis(dialkylamino)ethenes[26,27] such as **3** are more electron rich than silylated 1,4-dihydropyrazines.[10]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The −0.42-V oxidation potential of **1** is in good agreement with the ionization energy of 6.16 eV measured for the structurally related trimethylsilyl derivative;[9,10] the good fit of these values with a correlation obtained for mainly aromatic hydrocarbons[28] indicates relatively little geometry change after oxidation to the cation radical.[29] In fact, a recent crystal structure determination of the *N,N'*-diethylpyrazinium radical cation has also shown a planar six-membered ring with only small yet significant changes of distances between ring atoms relative to those of **1**.[30] These small geometry changes as calculated also for the parent redox pair $C_4N_2H_6/C_4N_2H_6^{\bullet+}$ [31] mean a small structural contribution to the reorganization energy λ, which plays an important role in the Marcus equation (5) for electron transfer.[1]

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2 \qquad (5)$$

Electrochemical potentials obtained for a number of other 1,4-dihydropyrazine systems[14,32,33] show that the *N*-silyl-substituted derivative **1** has a lower oxidation potential than *N*-acyl, *N*-ester, or *N*-thiophosphinic amide derivatives,[32] whereas the *N*-ethyl-substituted compound (which is unstable in the 8π-electron form) exhibits a more negative potential of −0.67 V vs SCE.[33]

A comparison between **1** and **3** (Table III) demonstrates the suitability of **1** for outer-sphere single-electron transfer. While the second oxidation of **3** to the dication occurs reversibly at only slightly higher potentials than the first electron loss,[26] the dihydropyrazine cation radical $\mathbf{1}^{\bullet+}$ exists in a much larger potential range until irreversible (dissociative) oxidation to the dication takes place.

Compounds **1** and **2** form isoelectronic radical ions[8,34] on oxidation (**1**) and reduction (**2**), respectively, the ESR parameters of $\mathbf{1}^{\bullet+}$ [8] and $\mathbf{2}^{\bullet-}$ being virtually identical with those reported for the trimethylsilyl or -aluminum derivatives.[10] While **2** is largely dissociated in the polar solvents THF and DMF and to a small extent also in 1,2-dichloroethane, its stable anion-radical $\mathbf{2}^{\bullet-}$ is always reoxidized at a rather positive potential of about −0.6 V

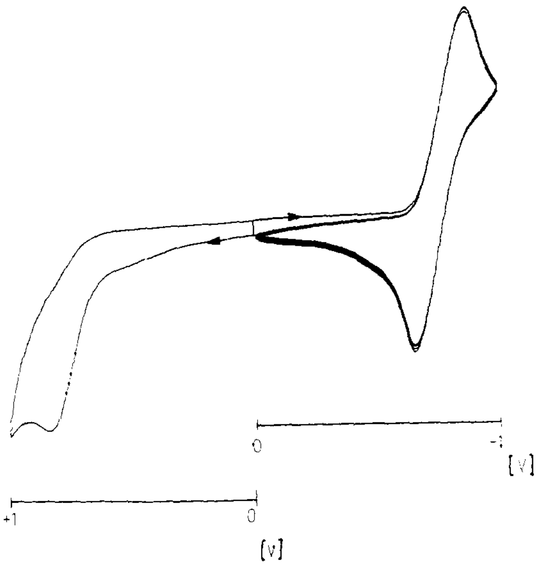

Figure 4. Cyclic voltammograms for the reduction (+0.0 to −1.0 V) and oxidation (+0.0 to +1.0 V vs SCE) of **2** in 1,2-dichloroethane solution/0.1 M tetrabutylammonium perchlorate.

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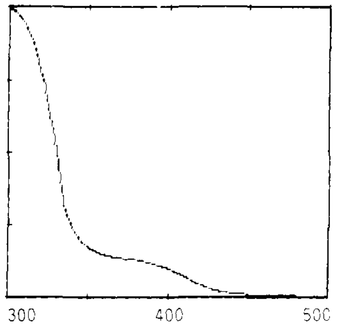
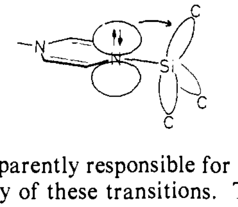


Figure 5. UV/vis absorption spectrum of **1** in THF.

vs SCE (Figure 4).[35] This value means that an anodic shift of about *1.5 V* has occurred for the reduction of pyrazine as a result of coordination of two neutral Lewis acidic molecules Al^{i}Pr$_3$, which makes this complex as reducible as *p*-quinones. Since irreversible oxidation of **2** occurs at a peak potential of +0.85 V vs SCE at 100 mV/s scan rate, the electrochemical potential range for **2** has now been reduced to about 1.5 V (Figure 4); the propensity of such primary charge-transfer complexes (1) between carbanions and organic π acceptors to undergo complete intracomplex electron transfer is thus quite obvious.

The binuclear triorganoaluminum complex **2** is already susceptible to an "inverse inner sphere" electron-transfer process: Under ambient conditions (room temperature, laboratory light) in toluene, a radical is formed from **2** as evident from a very complicated ESR signal. Although a full analysis of that spectrum will require double-resonance techniques, this apparently unsymmetrical species may be tentatively identified as the primary escape product of an SET reaction, viz., as the neutral radical $[^i\mathrm{Pr}_3\mathrm{Al}(\mathrm{pz})\mathrm{Al}^i\mathrm{Pr}_2]^\bullet$ obtained after dissociation of an isopropyl radical from **2**. Related unsymmetrical radical products have been detected after the rapid electron-transfer reactions of diorganomagnesium compounds with pyrazine or 4,4′-bipyridine.[3]

Electronic Absorption Spectroscopy. The most conspicuous property of the highly electron-rich organometal-stabilized 1,4-dihydropyrazines is their color, which can vary from yellow (Si compounds)[10] to red (Ge derivatives).[9] The stability of the triisopropylsilyl derivative **1** has now enabled us to obtain an absorption spectrum (Figure 5), which shows that the color originates from a weak (ϵ = 100 M^{-1} cm^{-1}) band at the long wavelength side of intense $\pi \rightarrow \pi^*$ transitions in the ultraviolet region. We attribute this small feature to a transition from the highly destabilized π MO of the very electron rich heterocycle to low-lying unoccupied orbitals at the organosilicon substituent. The presence of such low-lying molecular orbitals has been inferred for second and higher row main-group element substituents from electron transmission spectroscopy (ETS)[36,37] and a number of arguments point toward a σ^*(E–C) character of these orbitals (6); their quite



(6)

diffuse nature is apparently responsible for the poor overlap and for the low intensity of these transitions. The apparent bathochromic shift in the red trimethylgermanium derivative[9] is in good agreement with the ETS-spectroscopically determined lowering of the attachment energy for an electron on going from silicon to germanium compounds.[36]

Whereas the long-wavelength transition of the silicon-substituted dihydropyrazine **1** may then be described as a special variety of ligand-to-metal charge transfer or LMCT,[38] the reverse kind of transition (7) is responsible for the red color of the isosteric

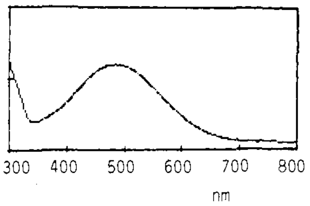
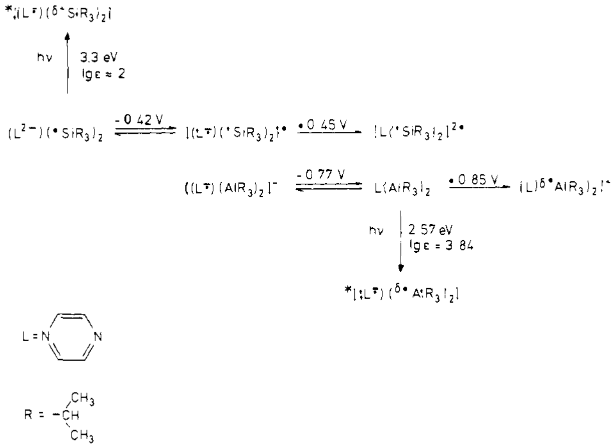
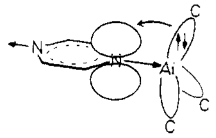


Figure 6. UV/vis absorption spectrum of **2** in heptane.



(7)

bis(isopropylaluminum) complex **2** of pyrazine. This species with an absorption maximum (Figure 6) at 483 nm in heptane (ϵ = 6900 M^{-1} cm^{-1} owes its low-energy absorption to a transition (8)



(8)

from the electron-rich aluminum–carbon σ bonds[39] to the low-lying π^* orbital of the 6π-electron heterocycle.[40] The high intensity of this transition[41] stands in contrast to the rather weak $\sigma \rightarrow \pi^*$ bands observed for trialkylsilyl derivatives of electron-deficient π systems such as azo compounds, quinones, or quinonediimines.[42] The intensity of the MLCT band of **2** indicates effective σ/π^* orbital overlap, which in turn explains the notable propensity of organo- and hydridoaluminum reagents for single-electron-transfer reduction of organic substrates.[3,8,43–46] If one locates the origin of this transition at the metal alkyl groups as implied by the term carbanion reagents for such organometallics,[4] this intramolecular electron-transfer process may be designated as ligand-to-ligand charge transfer (LLCT). The role of the metal would then be

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to bring the acceptor and donor ligands together in a defined conformation for such an *inverse inner-sphere electron transfer* and to provide the necessary polarization.

Evidence for the assignments (6–8) for the long-wavelength transitions of **1** and **2** in the visible region comes from ESR spectra of the cation radical of **1** and the anion radical of **2** and of related species.[8,10,34] Previous work has clearly shown the very similar nature of the isoelectronic radical ions (9),[8,10,34] implicating that


(9)

the HOMO of **1** has essentially the same electron distribution as the LUMO of **2**. While the two charge-transfer excited states (7) are clearly not isoelectronic, there is a similarity in the overall charge distribution (7), which involves the 7π-electron form[10,14] of the heterocyclic ligand.

Electron-Transfer Reactivity of Electron-Rich Organosilicon Compounds. The silylated 1,4-dihydropyrazines and especially compound **1** are unique among main-group organometallics in their ability to act as outer-sphere single-electron-transfer reagents, forming stable cation-radical products in the presence of acceptor radical anions.[3,8] Reactions with the small prototypical molecular acceptor tetracyanoethylene (TCNE) serve to illustrate the variability of electron-transfer reactivity[1-3] of electron-rich organometallic compounds with organic acceptors (Scheme I).

(i) Very bulky organosilicon donors such as $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexakis(trimethylsilyl)-*p*-toluene[47] or 1,1,4,4-tetrakis(trimethylsilyl)-2-butene[48] (Scheme I) do not interact at all with TCNE despite low enough oxidation (and ionization) potentials.[47,52] The distance between donor and acceptor must fall below a critical value for frontier orbital interaction to take place.

(ii) If sufficient overlap is possible, the interaction between an acceptor molecule and the organometallic donor may lead to a σ- or π-coordinated charge-transfer complex,[49] which exhibits electronic transitions due to electron exchange in the excited state (1).[38] Many organosilicon compounds[50,51] including the silylamine[52] shown in Scheme I exhibit this behavior.

(iii) Electron exchange may occur in the ground state if energy differences and (inner-sphere) donor/acceptor interactions favor such a situation.[1-3] The primary pair of oppositely charged radical ions may collapse to form diamagnetic ("cage") products (1) or dissociate to be detected as "escape" products.[3] In the case of main-group organometallic donors, the cation-radical escape products have never been obtained as stable species before the studies described with reagents such as **1**;[6,21,53] metal–element bond cleavage was found to occur as a dominant follow-up process after single electron transfer (Scheme I).[6]

(iv) Protection of the sensitive bonds liable to dissociate after SET is possible as shown in this work, leading to the observation of the pair of oppositely charged radical ions e.g. as solvent-separated species by ESR (2).[8] The steric shielding needed in such cases also implicates the involvement of an outer-sphere electron-transfer mechanism and the requirement for a rather extreme redox potential in order to make such a probe useful for SET studies; all these requirements are apparently met by compound **1**.

(v) An alternative result of single-electron transfer between organometallic compounds and acceptors such as TCNE is possible in the transition-metal series where the metal center itself can be 1e-oxidized reversibly and then can bind more or less convalently to the anion radical of the acceptor;[49,54] however, such an alternative is clearly not possible for the silicon(IV) compounds described here or for other main-group metallic systems.

Conclusions. In a more quantitative extension of previous work based on radical detection and characterization,[3] we have shown by crystal structure analysis and energy-measuring techniques such as electrochemistry and absorption spectroscopy that the planar, organometal-stabilized 8π-electron heterocycle **1** and its pendant **2** are extremely suitable substrates for detailed studies of electron-transfer reactions involving main-group organometallics. The reason for this suitability lies in a unique combination of steric protection (without geometrical distortion) and efficient electronic interaction between the main-group organometallic fragments and a small bifunctional N-heterocycle. The results emphasize the crucial role of coordination and of the charge-transfer complexes as immediate precursors to the primary electron exchange products; first indications for a correlation between charge-transfer transition energies of main-group organometallic complexes and the reactivity in synthetically useful electron-transfer reactions have meanwhile been obtained.[55]

Experimental Section

All operations were carried out under vacuum or argon. Solvents were predried and used freshly distilled. ^{1}H NMR spectra were measured on a Varian A 60 spectrometer, ESR spectra on a Varian E9 system, and absorption spectra on a Shimadzu UV160 spectrophotometer. Cyclic voltammetry was performed in 0.1 M solutions of $Bu_4N^+ClO_4^-$ in 1,2-dichloroethane, tetrahydrofuran, or *N,N*-dimethylformamide. A three-electrode configuration was used with a glassy-carbon working electrode and an SCE reference electrode. The typical scan rate was 100 mV/s; a potentiostat/ramp generator POS 73 of Bank/Wenking (Göttingen, West Germany) was employed.

1,4-Bis(triisopropylsilyl)-1,4-dihydropyrazine (**1**) was prepared by combining 1 equiv of pyrazine, 2 equiv of triisopropylchlorosilane, and about 2.5 equiv of potassium metal in THF solution. After 24 h, precipitated KCl and unreacted potassium metal were separated by filtration; the yellow, slightly air-sensitive product was obtained by evaporation of the solvent and sublimation at 130 °C (10^{-4} Torr) in typically 70% yield. Anal. ($C_{22}H_{46}N_2Si_2$) C, H, N. ^{1}H NMR ($CDCl_3$): δ 1.13 (ps, 42 H, $SiCH(CH_3)_2$), 4.78 (s, 4 H, NCH).

Reaction between **1** and TCNE in dichloromethane produces a solution of solvent-separated pairs of ion radicals $TCNE^{\bullet-}$ and $1^{\bullet+}$.[8] Attempts to isolate a crystalline product from this reaction by evaporation of the solvent were not successful; a tarry black material was invariably obtained.

1,4-Bis(triisopropylaluminum)pyrazine (**2**) was obtained as a highly air-sensitive deep red solid by combining pyrazine and 2 equiv of triisopropylaluminum in heptane and precipitating the complex by cooling to −78 °C. An elemental analysis could not be performed due to the sensitivity of the compound. ^{1}H NMR ($CDCl_3$): δ 0.54 (sept, 6 H, $CH(CH_3)_2$, 1.08 (d, 36 H, $CH(CH_3)_2$), 8.86 (s, 4 H, NCH).

X-ray Crystallography. A crystal of **1** with the dimensions 0.4 × 0.4 × 0.6 mm, as grown by slow sublimation under vacuum, was sealed in a glass capillary under argon. Space group, symmetry, and cell dimensions were determined by a combination of photography and the centering of reflections using a Syntex $P2_1$ diffractometer. Crystal data for **1**: $C_{22}H_{46}N_2Si_2$, MW = 394.79; triclinic, $P\bar{1}$; $a = 772.6$ (2), $b = 830.2$ (1), $c = 1002.7$ (2) pm; $\alpha = 93.12$ (1), $\beta = 98.32$ (2), $\gamma = 105.88°$; $Z = 1$; $d_{calcd} = 1.07$ g/cm^3; Mo Kα radiation (graphite monochromator), scan $2° < 2\theta < 60°$; 3552 unique reflections (3068 observed with $I > 2\sigma(I)$). The C, N, and Si atoms were refined anisotropically, and the hydrogen atoms, isotropically; the function minimized was $\sum(|F_o| - |F_c|)^2$. Final R and R_w values were 0.038. The structure was solved using direct methods,[56] the program X-ray[57] was used on the Cray 2 computer of

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Supplementary Material Available: Listings of atomic coordinates and temperature factors for hydrogen and non-hydrogen atoms (Tables IV and V) (2 pages). Ordering information is given on any current masthead page.

Reactions of Trisodium Tetracarbonylmetalates(3–) of Manganese and Rhenium with Brønsted Acids and Other Electrophiles. Synthesis of $H_2M(CO)_4^-$ (M = Mn and Re), $(CH_3)_2Re(CO)_4^-$, the First Dialkyl Derivative of a Carbonylmetalate Trianion, and Related Anionic Species[1]

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Abstract: Treatment of hexamethylphosphoramide (HMPA) solutions of the trisodium tetracarbonylmetalates(3–) of manganese and rhenium with excess liquid ammonia causes precipitation of very thermally stable materials (dec ≥300 °C) that are isolated in high yields (85–95%) and represent the first available pure samples of unsolvated $Na_3[M(CO)_4]$. Infrared and ^1H NMR spectral studies of the protonation of $Na_3[M(CO)_4]$ in HMPA show initial formation of the new monohydrides, $HM(CO)_4^{2-}$, which are then converted quantitatively to the dihydrides, $H_2M(CO)_4^-$. The new manganese dihydride, which is isoelectronic with the first known carbonyl hydride, $H_2Fe(CO)_4$, and the previously established rhenium complex are isolated in high yields (75–80%) as the pure salts, $[Ph_4As][cis\text{-}H_2M(CO)_4]$. The monohydride dianions, $HM(CO)_4^{2-}$, also react with Ph_3SnCl to provide $cis\text{-}H(Ph_3Sn)M(CO)_4^-$, which can be isolated as the Et_4N^+ salt for rhenium. The initial successful alkylation reactions of carbonylmetalates(3–) are also reported. Treatment of $Na_3[Re(CO)_4]$ with methyl *p*-toluenesulfonate (MeOTs) in HMPA first provides $MeRe(CO)_4^{2-}$ (identified by IR), which can be protonated or further methylated to give $cis\text{-}H(Me)Re(CO)_4^-$ or $cis\text{-}(Me)_2Re(CO)_4^-$, both of which are isolated in good yields (70–80%) as Ph_4E^+ (E = P, As) salts. These represent the first isolated alkyl derivatives of metal carbonyl trianions. IR, ^1H, and ^{13}C NMR spectra also confirm that $Na_3[Re(CO)_4]$ reacts with 1,4-butaneditosylate to provide solutions of the somewhat thermally unstable rhenacyclopentane $\overline{CH_2CH_2CH_2CH_2Re}(CO)_4^-$, the initial example of an anionic 18-electron metallacycloalkane. Infrared, ^1H, and ^{13}C NMR spectral data have been obtained for many of these compounds and are compared with those of analogous previously known iron and osmium species.

Before 1975, numerous binary and substituted carbonylmetalate mono- and dianions were well established and shown to be quite useful reagents in chemical synthesis.[2] Such materials were known for all d-block transition elements except for the very early (Sc, Y, La, Ti, Zr, Hf) and very late (Cu, Ag, Au) triads.[3] Although carbonylmetalate trianions were unknown, several formal derivatives of these materials did exist as well as electronically equivalent (or isolobal) main group analogues such as P^{3-} and As^{3-}.[4] For these reasons, the reduction of $Mn(CO)_5^-$ was examined with the hope of preparing $Mn(CO)_4^{3-}$, the manganese analogue of $Fe(CO)_4^{2-}$, the first characterized carbonylmetalate.[2]

In the unusually effective reducing medium of sodium hexamethylphosphoramide (HMPA), $Mn(CO)_5^-$ underwent facile reduction to form a golden yellow to yellow brown solution. On the basis of derivative chemistry and infrared spectra, the major soluble component was formulated as "the superreduced species" $Na_3[Mn(CO)_4]$.[5] Related studies resulted in the syntheses of carbonyl trianions of V, Nb, Ta, Re, Co, Rh, and Ir.[6] While good evidence for the existence of the trianions of the group 5 metals has been obtained recently,[7] until now, the case for the mononuclear tetracarbonylmetalates(3–) of Mn and Re has been less satisfactory. Our inability to obtain pure samples of these trianion salts and the inherent uncertainty in distinguishing between anions

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