binding substrates, the two domains move toward each other. During these conformational events, the coordination site of Mg^{2+} could easily change. Spectroscopic and crystallographic results support such changes and differences in coordination as part of the catalytic action of kinase.[29–33]

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Registry No. NAD, 53-84-9; ADP, 58-64-0; ATP, 56-65-5; Na, 7440-23-5; Mg, 7439-95-4; Ca, 7440-70-2; Ba, 7440-39-3; Zn, 7440-66-6.

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Multinuclear Magnetic Resonance Study of Tris(cyclopentadienyl)scandium: A Fluxional Dimer with Bridging Cyclopentadienyl Groups

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$(C_5H_5)_3Sc$ is known to be associated via bridging cyclopentadienyl groups in the solid state, but hitherto nothing was known as to the nature of the compound in solution. ^1H NMR studies of the compound in THF show that it exhibits two fluxional processes. The first process observed on cooling is an exchange between the π- and σ-bonded rings. The second process, which can only be slowed and not completely stopped on the NMR time scale, is a metallotropic 1,5-shift of the Cp_2Sc moiety around the σ-bonded cyclopentadienyl ligand. The existence of only one species in THF, over the temperature range +30 to −80 °C is shown by ^{45}Sc NMR. In toluene, however, the exchange between σ- and π-bonded cyclopentadienyl ligands is complicated by the onset of dimer formation via bridging cyclopentadienyl groups at low temperature. The presence of two different scandium environments at low temperature is shown by variable-temperature ^{45}Sc NMR spectra.

In recent years the organometallic chemistry of the early transition metals has received considerable attention.[1] However, data in certain areas are still rather fragmentary. In the case of scandium, the widest group of compounds characterized are those in the $(C_5H_5)_2ScX$ series, where X is a monovalent ligand. In solution, when strongly coordinating solvents are present, monomeric species are formed.[2] However, in nonpolar solvents dimeric species are observed.[2a]

Crystallographic investigation of $(C_5H_5)_2ScCl$ and $(C_5H_5)_3Sc$ by Atwood has shown not only that $(C_5H_5)_2ScCl$ is dimeric[3] but also that$(C_5H_5)_3Sc$ is associated via bridging cyclopentadienyls in the solid state.[4] Indeed, the structure of $(C_5H_5)_3Sc$ is particularly interesting and can be interpreted in several ways. One possible description would be to regard the bridging cyclopentadienyl ligands as three-electron donors, i.e., σ bonding to one scandium and π bonding to the other as in the purported dimer (Figure 1a). An alternative, and somewhat extreme, view would be to take the dimer as a zwitterionic system (Figure 1b) comprised of $(C_5H_5)_2Sc^+$ and $(C_5H_5)_4Sc^-$ fragments. This unrealistically extreme view does, however, provide a formal analogy between the isoelectronic $(C_5H_5)_4Sc^-$ and $(C_5H_5)_4Ti$ systems; the relevance of such a comparison will shortly become apparent.

We now present some ^1H and ^{45}Sc NMR data on $(C_5H_5)_3Sc$ that give us some insight into the molecular dynamics of this interesting system.

Experimental Section

^1H NMR spectra were obtained on Bruker WM 400 and WM 250 spectrometers operating at 400 and 250 MHz, respectively. ^{45}Sc NMR spectra were obtained on Bruker WM 250 and WH 90 spectrometers operating at 60.735 and 21.964 MHz, respectively. Mass spectrometry was perfomed on a VG micromass 7070 F spectrometer equipped with a VG 2035 data system; the electron energy was 70 eV, and the ion source temperature was 200 °C.

The synthesis and manipulation of Cp_3Sc was carried out in an atmosphere of prepurified nitrogen with rigorous exclusion of air and moisture. Tetrahydrofuran was freshly distilled before use from sodium benzophenone ketyl.

Preparations. Anhydrous Scandium Trichloride. Anhydrous scandium trichloride was prepared by heating Sc_2O_3 (Nucor, Phoenix, AZ) with NH_4Cl in a furnace at 200 °C for 6 h. The excess NH_4Cl was removed by vacuum sublimation at 300 °C.

Cp_3Sc. To a suspension of anhydrous scandium trichloride (0.53 g, 3.5 mmol) in dry tetrahydrofuran (50 cm^3) was added freshly sublimed cyclopentadienylthallium (3.1 g, 11.5 mmol). The resulting mixture was refluxed for 3 h, allowed to cool, and filtered. The solvent was removed under vacuum and the resulting white solid pumped for several hours, to ensure complete removal of solvent. Data: ^1H NMR (C_6D_6) δ 6.3 (Cp); ^{45}Sc NMR (C_6D_6) δ 13.5 ($w_{1/2}$ = 280 Hz); mass spectrum (m/e (%)) 175 (Cp_2Sc^+, (100), 110 ($CpSc^+$, (20), 65 (Cp^+, 15).

Results and Discussion

In the solid state tris(cyclopentadienyl)scandium is associated via bridging cyclopentadienyl groups.[4] Comparison of the X-ray crystallographic data for $(C_5H_5)_3Sc$ and $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$[5] reveals structural parallels and lends credence to the proposition that in the solid-state structure the bridging cyclopentadienyl ligands can be regarded as three-electron donors.

In solution, however, the degree of association in $(C_5H_5)_3Sc$ had not been established. One might, therefore, envisage that, in a coordinating solvent such as tetrahydrofuran, the monomeric species $(C_5H_5)_3Sc(THF)$ would predominate whereas in a non-

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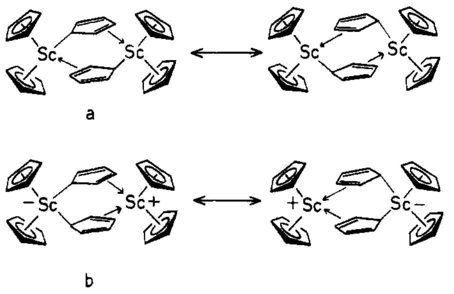

Figure 1. Possible representations of dimeric $(C_5H_5)_3Sc$.

coordinating solvent, toluene, a dimeric structure such as in Figure 1a is potentially viable.

The variable-temperature 250-MHz ^1H NMR spectrum of $(C_5H_5)_3Sc$ in THF showed that the single cyclopentadienyl resonance, observed at room temperature, separated into two peaks at δ 6.3 and 6.2 at −30 °C, reminiscent of Cp_4Ti,[6] but in the ratio 1:2. Further cooling splits the smaller peak into a 2:2:1 pattern similar to the behavior of $Cp_2Fe(CO)_2$ and related systems discussed in now classic papers from Cotton's laboratory.[7] We can, therefore, interpret the data for the $(C_5H_5)_3Sc(THF)$ system as involving two fluxional processes. The high-temperature process is the σ–π exchange between two η^5 rings and one η^1 ring; the low-temperature process is then rationalized as a metallotropic 1,5-shift of the $(\eta^5\text{-}C_5H_5)_2Sc(THF)$ moiety about the third cyclopentadienyl ring. This result has ample precedent[7] and need concern us no further.

The variable-temperature 400-MHz NMR spectrum of $(C_5H_5)_3Sc$ in toluene-d_8 (Figure 2) showed additional features not observed in the analogous spectra in THF. The room-temperature singlet splits at 10 °C into a 2:1 peak pattern that, upon further cooling at −30 °C, shows a gradual reversal, giving a 1:2 intensity pattern. Continued cooling to −80 °C eventually splits out the smaller peak as in the THF solution. It is not possible to see clear proton–proton coupling, and we attribute this to quadrupolar broadening due to the presence of ^{45}Sc nuclei.

It is readily apparent that we are dealing with several processes that occur over the temperature range of these experiments, and we advance the following hypothesis: (1) At low temperature, −80 °C, we are observing the dimer (Figure 1a) in which the four terminal cyclopentadienyl groups are equivalent but the two bridging cyclopentadienyls are no longer symmetrically bonded to the scandiums, i.e., each bridging C_5H_5 group is σ bonded to one scandium and π bonded to the other. We thus expect to see five environments for protons in the bridging rings. (2) When the temperature is elevated, −40 °C, the bridging rings are now rotated so as to bond apparently symmetrically to the two scandium atoms. This leads to a 1:2 peak pattern for the bridging and terminal C_5H_5 resonances. (We note that Werner has prepared a series of dipalladium complexes containing bridging cyclopentadienyl ligands.[8] He raised the possibility of the cyclopentadienyl rings being bonded in a η^3 fashion to palladium but was unable to freeze out a limiting spectrum.) (3) Further heating leads to bridge cleavage and establishment of a dimer-monomer equilibrium that, naturally, favors the monomer with increasing temperature. (4) The final process equilibrates all the protons in the system via a σ–π (η^1–η^5) exchange of the cyclopentadienyl rings. We thus attribute the low-frequency (high-field) peak in the 10 °C spectrum to the σ-bonded ring of the monomer and the terminal rings of any remaining dimer; hence, the π-bonded rings of the monomer and the bridging rings of any remaining dimer give rise to the high-frequency (low-field) peak.

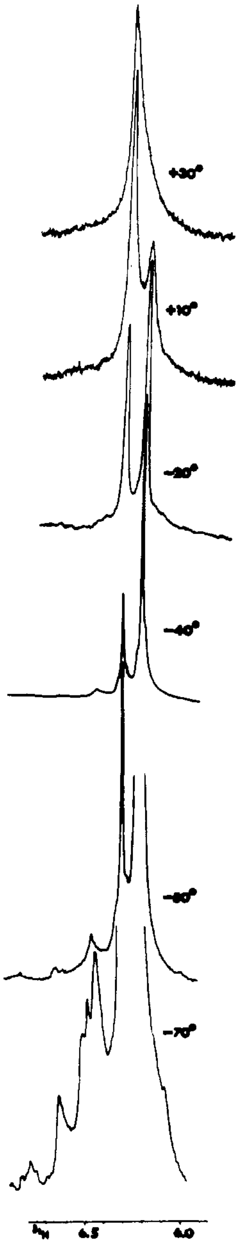

Figure 2. Variable-temperature 400-MHz ^1H NMR spectra of $(C_5H_5)_3Sc$ in toluene-d_8.

While this hypothesis readily accounts for the observed proton spectra, one must seek independent evidence of the monomer–dimer equilibrium. From our previous studies using ^{45}Sc NMR as a probe in scandium borohydrides,[9] we decided to apply this technique to the monomer–dimer equilibrium problem. (The observation of two separate lithium-7 resonances for a complex involved in monomer–dimer formation has recently been reported.)[10]

Scandium-45 is an excellent NMR nucleus.[11] It is 100% abundant and has a relative sensitivity 1708 times that of ^{13}C. Of all the NMR nuclei, only ^1H, ^{19}F, ^{51}V, ^{93}Nb, and ^{113}In are more favorable. The quadrupole moment of -0.22×10^{-28} m^2 is to some extent alleviated by the large nuclear spin value ($I = {}^7/_2$) so, even for systems of less than cubic symmetry, line widths are not a

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Table I. ^{45}Sc NMR Data for Some Ionic and Covalent Scandium Compounds

compd	δ^a	line width,^{b} Hz
$[\mathrm{Sc(OH_2)_6}]^{3+\,a}$	0	200
$\mathrm{Cp_2ScCl}^c$	−9.5	85
$\mathrm{Cp_3Sc}^c$	13.5	280
$\mathrm{Cp_2ScBH_4}^c$	67.5	250^d
$\mathrm{Sc(hfac)_3}^{c,e}$	73.0	1340
$\mathrm{Sc(acac)_3}^{c,f}$	89.3	570
$\mathrm{Sc(BH_4)_3}^c$	113.25	80^g
$[\mathrm{Sc(Me_2SO)_6}]^{3+\,h}$	115.5	690
$[\mathrm{Sc(CH_3CN)_6}]^{3+\,h}$	200	330
$[\mathrm{Sc(THF)_6}]^{3+\,h}$	203	610

[a] ppm relative to external 1.5 M aqueous $\mathrm{ScCl_3}$ where positive values represent high frequency. [b] Widths are measured at peak half-height with no proton decoupling. [c] Benzene solvent. [d] This decreases to 105 Hz on ^{11}B{^{1}H} NMR. [e] hfac = hexafluoroacetylacetonate. [f] acac = acetylacetonate. [g] This decreases to 20 Hz on ^{11}B{^{1}H} NMR. [h] Sample prepared by dissolving anhydrous $\mathrm{ScCl_3}$ in neat solvent.

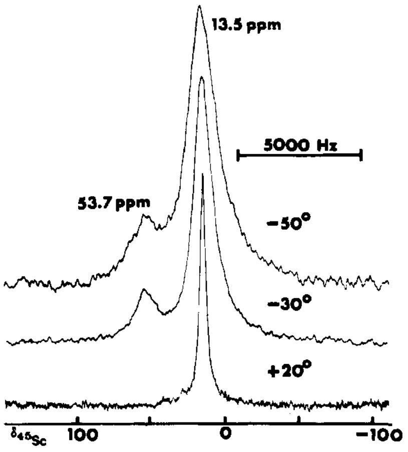

Figure 3. Variable-temperature 60.735-MHz ^{45}Sc NMR spectra of $(\mathrm{C_5H_5})_3\mathrm{Sc}$ in toluene-d_8.

particular problem. Some typical chemical shifts and line widths are listed in Table I, and it is clear that, for the $(\mathrm{C_5H_5})_2\mathrm{ScX}$ system, the ^{45}Sc resonance is sensitive to the identity of X. Indeed, we have previously noted that in the $(\mathrm{C_5H_5})_2\mathrm{MXY}$ systems, where M = ^{49}Ti and ^{91}Zr and X and Y are univalent groups, the ^{1}H and ^{13}C NMR shifts are almost identical and are of little diagnostic value while the metal shifts span a several hundred ppm range.[12]

With this in mind, we recorded the ^{45}Sc NMR spectra of $(\mathrm{C_5H_5})_3\mathrm{Sc}$ in THF and in toluene over a wide temperature range. In THF over the range +35 to −80 °C only a single resonance was observed consistent with the idea of a single scandium environment. In contrast, the spectra in toluene show a single resonance at room temperature that separates on cooling (Figure 3) into two resonances, the ratios of which change with temperature (presumably reflecting the increasing tendency to dimer formation at low temperature). Finally, the spectra broaden at low temperature, and this is attributed to quadrupolar relaxation effects.[13]

It is our contention, therefore, that in THF solution $(\mathrm{C_5H_5})_3\mathrm{Sc}$ behaves analogously to $(\mathrm{C_5H_5})_4\mathrm{Ti}$ in exhibiting a low-energy metallotropic shift of scandium around a η^1 ring and a higher energy process involving interconversion of σ- and π-complexed cyclopentadienyl rings. In contrast, in a noncoordinating solvent such as toluene the situation is complicated by association of the monomer units via bridging cyclopentadienyl ligands, as is known to occur in the solid state.

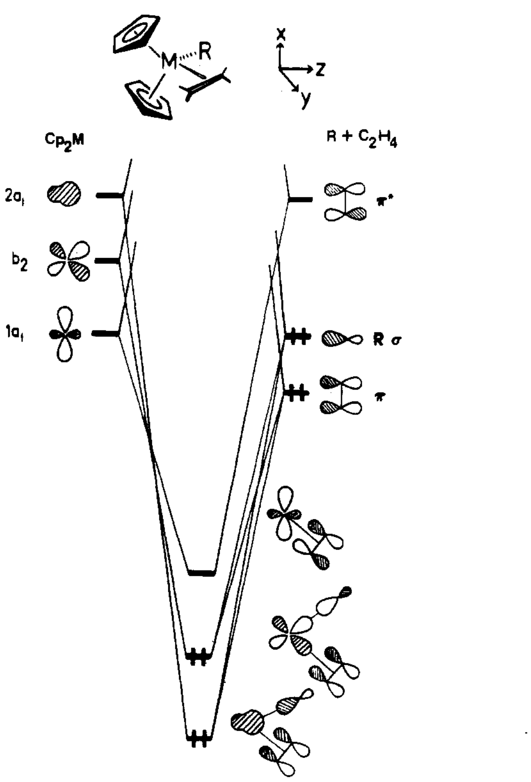

Figure 4. Frontier molecular orbital diagram of the $(\mathrm{C_5H_5})_2\mathrm{M(C_2H_4)R}$ system.

Finally, we comment briefly on the bonding in such a dimer. Lauher and Hoffmann have presented an extremely useful picture of the interaction of a bent $(\mathrm{C_5H_5})_2\mathrm{M}$ fragment with a variety of ligands.[14] Our description of the bridging cyclopentadienyls as involving one σ and one π interaction is readily handled by using the Lauher–Hoffmann approach. In the axis system in Figure 4 we show the three low-lying frontier orbitals of the $\mathrm{Cp_2M}$ fragment and note that they all lie in the yz plane.[14] We see that suitable in-phase and out-of-phase ligand σ orbitals can donate into the vacant $2a_1$ and b_2 metal orbitals. Furthermore, π back-bonding from the fragment $1a_1$ orbital is possible, but of course, this requires the $1a_1$ orbital to be filled as in the d^2 system $\mathrm{Cp_2Nb^+}$. Such a favorable interaction would constrain the olefin to the yz plane since rotation about the metal–olefin σ-bond axis would cause the π back-donation to be lost. However, in the d^0 $\mathrm{Cp_2Sc^+}$ case there is no such hindrance to rotation. Of course, there is no extra stabilization either so the olefin–metal interaction is essentially just a σ bond and consequently rather weak. Hence, the η^2-bonded $\mathrm{C_5H_5}$ ligand is not constrained to the yz plane (which would also give rise to steric problems with the other bridging ring) but is also not very firmly bonded to scandium. It is not surprising then that association via bridging cyclopentadienyls is only found in the solid state or in a weakly coordinating solvent at low temperature. In agreement with this picture, the electron-impact mass spectrum of $(\mathrm{C_5H_5})_3\mathrm{Sc}$ shows peaks attributable solely to the monomer whereas $(\mathrm{C_5H_5})_2\mathrm{ScCl}$ gives clear evidence of dimer formation even in the gas phase.

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Registry No. $(\mathrm{C_5H_5})_3\mathrm{Sc}$, 1298-54-0; $(\mathrm{C_5H_5})_3\mathrm{Sc(THF)}$, 93473-56-4.

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