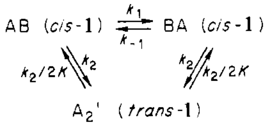
Table I. Activation Parameters[a] for $[MoI(CO)_2(dmdepe)_2]I$ from NMR Exchange Studies

	$^{13}C\{^{31}P, ^1H\}$[b]	$^{31}P\{^1H\}$[b]	$^1H\{^{31}P\}$[c]
$\Delta G^\ddagger$, kcal/mol (298 K)	13.50 (10)	13.60 (6)	13.5 (4)
$\Delta H^\ddagger$, kcal/mol	11.0 (20)	12.1 (13)	
$\Delta S^\ddagger$, cal/(mol K)	−8.4 (69)	−5.1 (46)	

[a] Uncertainties are 95% confidence limits in the last significant figure. Parameters are relative to the *cis*-**1** isomer since the rate constants used (k_2) refer to the forward reaction *cis*-**1** → *trans*-**1**. [b] This work. [c] Reference 1; uncertainty is the standard error from least-squares fit.

identical with those of the previous work.[1,4] The exchange-broadened spectra were fit to a two-site nonmutual-exchange model by using a complete density matrix approach.[5] Relative populations of the two isomers were fixed to values extrapolated from the slow-exchange spectra; thus, the rate constants were the only variables in the fits. Derived rate constants were fit to the Eyring equation[6] to obtain the activation parameters tabulated in Table I. This more rigorous treatment gives more accurate activation parameters than does the simple use of the Gutowsky–Holm[7] equation in ref 1.

The $^{13}C\{^{31}P,^1H\}$ NMR signals of **1** broaden above −30 °C and coalesce to a single line at about 20 °C. The exchange-broadened spectra were fit as a nonmutual-exchange problem by using the density matrix treatment described above.[5] The three-configuration model in eq 5 was used, where K is the equilibrium constant of eq 1.



Use of this model maintains an internal consistency with the rate constants used in the ^{31}P-exchange problem. Note that the model allows both carbonyl-edge rotation, k_1, and cis–trans exchange, k_2, to occur independently. The rates for cis–trans exchange were initially estimated from the rates obtained from the ^{31}P data, and the rate of carbonyl-edge rotation was varied to accommodate the spectra. Minimum deviations occurred when $k_1 \ll k_2$; larger values of k_1 produced calculated spectra which were markedly at variance with the experimental data. Subsequently, k_1 was fixed at zero, and the k_2 values were refined. A representative sample of experimental spectra and simulations is shown in Figure 1. A minor impurity in the downfield portion of the spectrum is evident but does not interfere significantly with the visual matching. Uncertainties in the rate constants were estimated from the range of values yielding acceptable comparisons.

These data establish that carbonyl-edge rotation of the type in eq 2 is slower than the process responsible for cis–trans exchange, if it occurs at all. That is, because carbonyl-edge rotation does not occur at an appreciable rate, we conclude that *any* mechanism based on the geometric transformation of path I of ref 1 is unlikely. It is important to note that the least motion transformation of path I simply depicts the equivalence of a unique edge rotation in a capped trigonal prism and an interchange of adjacent equatorial sites in a pentagonal bipyramid. The values for the activation parameters for cis–trans exchange from the independent ^{13}C and ^{31}P data are in good agreement. In both cases the magnitude of $\Delta S^\ddagger$ is consistent with a nondissociative, polytopal rearrangement.

Because of the inequality of competing rate constants, we conclude that multistep mechanisms, invoking path 1 of Figure 5 in ref 1, as suggested in the second step of Figure 6 of ref 1, are unlikely to be responsible for cis–trans exchange.[1,8] The simplest nondissociative mechanism capable of accounting for cis–trans exchange is a ligand twist of the bidentate phosphine.

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Registry No. *trans*-**1**, 65015-74-9; *cis*-**1**, 65058-47-1; $Mo(N_2)_2(dmdepe)_2$, 73544-69-1.

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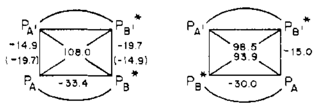
(4) Revised constants from ^{31}P data are



(5) The computer program PZDMX was kindly supplied by Dr. Paul Meakin. The general methods have been documented in several publications. See, for example: Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *17*, 729 and references therein.

(6) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107. A modified form of the program ARH2, supplied by J. D. Roberts, was used for the fit.

(7) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1966**, *25*, 1228.

(8) This mechanism does, however, occur in some cases. See: Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

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Synthesis of a Bis(pentamethylcyclopentadienyl) Derivative of Neodymium

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Bis(cyclopentadienyl)lanthanide chlorides $[(C_5H_4R)_2LnCl]_2$ and $(C_5H_4R)_2LnCl{\cdot}C_4H_8O$[1,2] ($R = H, CH_3$) are valuable synthetic precursors in organolanthanide chemistry.[3] Unfortunately, these complexes are not available for the early members of the lanthanide series, La–Nd, a result which excludes these metals from the derivative chemistry associated with $(C_5H_4R)_2LnCl$ precursors. If, as is often claimed,[1,4] syntheses of bis(cyclopentadienyl) chloride complexes of the larger lanthanides fail for steric reasons, then the use of a bulky substituted cyclopentadienyl ligand such as $C_5(CH_3)_5$[5] should allow the isolation of these important intermediates and their subsequent use in organolanthanide synthesis.

We have investigated this approach to bis(cyclopentadienyl)lanthanide chlorides and have succeeded in isolating and characterizing a crystalline bis(pentamethylcyclopentadienyl) complex of neodymium. Surprisingly, the isolated product is the lithium salt $[(C_5Me_5)_2NdCl_2][Li(C_4H_8O)_2]$ instead of the expected neutral species $[(C_5Me_5)_2NdCl]_2$.

Experimental Section

C_5Me_5H was prepared following the procedure of Bercaw and Threlkel.[6] LiC_5Me_5 was prepared by the reaction of C_5Me_5H and

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(1) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.

(2) Gomez-Beltran, F.; Oro, L. A.; Ibanez, F. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1541.

(3) Tsutsui, M.; Ely, N. M. *J. Am. Chem. Soc.* **1975**, *97*, 1280, 3551. Tsutsui, M.; Ely, N. M. *Inorg. Chem.* **1975**, *14*, 2680. Holton, J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 480. Marks, T. J.; Grynkewich, G. W. *Inorg. Chem.* **1976**, *15*, 1302.

(4) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.

(5) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6629. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Ibid.* **1978**, *100*, 3939.

(6) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

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n-C_4H_9Li in pentane at room temperature for 6 h. $NdCl_3{\cdot}xH_2O$ (Research Chemicals, Phoenix, Ariz.) was dehydrated by the method of Taylor and Carter.[7] THF and toluene were distilled from potassium benzophenone ketyl. Pentane was washed with sulfuric acid, dried over $MgSO_4$, refluxed over finely divided $LiAlH_4$, and vacuum transferred. All reactions were performed under nitrogen or argon with standard Schlenk and drybox techniques as appropriate.[8]

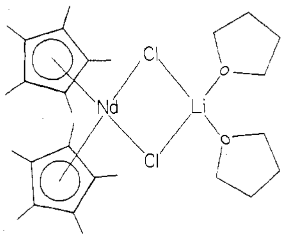
For $[(C_5Me_5)_2NdCl_2][Li(C_4H_8O)_2]$, addition of a white slurry of LiC_5Me_5 (1.66 g, 0.0117 M, in pentane) to a stirred slurry of $NdCl_3$ (1.46 g, 0.005 84 M, in THF) followed by stirring for 2 days at room temperature results in the formation of a cloudy aqua-blue solution. Removal of solvent from this mixture forms a sticky blue-green residue which is extracted with toluene to remove any unreacted $NdCl_3$ and byproduct LiCl. The blue powder obtained by rotary evaporation of the toluene from this solution is extracted with pentane to yield a blue solution from which blue-violet crystals form upon slight cooling (conveniently achieved by partial solvent removal with a rotary evaporator). The solution is quickly filtered, while cold, to isolate the crystalline product. Several crops of crystals are collected by repeating this procedure, leaving an increasingly green mother liquor. The combined microcrystalline product is further purified by cooling a saturated pentane solution at 0 °C until large purple crystals form. The final crystalline yield is 10–15%.[9] Anal. Calcd for $LiNdC_{28}H_{46}Cl_2O_2$: Li, 1.09; Nd, 22.65; C, 52.81; H, 7.28; Cl, 11.13; O, 5.02. Found:[10] Li, 1.01; Nd, 22.78; C, 52.82; H, 7.27; Cl, 11.28; O, 4.84 (by difference).

Results and Discussion

The reaction of $NdCl_3$ with 2 equiv of LiC_5Me_5 forms a crystalline product, I, formulated as $[(C_5Me_5)_2NdCl_2][Li(C_4H_8O)_2]$ based on complete elemental analysis and the following spectral data. Trivalent neodymium is indicated by the near-infrared–visible spectrum of I,[11] which exhibits a characteristic Nd^{3+} pattern, and by the room-temperature magnetic susceptibility,[12] $\chi_g = 8.536 \times 10^{-6}$ cm^3/g, $\mu_{eff} = 3.50$ μ_B, a value in the normal range for Nd^{3+}, 3.3–3.7 μ_B. The ^1H NMR spectrum of I in C_6D_6 exhibits broad resonances at δ 9.18, 1.13, and 0.11 (referenced to C_6H_6) which can be assigned to C_5Me_5 and THF, respectively. In THF, the resonance assigned to C_5Me_5 is found at δ 8.87 (referenced to THF or cyclohexane). The infrared spectrum of I exhibits several weak bands commonly observed in C_5Me_5 complexes,[13] and also displays absorptions at 1045, 915 and 895 cm^{-1} which are consistent with THF coordinated to a cationic center.[14]

The title compound is extremely air and moisture sensitive. Within seconds of air exposure, the complex decomposes to a green powder which turns red-brown upon further standing. These color changes are accompanied by a strong odor of C_5Me_5H. Hydrolytic decomposition of I is also rapid and yields C_5Me_5H.

Based on these data, the most probable structure for I is the chloro-bridged species shown below which allows for complete coordination of the lithium cation. A similar structure has been proposed by Lappert and co-workers for an yttrium complex, $[(Me_3SiC_5H_4)_2YCl_2][Li(C_4H_8O)_2]$.[14]



The attempted sublimation of I results in thermal decomposition at 270 °C. By analogy to the above yttrium case, the green decomposition product may be the neutral dimer, $[(C_5Me_5)_2NdCl]_2$. This latter product may also be present in the mother liquor from which I is obtained, since upon successive crystallizations of I, this solution becomes progressively greener. Removal of solvent from the green mother liquor leaves an oil, however, suggesting that a complex mixture is present as is found in bis(cyclopentadienyl)- and bis(methylcyclopentadienyl)neodymium chloride syntheses.[1] Since synthesis of I may be the only convenient solution route to a pure crystalline bis(cyclopentadienyl)neodymium chloride complex, we are investigating the use of I directly as a synthetic precursor.

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Registry No. I, 73597-12-3.

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(7) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.
(8) Shriver, D. F. "Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.
(9) There is some latitude in these reaction conditions. For example, stirring the reagents for 12 h at room temperature and 2.5 h at reflux, followed by THF removal and direct pentane extraction, constitutes a similarly successful synthesis. The initial microcrystalline product can be obtained in yields as high as 60%.
(10) Alfred Bernhardt Analytical Laboratories, D-5250 Engelskirchen, Germany.
(11) Near-IR–visible (in THF, λ_{max}, nm (relative intensity, scale 1–100)): 617 (4), 615 (7), 609 (10), 608 (10), 603 (32), 601 (19), 597 (100), 596 (60), 592 (21), 591 (11), 586 (8).
(12) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Becconsall, J. K. *Mol. Phys.* **1968**, *15*, 129.
(13) 1020 (w, sh), 800 (w) cm^{-1}. See: King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287 and ref 5.
(14) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140.

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Formation of 1,1,1-Trimethyl-*N*-sulfinylsilanamine from the Direct Reaction of SO_2 with Hexamethyldisilazane

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The direct, facile reaction between sulfur dioxide and the common silylating agent hexamethyldisilazane (HMDS) resulting in the formation of 1,1,1-trimethyl-*N*-sulfinylsilanamine, $(CH_3)_3Si{-}N{=}S{=}O$ (**1**), has not previously been reported, although sulfur dioxide is known to react with bis(trimethylsilyl)diimine[1] and $Me_3SiHgSiMe_3$[2] to form the unstable bis(trimethylsilyl) sulfoxylate $(CH_3)_3Si{-}O{-}S{-}O{-}Si(CH_3)_3$ (**2**). Compound **1** was first made in 1966 from the reaction of tris(trimethylsilyl)amine with thionyl chloride at 70 °C in the presence of $AlCl_3$ catalyst.[3] Since that time a number of other synthetic methods have also been reported for its formation.[4-8] It should be noted that the germanium

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(1) Wiberg, N.; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 374–87.
(2) Neumann, G.; Neumann, W. P. *J. Organomet. Chem.* **1972**, *42*, 293–306.
(3) Scherer, O. J.; Horning, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 729–30.
(4) Scherer, O. J.; Schmitt, R. *Chem. Ber.* **1968**, *101*, 3302–12.
(5) Armitage, D. A.; Clark, M. J. *J. Organomet. Chem.* **1970**, *24*, 629–31.
(6) Armitage, D. A.; Sinden, A. W. *J. Organomet. Chem.* **1972**, *44*, C43–5.
(7) Appel, R.; Montenarh, M. *Chem. Ber.* **1975**, *108*, 2340–8.

0020-1669/80/1319-2191$01.00/0