arise from two diastereomers formed for each of two orientational isomers having the dansyl group located cis to the 3′ or 5′ guanosine of the dinucleoside monophosphate.[17] The absence of a significant intercalative interaction of the dansyl moiety with duplex DNA was demonstrated by unwinding titration experiments, which are sensitive to the mode of binding of platinum compounds.[18] An unwinding angle of 13.5 ± 1.5° was obtained for [Pt(dansen)Cl_2] bound to pUC19 plasmid DNA. This value is essentially identical to those observed for cisplatin and [Pt(en)Cl_2], excluding [Pt(dansen)Cl_2] from the class of complexes that exhibit both covalent and intercalative interactions. Together with the demonstration of bifunctional coordination to single-stranded DNA described above, the results make it extremely unlikely that a combination of monofunctional and intercalative binding modes exists for [Pt(dansen)Cl_2].

Further evidence for the structural similarity of [Pt(dansen)Cl_2]-DNA adducts to those formed by cisplatin was obtained from the ability of the protein HMG1 to bind to restriction fragments modified by the fluorescent analogue. HMG1 binds to DNA modified by platinum complexes that form 1,2-intrastrand d(GpG) or d(ApG) cross-links, as revealed by gel mobility shift assays.[19] Identical band shift studies of DNA modified with [Pt(dansen)Cl_2] indicated that HMG1 also recognizes its DNA adducts (Figure S2).

The emission spectrum of [Pt(dansen)Cl_2] is shown in Figure 1A along with that of dansylamide for comparison. The electronic absorption (dansylamide, λ_{max} 328 nm, ϵ 7060 M^{-1} cm^{-1}; [Pt(dansen)Cl_2], λ_{max} 334 nm, ϵ 5220 M^{-1} cm^{-1}) and emission spectra of the two compounds are not appreciably affected by the presence of a sulfone, rather than a sulfonamide, link in the dansyl moiety. The ratio of emission intensity maxima for dansylamide and [Pt(dansen)Cl_2] at 344 nm, a wavelength where the extinction coefficients are identical, is 0.44. Apparently, the propylene tether prevents efficient quenching of the fluorescence by the platinum metal center. Moreover, the emission spectrum for [Pt(dansen)Cl_2] bound to calf thymus DNA is similar to that for the free complex, as expected in the absence of intercalative binding.

The [Pt(dansen)Cl_2] compound is taken up by bacterial cells in a similar fashion to cisplatin. Figure 1B shows emission spectra for pUC19 plasmid DNA recovered from 100-mL cultures of XL1-Blue *Escherichia coli* treated with 5×10^{-5} M solutions of the complex [Pt(dansen)Cl_2] or with the free ligand dansen in phosphate-buffered saline. An emission band centered at 534 nm was observed for DNA recovered from cultures treated with [Pt(dansen)Cl_2], but not for samples isolated from cultures treated with equimolar concentrations of dansen or cisplatin. In these latter two cases, only a weak background signal due to DNA was observed. Analysis by atomic absorption spectroscopy of pUC19 DNA obtained from platinum-treated cells revealed ratios of bound drug to nucleotide (r_b) of 10^{-4} for cisplatin and 10^{-5} for [Pt(dansen)Cl_2]. Quantitation of [Pt(dansen)Cl_2] in the latter samples by fluorescence spectroscopy agreed with the atomic absorption results, confirming that the ligand remains bound to the platinum center in vivo.

The luminescence, cellular uptake, and DNA binding properties of [Pt(dansen)Cl_2] should facilitate a variety of interesting applications. In particular, this cisplatin analogue might be used to investigate its intracellular distribution, processing by DNA repair enzymes, recognition by HMG-box proteins, and other aspects of its biological chemistry in vivo.[1,13,19] Compounds with similar optical properties, including the structurally uncharacterized compound *cis*-bis(6-aminoquinoline)dichloroplatinum(II),[20] have been employed to follow the compartmental localization of substrates within single cells.[21,22] Applications requiring the analysis of a cisplatin analogue bound to cellular DNA at r_b values considerably lower than those employed in this preliminary study should be possible with [Pt(dansen)Cl_2] or a related compound by laser excitation and recently developed, highly sensitive detection systems.[21,23]

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Supplementary Material Available: Preparation of compounds **1–4** including spectroscopic and analytical data, Figure S1 showing the results of the digestion/HPLC analysis of a dodecanucleotide platinated with [Pt(dansen)Cl_2], and Figure S2 displaying the gel mobility shift of DNA platinated with [Pt(dansen)Cl_2] in the presence of the protein HMG1 (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Neutral Lanthanide Silyl Complexes $(\eta^5\text{-}C_5Me_5)_2LnSiH(SiMe_3)_2$ (Ln = Nd, Sm)

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A number of key advances in transition-metal silicon chemistry have resulted from studies with the early transition metals.[1] In particular, it has been observed that d^0 M–Si σ bonds readily participate in insertion[2] and σ-bond metathesis[3] reactions, which appear to proceed via four-center, concerted additions. This suggests that f-element metal–silicon bonds would also be reactive, since they should be electronically similar to early metal–silicon

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bonds, and since four-center addition processes are closely associated with f-element chemistry.[4] It has recently been reported that lanthanocene complexes are catalysts for the dehydrocoupling of primary silanes to polysilanes,[5] possibly via a σ-bond metathesis mechanism involving four-center transition states.[3] In order to explore the potentially rich chemistry of lanthanide–silicon-bonded compounds, we have attempted to develop general syntheses for silyl complexes that are amenable to detailed investigations. The only lanthanide silyl derivatives to be previously reported are of the type $[Li(DME)_3]^+[Cp_2Ln(SiMe_3)_2]^-$ and have been obtained by reaction of $[Cp_2LnCl_2]^-$ complexes with $LiSiMe_3$.[6] Here we describe the synthesis of neutral neodymium and samarium silyl complexes via a σ-bond metathesis route.

We have previously shown that group 4 transition-metal silyl complexes can be obtained via σ-bond metathesis reactions involving hydrosilanes.[3a,e] Reactions of silanes with lanthanide alkyl complexes were therefore examined, in search of Ln–Si bond formation. In general, such reactions appear to be highly sensitive to steric effects. The yttrium complex $Cp^*_2YMe(THF)$ converts $PhSiH_3$ to $PhMeSiH_2$, indicating that the primary σ-bond metathesis process involves a four-center transition state that transfers the silyl group to carbon, rather than to yttrium.[7] To sterically direct transfer of the silyl group to the metal, the bulkier alkyl derivatives $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Sm, Nd)[4d] were employed. These complexes do not react with Ph_3SiH or Ph_2MeSiH (room temperature, 8 days), but do react with less hindered silanes such as $MesSiH_3$ (Mes = mesityl; over 10 min at 70 °C) to produce $CH_2(SiMe_3)_2$ (quantitatively), the corresponding hydrides $[Cp^*_2LnH]_2$,[4d] and a disilane (e.g., $MesH_2SiSiH_2Mes$). Such reactions probably involve intermediate lanthanide silyls, which undergo rapid dehydrocoupling reactions (bimolecularly[3b,g] or with the hydrosilane) that give the hydride and the disilane. It therefore appears that silanes with intermediate steric properties are required, to allow reaction with $Cp^*_2LnCH(SiMe_3)_2$ to occur while providing steric protection from further σ-bond metathesis reactions for the resulting silyl complex.

The alkyls $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Sm, Nd) react with neat $SiH_2(SiMe_3)_2$ (ca. 5 equiv) at 85 °C to give the new silyl complexes $Cp^*_2LnSiH(SiMe_3)_2$ as red (**1**, Ln = Sm) or blue-green (**2**, Ln = Nd) crystals from pentane (eq 1). The high silane

$$Cp^*_2LnCH(SiMe_3)_2 + SiH_2(SiMe_3)_2 \longrightarrow Cp^*_2LnSiH(SiMe_3)_2 + CH_2(SiMe_3)_2 \quad (1)$$

1, Ln = Sm
2, Ln = Nd

concentration is necessary to suppress the competing thermal decomposition of $Cp^*_2LnCH(SiMe_3)_2$. The infrared spectra for **1** and **2** are essentially identical and display a low ν(SiH) stretching frequency (1960 cm^{-1}; cf. 2085 cm^{-1} for the silane) that results from bonding of the silicon to an electropositive element. Preliminary mechanistic studies have shown that these reactions proceed according to a second-order rate law, but only after a pronounced, variable induction period. Therefore these σ-bond metathesis reactions appear to proceed via a relatively complex mechanism, which is currently under investigation.

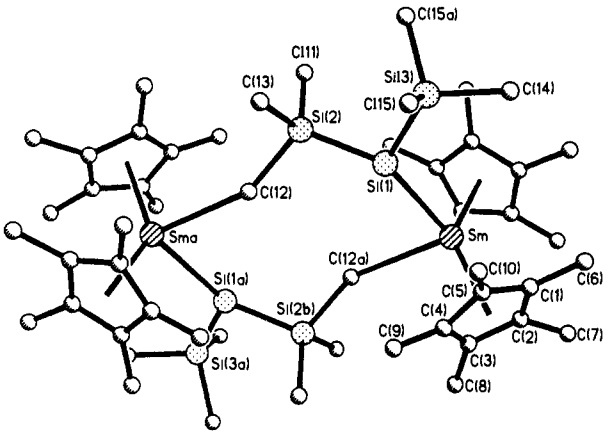

Figure 1. ORTEP view of **1**. Important bond distances (Å) and angles (deg): Sm–Si(1) 3.052 (8), Sma–C(12) 2.970 (22), Si(1)–Si(2) 2.214 (11), Si(1)–Si(3) 2.375 (12), Si(2)–C(11) 1.881 (37), Si(2)–C(12) 1.996 (22), Si(2)–C(13) 1.937 (28), Sm–CNT 2.43 (1); Sm–Si(1)–Si(2) 131.0 (4), Sm–Si(1)–Si(3) 124.2 (4), Si(2)–Si(1)–Si(3) 100.9 (4), Si(1)–Si(2)–C(11) 108.2 (12), Si(1)–Si(2)–C(12) 109.4 (7), Si(1)–Si(2)–C(13) 114.52 (8), Si(1)–Sm–C(12a) 88.1 (5), CNT–Sm–CNT 135.7 (2). CNT is the centroid of a Cp* ring.

Dimers of **1** in the solid state form via intermolecular Sm···C-H_3–Si interactions (Figure 1),[8] which result in Sm–C(Me) distances of 2.97 (2) Å. A number of related compounds, containing intramolecular coordination of an $SiMe_3$ group to a lanthanide metal center, are known.[9] In particular, it is interesting to compare the structures of $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Ce,[9b] Nd,[4d] Y[9c]), which are monomeric in the solid state and contain one intramolecular Ln···CH_3–Si interaction. Intermolecular interactions of this kind have also been found in complexes such as $Cp^*Be(\mu\text{-}Me)YbCp^*_2$.[10] These interactions have been attributed to weak electrostatic attraction between the metal and the methyl carbon atom. The Sm–Si distance in **1**, 3.052 (8) Å, is longer than the Lu–Si distance of 2.888 (2) Å in $[Cp_2Lu(SiMe_3)_2]^-$.[6a,c] This difference (0.16 Å) is somewhat more than can be attributed to the lanthanide contraction (ca. 0.10 Å).[11]

Both **1** and **2** are monomeric in pentane solution at room temperature (by isothermal distillation) and exhibit singlet Cp* resonances in their ^1H NMR spectra, due to rapid rotation about the Ln–Si bond. As with other complexes that display Ln···CH_3–Si interactions in the solid state, evidence for these interactions in solution is not observed in NMR spectra. The ^1H NMR chemical shifts for **2** display Curie–Weiss behavior, indicating that **2** is monomeric down to −80 °C. The Cp* resonance for **2** decoalesces into two singlets at 10 °C, which corresponds to an activation barrier for rotation about the Nd–Si bond of 13.3 (1) kcal mol^{-1}. For comparison, the analogous rotation about the Nd–C bond of $Cp^*_2NdCH(SiMe)_2$ has a barrier of 19.9 (1) kcal mol^{-1}.

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The silyl complexes reported here, and others prepared similarly, should prove to be valuable in the characterization of Ln-Si bond reactivity. Initial reactivity studies indicate that these bonds are quite reactive. Both **1** and **2** react rapidly (≤5 min) with hydrogen (1 atm, benzene-d_6) to produce $[Cp^*_2LnH]_2$ and $SiH_2(SiMe_3)_2$, and with ethylene (1 atm, benzene-d_6) to produce polyethylene (by ^1H NMR spectroscopy). In the reactions with ethylene, all of **2** is consumed, but only 80% of **1**. Finally, **1** and **2** react much more rapidly with silanes than do the corresponding alkyls. For example, **1** reacts with $MesSiH_3$ (3 equiv, benzene-d_6) over 10 min at room temperature to afford $[Cp^*_2SmH]_2$, $SiH_2(SiMe_3)_2$, and $MesH_2SiSiH_2Mes$, while the analogous reaction of $Cp^*_2SmCH(SiMe_3)_2$ requires 10 min at 70 °C.

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Supplementary Material Available: Experimental procedures and characterization data for **1** and **2** and tables of crystal, data collection, and refinement parameters, additional ORTEP drawings, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1** (10 pages); listings of observed and calculated structure factors for **1** (9 pages). Ordering information is given on any current masthead page.

Catalytic Asymmetric Synthesis with Trans-Chelating Chiral Diphosphine Ligand TRAP: Rhodium-Catalyzed Asymmetric Michael Addition of α-Cyano Carboxylates

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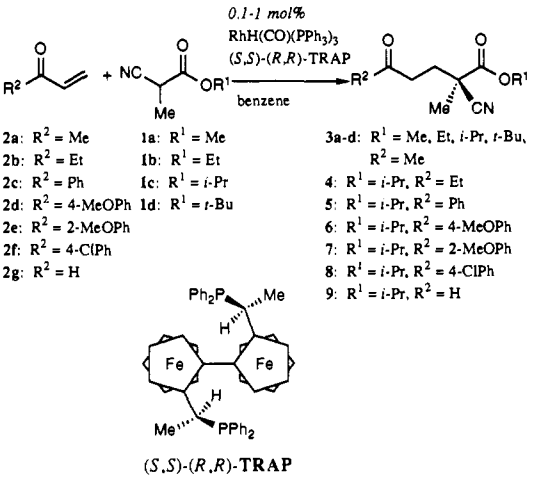
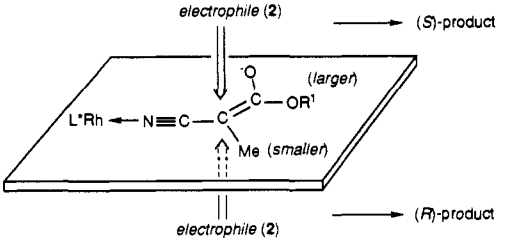
The synthesis of well-designed chiral phosphine ligands has played a predominant role in the recent development of catalytic asymmetric synthesis promoted by transition metal complexes.[1] Recently, we designed and synthesized a trans-chelating chiral diphosphine ligand, 2,2″-bis[1-(diphenylphosphino)ethyl]-1,1″-biferrocene (abbreviated to TRAP), which possesses planar chiralities as well as stereogenic centers.[2-4] Herein, we wish to report a successful application of "TRAP" to transition metal catalyzed asymmetric synthesis, in which the rhodium complex

Scheme I



Scheme II



prepared in situ from $RhH(CO)(PPh_3)_3$ and TRAP (0.1-1 mol %) was an effective catalyst for asymmetric Michael addition of α-cyano carboxylates (**1**) with vinyl ketones or acrolein (**2**) (Scheme I).[5] To the best of our knowledge, this is the first highly enantioselective Michael addition catalyzed by a chiral transition metal complex.[6,7]

Results are summarized in Table I. Enantioselectivities ranging from 83 to 89% were obtained for the reaction of **1c** with various vinyl ketones (**2a-f**) or acrolein (**2g**).[8,9] The enantioselectivity depends slightly on the structure of the ester group of **1** (entries 1-3, 5), with ispopropyl ester **1c** giving the highest selectivity.

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(3) The trans geometry of $PdCl_2$(TRAP) and $PtCl_2$(TRAP) was confirmed by the NMR and molecular weight studies (ref 2). Recently, the X-ray crystal structure of $PdBr_2$(TRAP) has been determined, where TRAP chelates to the palladium in a P-Pd-P bite angle of 164.4°, and *trans*-RhCl(CO)(TRAP) has been synthesized from $[RhCl(CO)_2]_2$ and TRAP (unpublished results: Sawamura, M.; Hamashima, H.; Ito, Y.).

(4) It has been reported that a DIOXOP-rhodium complex can adopt trans geometry in the asymmetric hydrogenation of dehydroamino acids, but the ligand coordinates to Rh(III) as a tridentate ligand. See: (a) Brown, J. M.; Chaloner, P. A.; Descotes, G.; Glaser, R.; Lafont, D.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1979**, 611. (b) Descotes, G.; Lafont, D.; Sinou, D.; Brown, J. M.; Chaloner, P. A.; Parker, D. *Nouv. J. Chim.* **1981**, *5*, 167. Recently, Burk et al. have reported the synthesis of a series of multidentate chiral phosphorane ligands, some of which were shown to chelate to rhodium in a trans manner as tridentate ligands. See: (c) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron: Asymmetry* **1991**, *2*, 569.

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(8) Similar Michael addition of **1** with methyl acrylate or acrylonitrile took a longer reaction time, resulting in the formation of respective Michael adducts with low enantiomeric excesses (<15% ee).

(9) The reactions with aryl vinyl ketones (**2c-f**) or acrolein (**2g**) are very fast. In these cases, higher enantioselectivities are obtainable when a benzene solution of **2** is slowly added to a mixture of **1** and the catalyst in benzene.

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